Generation of few-cycle and attosecond pulses and their use in probing ultrafast dynamics in gases and surfaces

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September 2010

Thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy of Imperial College London and the Diploma of Imperial College

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Declaration
I hereby certify that the material presented in this thesis, which I now submit for the award of Doctor of Philosophy of Imperial College London, is my own work unless otherwise cited or acknowledged within the body of the text.

Christopher Arrell
Abstract

A laser-based system to allow the temporal evolution of plasmonic fields on surfaces with attosecond resolution is presented.

Sub 7fs carrier envelope phase stabilised infra-red (IR) pulses with 450µJ have been generated using a hollow fiber compression system utilising self phase modulation to produce a 400nm FWHM bandwidth centred at 790nm and subsequent compression with chirped mirrors.

The isolated attosecond pulse was produced using spectra selection of a continuum of extreme ultraviolet (XUV) photons generated from a single half cycle emission from the IR driving field. The isolated XUV was characterised using the atomic streak camera technique and a pulse duration of 270as was retrieved using a frequency resolved optical gating algorithm.

An ultra high vacuum ($10^{-10}$ mbar) surface science system for attosecond pump-probe studies of surfaces was designed and built, connecting directly to the attosecond beamline. A sample manipulator was developed to precisely position surface samples in the IR and XUV foci. Novel vibrational decoupling mechanisms were developed, achieving only 10nm of motion measured of the sample head.

An electron spectrometer with a resolution of 0.05eV for 30eV was used to measure localised nanoplasmonic intensity enhancement of $10^3$ from a rough silver surface (4mm RMS roughness) by collecting 35eV photoelectrons emitted by a few-cycle IR field with an intensity of $\sim 10^{10}W/cm^2$.

A 2-photon photoemission XUV-IR cross correlation measurement probing hot electron dynamics in a gold surface is reported, revealing femtosecond dynamics of electron thermalisation.
Acknowledgments

I’ve had a great time in the Consortium, and this has been down to the people I’ve worked with. The early members of the group were particularly welcoming, Joe for being a great postdoc and having the time to fully explain everything, James for growing old disgracefully, and ‘standgesomething’ Phil. Hank has to be thanked for providing Sky TV in lab for long night scans, Natty for his interesting topics of conversation, and Sarah for her patience with Roland and estates.

The theory office needs to be thanked - not for any theory but for always welcoming a disturbance. Theory Senior for the coffee and whiskey, Theory Junior for never saying no to ‘just one’, Ryan for being a great sport and never letting a joke get to him. Narges has also been a very welcome touch of class to theory pit - sorry - office.

When not stealing tools the members of the 012 have been very helpful. Thank-you Tom for taking the role of ‘Crusher’ and always supplying a range of social outings, Leo for great quotes and a cheeky smile. Malte has brought a great sense of style and order to the other side of the wall which complemented Omair perfectly, with Amelle bringing a motherly French flare and the Red Dragon to heal. Hugo deserves a mention but I’m not really sure where he fits in, along with ‘in my country....’ Rashid. Thanks also to Richard and Leszek for becoming the new Stores.

The ‘Attoboy’s’ have made labtime like playtime! Tobi’s skills with Matlab have been a blessing making his other personal outputs more bearable, Jarlath brought a new light to the lab through his love of women’s dresses and water conservation. Will has been a great addition to the lab and will one day appreciate a morning of Eye of the Tiger. Felix has been a great friend throughout and I couldn’t have asked to work with anyone else (I did look into it but wasn’t allowed).
For the surface experiments, Thorsten has been an immense help and guidance in the experimental design and pitfalls of UHV. Eva has been great at keeping everything real, and has really pushed the streaking work forward. Thanks also to Dangyuan, Yannick and Stefan for sample production and useful discussions.

My supervisors John and Jon have been a great source of guidance and help. Thank-you John for reading and correcting this thesis in a matter of hours! Thanks also for your friendship and advice on everything from touching cloth, to squeaky floorboards to atto physics, nobody could ask for a better supervisor. Jon’s advice and direction has been most welcome along with all the presents - even though you did fine me when in Beit!

Peter, Andy, Bandu and Brian have been a great service to the Atto lab. I’m sure no other lab is so well served that you can vaguely talk about a project in the morning for a masterpiece is delivered in the afternoon.

Other and new members of the group (Roland, Misha, Henry, Mike, Marco ‘you’re weird when you’re in the office’, Sid, Simon, Stefan, Katalin and Suren) have made the Laser consortium a great place to be and work. Thanks also to Miriam for that capillary! Thanks also to all the members of the Beit Wardening team for making my three years in hall so enjoyable, and of course thank-you to my father for inspiring me to do a PhD.
‘Why you need a big one?’

Leonardo Brugnera
Contents

1 Introduction 9
   1.1 Introduction .......................................................... 9

2 Theory 15
   2.1 Ultrashort laser pulses ............................................ 15
   2.2 Carrier Envelope Phase .......................................... 21
   2.3 Self-Phase Modulation ........................................... 24
   2.4 Hollow fibre pulse compression .................................. 26
   2.5 Characterisation of few-cycle IR pulses ....................... 29
   2.6 Strong-field physics ............................................... 37
   2.7 High Harmonic Generation ....................................... 41
   2.8 Attosecond pulse generation .................................... 50
   2.9 Characterisation of attosecond pulses ......................... 54
   2.10 Theory of condensed matter processes related to this thesis 61

3 An attosecond source 67
   3.1 The drive laser - Chirped Pulse Amplification .................. 67
   3.2 Carrier envelope phase stabilisation ............................ 71
   3.3 Hollow fibre pulse compressor .................................. 74
CONTENTS

3.4 Pulse measurement - FROG ............................... 76
3.5 Summary of few-cycle IR light source ..................... 81
3.6 Overview of Beamline .................................... 81
3.7 High harmonic spectra ................................... 89
3.8 Summary of light sources produced by the ASB .............. 93

4 Attosecond metrology .................................. 95
4.1 Experimental setup ....................................... 95
4.2 IR and attosecond pulse trains .............................. 102
4.3 IR and isolated attosecond pulse - Atomic streak camera ... 106
4.4 Summary .................................................. 113

5 Surface Beamline ........................................ 115
5.1 Initial design criteria .................................... 118
5.2 Surface preparation chamber and sample transfer .......... 120
5.3 Experimental chamber and electron spectrometer .......... 123
5.4 Vibration isolation ....................................... 127
5.5 Achieving UHV .......................................... 132
5.6 Summary ................................................ 134

6 Surface investigations .................................. 137
6.1 Photoelectron spectra - rough silver surface ............... 137
6.2 Photoelectron spectra - gold surface with XUV ........... 145
6.3 Two-photon emission from a gold surface .................. 149
6.4 Summary ................................................ 157

7 Summary .................................................. 159

Bibliography ................................................. 163
Chapter 1

Introduction

1.1 Introduction

The atomic unit of time is 24 attoseconds and is defined as the time for an electron to complete 1 rad of an orbit in hydrogen. Attosecond science is rapidly approaching this fundamental unit of time with the shortest isolated pulse measured as 80as [47]. Hitherto instantaneous events can now be timed as a process occurring in terms of attoseconds. Recent experiments have measured a delay of 21 as in photoelectron emission from 2p and 2s orbitals in krypton [111], and a transit time of 100 as has been measured for emission of an electron from a core state in a metal [21].

These measurements have been achieved by using an isolated burst of extreme ultra-violet radiation with an attosecond duration. At field intensities of $10^{13}$ W/cm$^2$ an electron can tunnel ionise from an atom or molecule. Subsequent acceleration in the field and recombination to the parent ion can emit photons in the extreme ultra-violet a process referred to as high harmonic generation [25]. The use of
waveform controlled laser pulses containing only a few oscillations of the laser field [113] allow this process to be restricted to a single half cycle of the laser field, giving rise to the characteristic attosecond timescale of the XUV emission.

The term ‘Plasmonics’ was coined in 2001 [87] but related phenomena have been observed as far back at the 4th century (figure 1.1). Work throughout the 20th century unified ‘strange’ observations of light and radio waves interacting with metallic surfaces to explain the coupling of electromagnetic waves to two dimensional surfaces and sub wavelength dimensioned structures.

The recent development of nano-fabrication techniques allowing metallic shapes to be ‘written’ onto surfaces with nanometer precision has driven the recent boom in the area. For telecommunications, plasmonic effects have gone from being an irritation causing losses into metals to a hugely important topic. Nano structures are being developed to couple the large bandwidth of light needed for modern communications into small components on a chip smaller than the diffraction limit [36].

The localisation of fields gives rise to significant enhancement of an electric field which has been used to dramatically improve techniques such as Raman spectroscopy allowing sensing of single molecules [72], and of great relevance to this thesis a structured surface has been used to enhance an output of a femtosecond oscillator to allow high harmonic generation to occur [69].

My PhD has been focused on the interface between these two fields of physics. As part of a team, I have produced and measured an isolated attosecond pulse produced by high harmonic generation. As the foundation student on a new surface science initiative in the group, I have also designed and constructed a sophisticated ultra high vacuum system to allow ultrafast electron dynamics to be probed with our attosecond source. Through my work the attosecond beamline now has the
1.1. INTRODUCTION

(a) Illuminated from front  (b) Illuminated from back

Figure 1.1: Lycurgus cup. Plasmonic effects were utilised by Romans in the 4th century. Photons couple to plamsons on nanoscale particles of silver and gold in the glass, allowing transmission of the red photons and scattering of blue [5]

capability to measure the temporal dynamics of an enhanced plasmonic field.

Author’s contribution to work

I have played a major role in all the aspects of the experimental work detailed in this thesis. As part of a team I have built the atomic streak camera apparatus and developed the experimental method. I have maintained and optimised the few-cyle IR source used to produce an isolated attosecond pulse. I have been involved with all aspects of the atomic streaking measurements, while the analysis was conducted by Mr T Witting.

I have built the gas targets used to produce high harmonics and as a part of a team built and calibrated the XUV spectrometer.
I have designed and constructed the surface science apparatus described in this thesis, with Dr T Uphues being a source of advice throughout. I have been the principle coordinator for the surface science experiments and the point of contact for collaboration with Professor Stefan Maier’s group for the design and production of samples. I have carried out all the analysis of the data presented in this thesis relating to measurements from surfaces.

At the beginning of my PhD I was involved with collaborative experiments using the XUV source involving Reading, UCL and Birmingham universities. This work is not covered in my thesis.

As part of a team I have maintained the vacuum beamline and Femtolaser system throughout my PhD.

The following papers are in preparation from work carried out during my PhD:

**A system for doing ultrafast and attosecond science** Christopher Arrell et al.

**Band structure effects in highly non-linear photoelectron emission from graphite with femtosecond laser pulses** Emma L. Catton, Andrey Kaplan, Joseph S. Robinson, Miklos Lenner, Christophe Huchon, Christopher Arrell, Jonathan P. Marangos, John W. G. Tisch and Richard E. Palmer

**Interferometric studies of high kinetic energy electron emission generated by intense few-cycle laser pulses** Emma L. Catton, Andrey Kaplan, Joseph S. Robinson, Miklos Lenner, Christophe Huchon, Christopher Arrell, Jonathan P. Marangos, John W. G. Tisch and Richard E. Palmer

and have presented talks or posters at the following conferences:

Invited Speaker COAST Ultrafast Intense Laser Science Symposium, University
1.1. **INTRODUCTION**

of Tokyo, 2008

Speaker Ultrashort Pulse Sources Rank Symposium, Grasmere, 2009

Attosecond Source Development. Poster exhibited at Photons, Atoms and Qubits, Royal Society, 2007

Probing proton dynamics in molecules on an attosecond timescale. Poster exhibited at Attosecond Summer School, Bad Honef, 2007

**Organisation of thesis**

In Chapter 2 I present theory and background of the science relating to work described in this thesis. Chapter 3 presents the Attosecond beamline and details the light sources it produces. The atomic streak camera experiment is described in Chapter 4. Chapters 5 and 6 detail the surface apparatus constructed during my PhD and its use to study ultrafast electron dynamics of a surface. Chapter 7 summaries the work conducted during my PhD and discusses the possible future work in the Attosecond laboratory.
Chapter 2

Theory

Theory relating to the production, characterisation and control of few-cycle pulses is described in the first part of this chapter. The theory of high harmonic generation, isolated attosecond pulses and techniques for their measurement follows. The final section covers electron emission from surfaces and surface plasmon coupling.

2.1 Ultrashort laser pulses

Description of Ultrashort pulses

For few-cycle pulses it is useful to describe the electric field as a product of a slowly changing envelope and an oscillating carrier:

\[ E(z, t) = A(z, t) e^{i(\omega t - kz + \phi_0)} \]

where \( A(z,t) \) describes the varying amplitude of the envelope, \( k = \omega/c \) is the wavenumber and \( \phi_0 \) is called the carrier envelope phase (CEP). The quantity

\[ E(z, t) = A(z, t) e^{i\phi(z,t)} \]  \hspace{1cm} (2.1)
\( \phi(z,t) \) is called the temporal phase, which describes the instantaneous frequency (the time dependent evolution of the carrier) as:

\[
\omega(z,t) = \frac{\partial \phi(z,t)}{\partial t} .
\]  

(2.2)

One can also describe the pulse in the spectral domain by taking the fourier transform of equation 2.1. This description is useful for few-cycle pulses where we will see relative separation or chirp between frequency components needs to be addressed. The electric field can be written in the spectral domain according to:

\[
E(z,\omega) = A(z,\omega)e^{-i\phi(z,\omega)} = \int_{-\infty}^{\infty} E(z,t)e^{-i\omega t} dt ,
\]

(2.3)

where \( \phi(z,\omega) \) is the spectral phase.

There is a fundamental limit to how short a pulse can be for given bandwidth. This is encapsulated in the time bandwidth product (TBP):

\[
\Delta \omega \Delta t \geq a ,
\]

(2.4)

where \( \Delta \omega \) is the FWHM of the frequency spectrum and \( \Delta t \) is the temporal FWHM of the pulse. The constant \( a \) is unique to different pulse shapes, as shown in table 2.1. The minimum pulse duration or ‘transform limited’ pulse is only achieved when there is no temporal spreading or chirp of the different frequency components of a pulse. In other words the spectral phase \( \phi(z,\omega) \) of the pulse needs to be flat across the entire bandwidth of the spectrum. Whereas this issue may be overlooked for longer pulses of several hundreds of femtoseconds, equation 2.4 shows us that for a few femtoseconds one requires a spectrum of several hundred nanometers. In order to preserve a close to transform limited pulse one needs to maintain the flat spectral phase and pay close attention to how different wavelengths propagate through a medium, in other words the chromatic dispersion.
2.1. ULTRASHORT LASER PULSES

Table 2.1: Temporal intensity profiles and their time-bandwidth product of commonly used pulse shapes for few-cycle pulses

<table>
<thead>
<tr>
<th>Pulse shape</th>
<th>Temporal intensity profile (FWHM)</th>
<th>Time bandwidth product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gaussian</td>
<td>$e^{-(4\ln 2)\Delta t^2}$</td>
<td>0.441</td>
</tr>
<tr>
<td>Sech$^2$</td>
<td>$\text{sech}^2 \left( \frac{2n(1+\sqrt{2})\Delta t}{\Delta \tau} \right)$</td>
<td>0.315</td>
</tr>
<tr>
<td>Square</td>
<td>1 for pulse, 0 outside</td>
<td>0.886</td>
</tr>
</tbody>
</table>

Dispersion

The common expression for wavenumber:

$$k(\omega) = \frac{\omega}{c}, \quad (2.5)$$

is only valid for the propagation of light in a vacuum. One must include the wavelength dependent term for the refractive index $n(\omega)$ to fully describe the dispersion of broadband pulses close to the transform limit.

$$k(\omega) = \frac{\omega n(\omega)}{c}. \quad (2.6)$$

One can see that the group velocity $v_g$ and phase velocity $v_p$ of a pulse has a wavelength dependence in a medium (air or glass) with the expressions becoming:

$$v_p = \frac{c}{n(\omega)} \quad \text{and} \quad v_g = \frac{c}{n(\omega) + \omega \frac{dn(\omega)}{d\omega}}. \quad (2.7)$$

We are interested in the effect this wavelength dependence will have across the pulse. To see this one can use a Taylor expansion of the spectral phase given by:

$$\phi(\omega) = \phi_0 + \sum_{n=1}^{\infty} \frac{1}{n!} \frac{d^n \phi(\omega)}{d\omega^n} \bigg|_{\omega_0} (\omega - \omega_0)^n. \quad (2.8)$$

As we saw before $\phi_0$ is the carrier envelope phase. The second term of the expansion $\frac{d^n \phi(\omega)}{d\omega^n} \bigg|_{\omega_0}$ is the time taken for the pulse to propagate through a material and is
called the group delay. Neither of these terms alter the shape of the pulse envelope.
The third term, \( \frac{d^2\phi(\omega)}{d\omega^2} \mid_{\omega_0} \), is called the group delay dispersion (GDD) and describes the stretching of a pulse in a medium. For higher bandwidths the third and fourth orders also introduce dispersion and are called third order dispersion (TOD) and fourth order dispersion (FOD).

When the GDD is positive a pulse is positively chirped with longer wavelengths arriving before shorter ones, this is called positive dispersion and is common for materials at 800nm. One can pre-compensate for positive dispersion by negatively chirping a pulse beforehand. This technique is commonly used in modern lasers: a negative chirp is applied to a pulse in the oscillator to pre-compensate for positive dispersion of optics in the amplifier and compressor, resulting in an output pulse with relatively flat phase.

**Generation**

Femtosecond lasers all rely on the production of short broadband pulses from a laser cavity in an oscillator. In the cavity a gain medium is pumped by a light source causing a population inversion. Amplification occurs when a photon in the cavity is resonant with an allowed transition in the gain medium releasing a photon into the cavity. Inside the cavity one will have a series of modes with different phases propagating back and forth through the gain medium between the end cavity mirrors. The wavelength of the different modes is given by \( L = \lambda_n/2n \) where \( L \) is the cavity length. Only modes with a frequency within the gain bandwidth of the gain medium will be amplified in the cavity. The output of this cavity will be CW and fluctuate as the modes are adding constructively and destructively with the average power given by:
\[ I_{CM} = \left| \sum_{0}^{N} E_n e^{i(n\omega_0 t + \phi_n)} \right|^2, \]  

(2.9)

where \( N \) is the number of modes in the cavity, \( E_n \) is the electric field of the \( n^{th} \) mode and \( \omega_0 \) is the fundamental mode of the cavity. The average output of such a cavity is \( \propto N E_0^2 \) where an increase in the number of modes oscillating in the cavity would increase the intensity of the output.

Forcing all the modes in a cavity to lock to a single phase or ‘mode-locking’ allows this output to be increased so the intensity is \( \propto N^2 E_0^2 \) [79]. If all the longitudinal modes are forced to oscillate with the same phase then they will constructively interfere at one location in the cavity. Several methods have been developed over the years to passively or active mode-lock a cavity. Passive methods include using a saturable absorber which has a decreasing loss for increasing intensity, favouring the production of short intense pulses. Active methods include using acusto-optic crystals to modulate cavity losses to promote intense pulses. These methods work well for oscillators producing longer pulses, but are limited by the larger bandwidth one needs to support a ultra-short pulse. The following references provide a review of the development of different mode locking methods and ultra fast laser technology [30, 44, 65]

In 1991 Kerr-lens mode locking was developed to preferentially amplify the most intense mode [118]. If random modes are set oscillating in the cavity (by quickly distorting the length of the cavity) one will have many modes passing through the gain medium. As the intensity increases, the more intense modes will have a high enough intensity to alter the refractive index of the gain medium by:

\[ n = n_0 + n_2 I. \]  

(2.10)
For higher intensities the altered refractive index will focus that mode, increasing the overlap with the pump beam and hence the gain of that mode. After many round trips through the gain medium the intensity of a single mode will be significantly greater than the others.

**The B-integral**

As the intensity of laser pulses increases one has to account more and more for non-linear process which can influence the pulse. The intensity dependent refractive index $n_2$ will introduce non-linear phase which can cause a change in a beam divergence and ultimately self focusing. Over a length $L$ the accumulated non-linear phase is given by [117]:

$$B = \frac{2\pi}{\lambda} \int_0^L I(z)n_2(z) \, dz ,$$

(2.11)

where $I(z)$ is the intensity of the laser. To avoid damage and distortion of the beam profile laser systems are designed to limit the value of $B < 1$.

**Chirped Pulse Amplification**

To generate broadband intense femtosecond pulses one has to carefully consider damage to the laser optics caused by the high intensities being produced, especially the dangers of an increasing B-integral causing self focusing. One can either increase the beam diameter, and build a laser with large diameter optics, or use a more economical approach—chirped pulse amplification (CPA)—which was proposed in 1985 to combat this problem [121].
The short broadband near transform limited pulses that were discussed in the previous section are given a chirp by some frequency dependent process such as dispersion in a material or angular dispersion from gratings. This is called pulse stretching and greatly reduces the peak power of the pulse by increasing the pulse length by several orders of magnitude. This pulse can now pass through the amplifier without damaging any of the optics. After amplification the energetic pulses can be compressed down to near transform limited pulses using prisms or gratings just to the limit where self-focusing may occur. CPA systems have allowed table-top laser systems to reach peak intensities of $10^{18}$ W/cm$^2$ [13] and facility based CPA systems can achieve intensities three orders of magnitude greater [27]. The CPA laser used for the experiments described in this thesis has the following stretching and compression characteristics:

$$\text{Oscillator} - 10\text{fs} \xrightarrow{\text{Stretcher}} \text{Amplifier} - 3\text{ps} \xrightarrow{\text{Compressor}} \text{Output} - 30\text{fs}.$$

### 2.2 Carrier Envelope Phase

Carrier envelope phase (CEP) is the relative difference in the peak of the carrier of a pulse and the peak of the envelope and is given in the description of the electric field of a laser pulse:

$$E(t) = E_0(t)\cos(\omega t + \phi_0),$$

where $E_0(t)$ is the carrier envelope and $\omega$ is the carrier frequency and $\phi_0$ is the carrier envelope phase. Small temperature variations, vibrations and air flow in the oscillator cause the CEP to vary as the beam passes through dispersive material. The offset is caused by the difference in the propagation speeds of the carrier wave and pulse envelope in the dispersive material [51, 59].
CEP can be neglected for many-cycle pulses where there is a slow decay of the envelope, however for few-cycle pulses the offset between the peak of the carrier and envelope has a significant effect on the overall intensity of a pulse and is evident in non-linear processes [99].

One can see in figure 2.3 that there is a significant difference (∼ 10%) in the intensity when there is a π/2 offset in the CEP causing significant differences between pulses for non-linear process. This variation has led to a requirement that modern state of the art few-cycle laser systems need their CEP locked to a set value. This can be achieved by carefully examining the source of the CEP.

Figure 2.1: A 3fs 800nm pulse with different CEP, top left at a CEP value of 0, top right a CEP value of π/2, the lower figures show the intensity profile of the pulses.
2.2. CARRIER ENVELOPE PHASE

Figure 2.2: In red, schematic of the frequency comb associated with an oscillator output, with discreet peaks separated by $\omega_{rep}$, the repetition rate of the oscillator. Shown in black is a representation of the comb extending down to zero frequency where the first non zero spectral component is given by $\omega_{CEP}$. In reality the components shown in black have no power. Figure adapted from [105]

The pulse spectrum from an oscillator cavity is made of many modes of integer multiples of the repetition frequency, $\omega_{rep}$ of the oscillator. While in practice the intensity of these modes goes to zero at the extremities of the oscillator bandwidth, one can imagine them extending to zero frequency. If the carrier and envelope velocities in the oscillator were perfectly matched there would be a zero offset in the CEP and the lowest mode would be at zero. In reality, the lowest order mode is offset from zero by an amount $\omega_{CEP} = d\phi_0/dt$ [125] hence:

$$\omega_n = n\omega_{rep} + \omega_{rep}.$$  \hspace{1cm} (2.13)

By broadening the oscillator spectrum to a whole octave (where the modes $\omega_n$ and $2\omega_n$ are contained) and then frequency doubling a replica a beat signal is seen where the two spectra overlap given by $2\omega_n - \omega_m$. This is equal to:
Figure 2.3: A schematic of the f - 2f measurement of CEP. The original spectrum is broadened to span an octave and a replica is frequency doubled. The interference of the two produces a beat signal with contains a component of $\omega_{\text{CEP}}$.

$$2\omega_n - \omega_m = 2n\omega_{\text{rep}} + 2\omega_{\text{CEP}} - 2n\omega_{\text{rep}} - \omega_{\text{CEP}} = \omega_{\text{CEP}}, \quad (2.14)$$

where $m$ corresponds to the $m^{th}$ mode of the doubled spectrum. This beat signal can be stabilised by a fast electronic feedback system to the oscillator to control the value of $\omega_{\text{CEP}}$. The is commonly done by feedback to an acousto optic modulator in the pump laser beam. Small alterations in the pump beam intensity change the non-linear refractive index of the Ti:saph crystal causing small changes to the group and phase velocities of pulse in the oscillator cavity therefore controlling the CEP.

### 2.3 Self-Phase Modulation

Self-phase modulation (SPM) is a non-linear process where the spectral bandwidth of a pulse can be broadened by a time dependent modulation of the refractive index of a medium known as the Kerr effect. SPM is routinely used to generate ultra short pulses where an initial laser intensity is high (for example $10^{13}\text{Wcm}^{-2}$ in a gas) an intensity which can easily be achieved with table top CPA systems. At
these intensities the second term of the refractive index (as shown in equation 2.10) is relevant:

\[ n(I) = n_0 + n_2 I(t) \]

where \( n_0 \) is the material refractive index and \( n_2 \) is the non-linear refractive index:

\[ n_2 = \left( \frac{2\pi}{n_0} \right)^2 \chi^{(3)}(\omega) \]

\( \chi^{(3)} \) is the third order non-linear susceptibility with typical values for gases given in Table 2.2. Writing the instantaneous frequency as the rate of change of the temporal phase we get:

\[ \omega(z,t) = \frac{\partial \phi(z,t)}{\partial t} = \omega_0 - \frac{\omega_0 n_2 z dI}{c dt} \]

where one can see the frequency of the pulse depends on the rate of change of the intensity. For a short pulse with a rapidly changing envelope at the rising edge we will have \( dI/dt > 0 \) causing a decrease (red shift) in the frequency. Conversely when \( dI/dt < 0 \) there is an increasing (blue shifting) in frequency.

Table 2.2: Ionisation potentials and third order hyperpolarisability for gases typically used for SPM. Data from [53]

<table>
<thead>
<tr>
<th>Gas</th>
<th>Ionisation potential [eV]</th>
<th>( \chi^{(3)}_{1111}(-\omega_2,\omega_1,\omega_1,\omega_1) \times 10^{-39} \text{ esu} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xenon</td>
<td>12.1</td>
<td>217</td>
</tr>
<tr>
<td>Krypton</td>
<td>14.0</td>
<td>69.8</td>
</tr>
<tr>
<td>Argon</td>
<td>15.8</td>
<td>24.8</td>
</tr>
<tr>
<td>Neon</td>
<td>21.6</td>
<td>1.79</td>
</tr>
<tr>
<td>Helium</td>
<td>24.4</td>
<td>1.00</td>
</tr>
</tbody>
</table>
2.4 Hollow fibre pulse compression

Pulse compression systems using SPM in solid materials have been able to produce sub 10fs pulses. However such methods are limited for higher energies by surface damage and damage caused to the bulk material through self-focusing. Gas is now commonly used in hollow fibre wave guides at higher energies (upto 5mJ) to broaden a pulse where an increase in the bandwidth of several hundred nanometers can be achieved at transmission of $\sim 60\%$. The wave guide also acts to maintain a high intensity along the fibre.

To design a hollow fibre pulse compression system one needs to balance different factors, namely increased broadening compared to decreasing transmission along a fibre.

Many modes can propagate along a hollow fibre wave guide when the beam is coupled into the fibre entrance. For a dielectric hollow waveguide the lowest losses are found at the $EH_{11}$ mode described by [8]:

$$I(r) = I_0 J_0^2\left(\frac{2.405r}{a}\right),$$  \hspace{1cm} (2.18)

where $I_0$ is the peak intensity, $J_0$ is the zero order bessel function, $a$ is the radius of the hollow fibre and $r$ is the distance from the fibre centre. The coupling efficiency of the laser will depend on the diameter of the focused beam at the entrance of the hollow fibre. A tightly focused beam will quickly diverge in the fibre coupling into less efficient modes, and a too large beam will cause losses at the fibre entrance. The optimum beam size is give by [95]:

$$\eta = \frac{4\left[\int_0^\infty r J_0(\frac{u1m_r}{a})exp\left(-\frac{r^2}{w^2}\right)dr\right]^2}{w^2 \int_0^\infty r J_0^2(\frac{u1m_r}{a})dr},$$  \hspace{1cm} (2.19)
where \( u_{1m} \) is the \( m^{th} \) root of \( J_0(u_{1m}) = 0 \) and \( w \) is the \( e^{-2} \) beam radius. \( \eta \) is greatest when \( w = 0.65a \). In this case coupling into the fibre is around 98%.

As the wave propagates along the fibre there will be losses into the fibre wall. For the \( EH_{11} \) mode the attenuation coefficient is given by [94]:

\[
\alpha = \left( \frac{2.4}{2\pi} \right)^2 \frac{\lambda^2}{a^3} \frac{v^2 + 1}{\sqrt{v^2 + 1}}, \tag{2.20}
\]

where \( v \) is the ratio of the refractive index of the fibre wall and the internal medium \( i.e. \) gas. Equation 2.20 shows the transmission can be increased by increasing the refractive index of the fibre wall by for example coating the inside of the fibre with a metallic surface \( e.g. \) silver. Increasing the diameter of the fibre \( a \) would also decrease the losses into the wall, however this would decrease the peak intensity in the fibre.

The laser intensity is another important consideration. If the intensity is too high the gas in the fibre will be ionised causing defocusing of the beam in the fibre. A novel method has been introduced to overcome this problem - by matching the decreasing laser intensity along the fibre with increasing gas pressure [106]. This is achieved by a differentially pumped system pumping gas along the fibre instead of a more conventional statically filled system. The lower gas pressure at the entrance to the fibre also reduces plasma formation before the entrance which will reduce coupling. The pumping sets up a pressure gradient described by:

\[
p(z) = \left[ p_0^2 + \frac{z}{L}(p_L^2 - p_0^2) \right]^{1/2}, \tag{2.21}
\]

substituting this in for the pressure into the relation:

\[
\Delta \omega = \frac{0.86}{T_0} \int_0^L \gamma(z)P(z)dz \quad \text{where, } P(z) = P_0 e^{-\alpha z}, \tag{2.22}
\]
where:

$$\gamma z = \eta_2 p(z)\omega_0/cA_{eff},$$  \hspace{1cm} (2.23)

given by [106] for the bandwidth produced by SPM where $z$ is the distance along the fibre, $L$ is the length of the fibre, $T_0$ is the temporal half width of the pulse and $P(z)$ is the peak power $\xi$ is the coupling efficient and $\alpha$ is the coefficient of attenuation along the fibre, one gets:

$$\Delta \omega = \frac{0.86\omega_0 n_2 I_0 \xi P_0 p(L)}{T_0 c A_{eff}\sqrt{L}} \int_0^L \sqrt{ze^{-\alpha z}} \, dz,$$  \hspace{1cm} (2.24)

where $\eta_2$ is the non-linear response of the medium, $A_{eff}$ is the effective mode area of the fibre. It is assumed that $p_0$ is zero (i.e. the pressure at the entrance to the fibre). One can see from equation 2.24 that the total broadening is linear with pressure and initial intensity and non-linear with fibre length. Suitable gases for spectral broadening are argon and neon. Argon is better suited to lower intensities as $n_2$ of Ar is approximately 14 times larger than Ne (see table 2.2), however its lower ionisation potential (15.8eV) causes ionisation at the fibre entrance for moderate intensities. For this reason neon is preferred for more energetic pulses.

The spectrally broadened pulse out of a hollow fibre will have a positive chirp. To compress this pulse to have near flat spectral phase a negative GDD needs to be applied. Multilayer chirped mirrors have been used since the late 60’s for this purpose [126]. These are multi-layer dielectric highly reflective broadband mirrors with layer thicknesses that vary in a controlled manner. Different wavelengths are reflected at different interfaces in a mirror (figure 2.4). The chirped mirrors in our few-cycle laser system introduce $\simeq -50fs^2$ per reflection. A chirped mirror compressor can be built from several mirrors allowing a different number of reflections to introduce the desired value of negative GDD to a pulse. Modern mirrors can
2.5. Characterisation of few-cycle IR pulses

Autocorrelation

Common electrical devices such as photodiodes are too slow to measure a femtosecond pulse (state of the art oscilloscopes can measure 10’s of ps). The simplest method for measuring femtosecond and picosecond pulses is autocorrelation. This method uses the interaction of a pulse with itself in a nonlinear medium to ascertain the time duration of the pulse.

The initial autocorrelation technique (Figure 2.5a) overlaps two pulses collinearly
in a non linear medium such as β-barium borate (BBO) or potassium dihydrogen phosphate (KDP) [14]. By delaying one pulse relative to the other and measuring the intensity of a second harmonic signal created in the crystal an interferometric trace is produced, giving an autocorrelation function which can be measured on a slow detector.

\[ I_{ac}(\tau) \propto \int_{-\infty}^{\infty} |(E(t) + E(t - \tau))|^2 dt. \]  

(2.25)

This approach allows some phase information and chirp to be retrieved - but is still unreliable for short pulses as different shaped pulses of equal length will produce different interferometric traces [31]. The autocorrelation trace is also constrained to be symmetric reducing retrieved information about a pulse shape.

Interferometric or scanning autocorrelation can also be applied to other intensity related processes. Figure 2.6 is an autocorrelation of two 30fs pulse replicas focused and overlapped in a neon gas. This data was taken in the gas phase experimental chamber with experimental details given in section 4.1. Photoelectrons produced by above threshold ionisation (see section 2.6) are collected from different delay positions.

Interferometric autocorrelation was a large step forward in time resolved measurement by using devices with a response time far longer than the pulse being measured. However it does require a large number of laser pulses and tells us nothing about shot to shot fluctuations. A single-shot autocorrelator (figure 2.5b) allows the temporal profile of a pulse to be measured in a single shot [97].

In this device, replica pulses enter a non linear crystal with angle \( \theta \) creating a second harmonic signal along the bisector of the two beams. Figure 2.7 shows that the spatial dimension of this autocorrelation signal is given by the duration of the
2.5. CHARACTERISATION OF FEW-CYCLE IR PULSES

(a) Scanning autocorrelator  (b) single-shot autocorrelator

Figure 2.5: Schematics of a scanning (a) and single-shot autocorrelators (AC) (b). A scanning AC temporally and spatially overlaps two pulse replicas in a non-linear medium. The envelope of the resulting signal gives information about the pulse envelope. A single-shot autocorrelator maps the temporal envelope of two pulse replicas into the width of the signal from a non-linear medium such as a BBO crystal.

Figure 2.6: An interferometric measurement of ATI photoelectrons from neon gas. Two pulse replicas of a 30fs IR pulse are temporally overlapped in a gas target.
Figure 2.7: Pulse replica overlap in a second harmonic crystal. The duration of the pulse is mapped into the spatial profile of the second harmonic signal measure on a CCD. A longer pulse will produce a broader second harmonic image on the CCD.

Pulses and the angle between them described by:

\[
x = \frac{c \tau}{\sin(\theta/2)}.
\]  

(2.26)

As \(x\) is proportional to \(\tau\) the device can easily be calibrated by inserting a known delay into one pulse (eg by moving a mirror by a set distance). The profile of the autocorrelation function is given by:

\[
I_{ac}(\tau) = \int_{-\infty}^{\infty} I(t)I(t - \tau) \, dt.
\]  

(2.27)

One can see that from equation 2.27 the autocorrelation function does not provide any phase information about the pulse being measured. While this method is reliable for longer (10s of fs) pulse, it is unreliable for few-cycle pulses.
2.5. CHARACTERISATION OF FEW-CYCLE IR PULSES

Frequency-Resolved Optical Gating

Frequency resolved optical gating was developed by Trebino in the early 1990s to remove the ambiguity of an autocorrelation measurement by retrieving both the intensity and phase of a pulse [127]. Various forms of FROGs have been developed using different optical gates [128, 62], but the most common in the field of few-cycle IR pulses is second harmonic generation FROG or SHG FROG [28]. Pulse measurements of the few-cycle source used for this thesis were routinely characterised by a SHG FROG (details are given in section 3.4).

A single-shot autocorrelator can be modified to become a FROG by spectral resolving the pulse in the plane perpendicular to the temporal resolution i.e. by adding a slit and grating before a CCD camera. Figure 2.8 shows a typical FROG trace.

Figure 2.8: A typical FROG trace of a 10fs pulse from the SHG FROG used in the thesis. The y-axis is spectrally resolved using a grating and slit before the camera. The x-axis is temporally resolved and is produced by two pulse replicas crossing in a second harmonic generating crystal.
The electric field is related to the FROG trace by:

\[ I_{\text{frog}}(\omega, \tau) = \left| \int_{-\infty}^{\infty} E(t) g(t - \tau) e^{-i\omega t} dt \right|^2, \tag{2.28} \]

where \( g(t - \tau) \) is the gating function. For a SHG FROG it is given by:

\[ g(t - \tau) = |E(t - \tau)|^2. \tag{2.29} \]

The pulse cannot be directly reconstructed from the FROG trace - an algorithm is used. The algorithm generates random pulses and then compares their SHG FROG trace to the measured FROG trace and iteratively reducing the error between the two [29]. This may seem a slow and blind approach at reconstruction. However the process can be improved to ensure what you reconstruct is real. For example integrating along the frequency axes of the trace gives the temporal marginal which can be used to ensure a reconstructed pulse is not shorter than the transform limit. By sampling the spectrum before the SHG crystal one can ensure that the correct spectral amplitudes are also used.

Similarly to a single-shot autocorrelator a FROG produces a symmetrical trace where the time direction can not be distinguished. However as the time evolved spectral phase is resolved one can see if a pulse has a sloping phase and can hence use the reconstructed pulse to check one has optimal compression.

**Spectral Phase and Intensity by Direct Electric field Reconstruction**

An alternative pulse diagnostic common in the few-cycle IR field is Spectral Phase and Intensity by Direct Electric field Reconstruction (SPIDER) [55]. A clear advantage of SPIDER over a FROG measurement is the ability to reconstruct the
2.5. CHARACTERISATION OF FEW-CYCLE IR PULSES

electric field of a pulse with a simple algorithm as opposed to the longer FROG reconstruction. SPIDER allows online pulse characterisation with full reconstructed phase. This is a very useful tool when trying to optimise the compression of a pulse produced by a complex system.

Figure 2.9 is a block diagram of a typical SPIDER set up. Initially three replicas of the pulse are created. Two are separated with a time delay $\tau$ and the third replica of the pulse is strongly chirped and stretched typically in a long rod of glass.

Figure 2.9: Schematic of a SPIDER. Three pulse replicas are created, two of which are temporally delayed by $\tau$ and then interfered in a non linear crystal with different frequencies of the third stretched replica. The output or ‘SPIDER signal’ is encoded with the phase of the original pulse, which is subsequently retrieved by performing a fourier transform of a interferogram, filtering and then an inverse fourier transform. Figure from [105]

The three pulses then overlap in a nonlinear crystal resulting in upconversion of their spectra. It is important that the time delay $\tau$ and the stretching of the third pulse is long enough to ensure that the two short pulses are upconverted with distinct frequencies. After the crystal the two spectrally sheared pulses are interfered in a spectrometer giving the following interference pattern which contains
information of the phase from the initial pulse:

\[ S(\omega) = |E_1(\omega)|^2 + |E_2(\omega)|^2 + 2|E_1(\omega)||E_2(\omega)|\cos[\delta\phi(\omega) + \omega\tau] \] . (2.30)

\( E_1 \) and \( E_2 \) refer to the electric field of the two short pulse replicas after the spectral upconversion and the difference in their spectral phase \( \delta\phi(\omega) \) where:

\[ E_1(\omega) = E(\omega + \omega_0) \] , (2.31)
\[ E_2(\omega) = E(\omega + \omega_0 + \Omega) \] , (2.32)
\[ \delta\phi = \phi(\omega + \omega_0 + \Omega) - \phi(\omega + \omega_0) \] . (2.33)

The first two terms of equation 2.30 describe the upconverted replica (shown in the figure) while the last term contains the phase information and \( \Omega \) is the spectral shear between the two pulses.

If we write equation 2.30 as:

\[ S(\omega) = A_{DC}(\omega) + A_{AC}(\omega)e^{i\omega\tau} + A_{AC}^*(\omega)e^{-i\omega\tau} \] , (2.34)

where \( A_{DC}(\omega) = |E_1(\omega)|^2 + |E_2(\omega)|^2 \) and \( A_{AC}^*(\omega) = |E_1(\omega)||E_2(\omega)|e^{-i\delta\phi(\omega)} \).

The Fourier transform gives us:

\[ S(t) = A_{DC}(t) + A_{AC}(t - \tau) + A_{AC}^*(t + \tau) \] , (2.35)

the phase information is now contained in the two terms \( \pm \tau \) around \( t \). By isolating a single phase term and performing an inverse fourier transform the phase of the pulse and intensity of the pulse is given for a set value of \( \Omega \). Stepping the process for several values of \( \Omega \) allows the temporal profile of the pulse to be extracted.
2.6. STRONG-FIELD PHYSICS

While SPIDER can be used as an online diagnostic of ultrashort pulses at kHz repetition rate [73, 74], the technique is very sensitive to the input spectrum. Any areas of the spectrum with a low intensity lead to difficulties in extracting the phase from the interferogram. Another practical consideration is creating three pulse replicas of the original pulse without introducing dispersion in one.

2.6 Strong-field physics

Ponderomotive energy

An oscillating electric field of a laser pulse $E_0 \cos(\omega t)$ exerts a force $qE_0 \cos(\omega t)$ on a charged particle causing it to oscillate. The cycle-averaged kinetic energy of the oscillating particle as it moves in the field is called the ponderomotive energy and for an electron is given by:

$$U_p [eV] = \frac{e|E_0|^2}{4m_e\omega^2} \approx 9 \times 10^{-14} I \lambda^2 , \quad (2.36)$$

where $m_e$ is the mass of an electron, $e$ the electron charge, $\lambda$ is given in microns and $I$ has units of Wcm$^{-2}$. $U_p$ is a useful unit in strong field physics and non-linear processes. It will be shown later that this value determines the maximum photon energy obtained in high harmonic generation or the highest electron energy release in above threshold ionisation.

Ionisation

At the high intensities ($I>10^{13}$Wcm$^{-2}$) produced by a laser field several ionisation processes are possible in gases. Electrons can be liberated from atoms and molecules despite an IR photon energy of 1.5eV being significantly lower than the
ionisation potentials of around 15eV. Two mechanisms, - above threshold ionisation (ATI) and multi-photon ionisation (MPI) overcome the ionisation barrier by using several photons to produce ionisation. Two other mechanisms rely on the high intensity of the electric field in a laser pulse to distort the potential of an atomic well to allow an electron to be liberated by either tunnel ionisation or over the barrier ionisation (OTBI).

Multi-photon mechanisms have been observed at laser intensities between $10^{12}$ - $10^{13}$ W cm$^{-2}$. At these intensities the photon flux is sufficient that it is probable an electron will absorb several electrons. The energy gained by the electron is sufficient for it to overcome the binding energy of the atom resulting in ionisation. The rate of this process is described by [132]:

$$\Gamma_N = \sigma_N I^N,$$  \hspace{1cm} (2.37)
where \( \sigma_N \) is the cross section and \( I \) is the laser intensity and \( N \) is the minimum number of photons required for ionisation. If the photon flux is higher the electron can absorb further photons leading to electrons being released with energies separated by the photon energy of the ionising field. This is called above threshold ionisation (ATI) with an example in figure 2.11 which is a spectrum of electrons detected from argon gas measured in the gas phase experimental chamber (see chapter 4) during the course of my PhD. The ionisation was produced by a 30fs IR pulse with an intensity of \( 5 \times 10^{14} \text{Wcm}^{-2} \).

![Figure 2.11: Electron spectrum from an argon gas target. The driving field was a 30fs IR pulse with an intensity of \( 5 \times 10^{14} \text{Wcm}^{-2} \). The peaks are spaced at 1.5eV (1.5eV = \( h\omega_0 \)).](image)

The rate of ATI is given by:

\[
\Gamma_{N+S} = \sigma_{N+S} I^{N+S},
\]

where \( S \) is the number of additional photons absorbed.
At intensities higher than $10^{13}\text{Wcm}^{-2}$ the electric field of the laser distorts the coulomb potential of an atom or molecule. This leads to two other ionisation mechanisms. Tunnelling ionisation is possible at intensities $10^{14}\text{Wcm}^{-2}$ as the potential barrier is lowered (figure 2.10) increasing the probability that an electron will be able to tunnel through and be freed from the atomic potential. The rate of this process in hydrogen is given by:

$$\Gamma(E(t)) = \frac{4}{E(t)} e^{-\frac{2}{3} \frac{E(t)}{U_p}}. \quad (2.39)$$

Rates for more complicated atoms and molecules have been modeled by ADK theory\[9\]. At intensities around $10^{15}\text{Wcm}^{-2}$ the potential barrier of an atom can be suppressed entirely such that the electron is freed from the potential well. This is called over-the-barrier ionisation \[85\]. The intensity that this is possible is given by:

$$I_{OTBI} = 4 \times 10^9 I_p^4 Z^2, \quad (2.40)$$

where $I_p$ is the ionisation potential in eV $I_{OTBI}$ is in Wcm$^{-2}$ and $Z$ is the charge of the ion after ionisation.

Tunnelling and OTBI typically occur at the peak of the laser field. The ionisation process must also occur before the electric field changes direction increasing the potential gradient. The Keldysh parameter, $\gamma$ is the ratio of the time for tunnelling ($T_{tunnel}$) to occur and the laser period ($T_{laser}$) \[64\]:

$$\gamma = \frac{T_{tunnel}}{T_{laser}} = \sqrt{\frac{I_p}{2U_p}}. \quad (2.41)$$

If $\gamma >> 1$ tunnelling ionisation will not be the dominant process as the time for
ionisation to occur is longer than the laser period. For $\gamma << 1$ tunnelling ionisation will dominate over multi-photon processes. For tunnel ionisation to dominate in argon ($I_{p,Ar} = 15.8eV$) a laser intensity of $1.4 \times 10^{14} \text{Wcm}^{-2}$ would be required: an intensity that is easily produced with modern Ti:Sa lasers.

2.7 High Harmonic Generation

Harmonic generation [37] has been observed since the sixties when Franken et al observed second harmonic from a ruby maser [43] and later when New et al predicted and observed third harmonic generation in a gas [93]. These lower order harmonic experiments are described by weak field perturbation theory. In a similar concept to ATI, the increasing harmonic orders are described by an electron absorbing several photons promoting it to a higher virtual state, releasing this gained energy as a single photon. A key characteristic of this regime is a rapidly decreasing intensity of higher harmonics as the probability of absorbing an increasing number of photons decreases, limiting the harmonic order observed to the mid teens [130]. When Ferray in 1988 [41] observed up to the 33rd harmonic with, surprisingly, a plateau in the intensities of the higher orders, it was clear this was a different regime, it was high order harmonic generation.

Single atom response

What was being observed in 1988 and subsequent years [83, 86] was with increasing laser intensity the atomic medium was undergoing tunnelling ionisation, where the electric field of the laser field distorted the atomic potential. A few years later Kulander [75] and Corkum[25] published a semi-classical explanation to explaining HHG, now commonly called the three step model(see figure 2.12):
CHAPTER 2. THEORY

1. First a potential of an atom or molecule is distorted by an intense laser field allowing tunnel ionisation to take place. Immediately after the ionisation the electron is born at the position of the ion with zero kinetic energy.

2. Second the electron experiences the intense laser field and is accelerated away from the ion. When the laser field changes direction the electron wave-packet is accelerated back towards the parent ion.

3. Third the returning wave packet may overlap with the parent ion and there is a probability of recombination occurring. If this takes place the kinetic energy gained by the electron during its excursion in the laser field can be released as a photon.

In a more rigorous quantum approach [82], the process is seen as the original wave function of the ground state electron splitting to form a bound and continuum part. While the electron is in the continuum this part spreads and is treated as a plane wave. A half cycle of the laser field later it returns, and if the laser’s polarisation is close to linear[32], will overlap with the bound wavepacket. This recombination creates an oscillating dipole which causes the harmonic spectrum.

This model is useful explaining many of the features observed in HHG. First the driving of the electron wavepacket through the continuum by the oscillating electric field presents a useful classical explanation of the extension of the cut-off observed with longer wave length driving fields, as the electron wave packet spends longer in the continuum. This excursion time and corresponding spreading of the electron wave packet explains the greatly reduced harmonic yield seen for longer wavelengths. The spreading of the electron wave packet reduces the overlap with the bound wavepacket resulting in a lower intensity of the harmonic emission.
The 3-step model also predicts many of the features observed in HHG. The model also has three stages of calculation using quantum and classical approaches. First Ammosov, Delone and Krainov theory is used to calculate the ionisation rate of the atom [10], giving the electron wavepackets produced and released in the continuum. Corkum’s model treats these wavepackets as being born into the continuum at the same point as the ion and with zero velocity. They are then treated classically in the electric field of the laser by:

\[ E(t) = E_0 \cos(\omega t) e_x + \epsilon E_0 \sin(\omega t) e_y , \]  

(2.42)

where \( \epsilon \) is the ellipticity of the laser field (\( \epsilon = 0 \) is linearly polarised and \( \epsilon = \pm 1 \) is circularly polarised). This already shows that if there is an electric field component in the \( y \) direction the electron will miss the ion on its return path. It is assumed that the intensity of the electric field is low enough to neglect the magnetic field. This is not the case for higher intensities \( \sim 10^{16} \text{Wcm}^{-2} \) where the magnetic field drives the electron away from the parent ion preventing HHG. The classical treatment of the electrons predicts that the highest kinetic energy and electron will gain in the continuum is 3.17 times the ponderomotive energy leading to a cut-off in the harmonic orders dependent on the laser intensity given by:

\[ E_{\text{cut off}} = I_p + 3.17U_p . \]  

(2.43)

The returning electron can recombine with the ion emitting a photon containing the energy gaining in the continuum. The model treats this step with a quantum approach. If the wave function is split into the continuum \( \psi_c \) and the ground state \( \psi_g \) the expectation value of the dipole operator can be written as:
CHAPTER 2. THEORY

Figure 2.12: A semi-classical model of High Harmonic generation. 1. A potential is distorted by an intense laser field allowing tunnel ionisation to take place 2. An electron is born into the laser field, initially accelerated away from the ion, then returning when the laser field changes direction 3. If the electron recombines with the ion the kinetic energy gained in the electron excursion is released as a photon

\[ <\psi|er|\psi>=<\psi_g|er|\psi_c>+<\psi_c|er|\psi_g>+c.c. \]  \hspace{1cm} (2.44)

If the wave function is then assumed to be similar to hydrogen and that the ground state is not depleted the first term of 2.44 dominates.

Corkum then accounts for the continuum wavepacket A, spreading as:

\[ \int A_0^2d^3x = \left[ \int_{E_h-h\omega}^{E_h+h\omega} P(E)dE \right]/V, \]  \hspace{1cm} (2.45)

where \( V = \pi r^2 p \delta t/m_e \) and \( P(E) \) is the probability per unit energy per laser period of the wavepacket crossing the ion with energy \( E \). This is used to calculate the continuum wavefunction as it passes the ion \( i.e. \) when \( x \approx 0 \) given by:
where \( q \) is the harmonic order and \( p_q(x \approx 0, t) \) is the momentum of the electron generating the harmonic order \( q \). This model reproduced many of the features seen including the plateau and the cut-off. Other models that solve the time dependent Schrödinger equation use a quantum orbit description and offer a fuller treatment of the electron in the continuum. Solutions using these approaches predict the relative amplitudes of individual harmonics [24]. They are also useful to study and predict the effect of other driving fields while the electron is in the continuum. Such fields can be introduced and modelled to allow an electron to gain more energy, extending the harmonic cut-off [23].

### Phase matching

The descriptions above deal with the response of a single atom to the HHG process. To observe and use high harmonics, the macroscopic response of a whole ensemble of emitter sources needs to be considered in order to have a meaningful flux of harmonics. HHG can occur at any point where there is overlap with a generating medium and a laser of sufficient intensity, \textit{i.e.} along a focal volume. For each of these emitter sites to contribute constructively their emission needs to be in phase. Other emission that is out of phase will interfere deconstructively.

Taking a simple model of a collimated source propagating along a continuous medium the phase mismatch between the fundamental and harmonic would be:

\[
\Delta k = k_q - q k_1 ,
\]
where $k_q$ is the wavenumber of the $q^{th}$ harmonic and $k_1$ is the wavenumber of the fundamental. If the harmonic propagated at the same phase velocity through the medium as the fundamental the mismatch would be zero. However if there is a difference the phase mismatch, $\Delta k$ is non-zero, then the harmonic intensity will only increase over a distance:

$$L_{\text{coherent}} = \frac{\pi}{\Delta k},$$

where $L_{\text{coherent}}$ is the coherence length.

There are several effects that influence the phase of the harmonics across the focal volume. As the laser is focused into the gas target there is a phase shift induced by the curvature of the wave fronts. The change is called the Gouy phase and the coherence length is given by:

$$L_{\text{gouy}} = \frac{\pi z_0}{q} = \frac{\pi^2 \omega_0^2}{q \lambda_0^2}.$$  \hspace{1cm} (2.49)

Another fundamental effect is caused by the ionisation of the gas medium by the fundamental beam. This produces a free electron population that causes a phase shift of both the laser and harmonics as the refractive index changes. The coherence length for this effect is given by:

$$L_{fe} = \frac{2\pi c \omega_0}{\omega_p(\tau)^2 q},$$

where $q$ is the harmonic order, $\omega_0$ is the laser frequency and $\omega_p$ is the plasma frequency given by:

$$\omega_p = \sqrt{\frac{e^2 n_e}{m \epsilon_0}},$$

where $n_e$ is the density of free electrons.
Calculating phase matching conditions

Phase matching conditions have been calculated across different sections of a focal volume by evaluating the modulus of $k_q$ in [16]. There is phase matching when there is constructive interference between the field at two positions across the medium given by $r_1$ and $r_2$ given by:

$$\text{arg} \left[ P_q(r_1) \exp(i k_q(r_2 - r_1)) \right] = \text{arg} \left[ P_q(r_2) \right] , \quad (2.52)$$

where $P_q$ is the $q$ fourier component of the atomic polarisability. When $r_1$ and $r_2$ are close equation 2.52 becomes [16]:

$$k_q = \nabla \text{arg}(P_q) , \quad (2.53)$$

for intensities used to generate high harmonics the wave vector of the atomic polarisation which is the right-hand side of equation 2.53 can be written as $qe^{ik_1z}$. The standard condition for phase matching is then achieved when:

$$k_q = qk_1^0, k_1^0 = \frac{\omega}{c} . \quad (2.54)$$

The phase matching for the atomic phase $K$ is given by:

$$K(r, z) = \nabla \Phi_{at}(r, z) , \quad (2.55)$$

where $\Phi_{at}$ is [16]:

$$\Phi_{at} = q \omega t_1 - \frac{1}{\hbar} S(p_{at}, t_i, t_0) , \quad (2.56)$$
where $S$ is the semiclassical action in the momentum space along the trajectory and $p_{\text{st}}$ is the canonical momentum of the electron. The wave vector for the Gouy phase is given by:

$$k_1(r, z) = k_0^0 e_z + \nabla \arg \left[ \frac{1}{b + 2iz} \exp \left( -\frac{k_0^0 r^2}{b + 2iz} \right) \right],$$

(2.57)
given in cylindrical coordinates, $e_z$ is the unit vector in the $z$ direction and $b$ is the confocal parameter. These values are plotted in figure 2.13. The plots show that the wave vectors considerably change over the laser focal volume. There will be distinct phase matched regions where:

$$k_q = qk_1 + K.$$  

(2.58)

Figure 2.14 is a vectorial representation of the different phased matched conditions that can be achieved in the focal volume. The figure shows that conditions for phase matching are not met at the focus but after the focus i.e. when the gas jet is placed after the focus of the beam there is phase matching for on-axis harmonics. When the gas target is before the focus, phase matching is met from off-axis harmonics but not for on-axis. These phase matching conditions are readily observable in the lab. Scanning the gas target in the $z$ direction one preferentially sees on or off axis harmonics as predicted.

Another important factor is the absorption of the harmonics by the generating medium, where a balance needs to be found between an increased interaction length and an increase absorption by the medium. In summary, efficient generation of high order harmonics requires careful consideration of the focusing gas targets. Positioning the gas target before or after the focus leads to preferential phase matching long or short trajectories [107]. A full review of this topic can be found in [45]. For the work conducted in this thesis harmonics were used as a light source where on-axis emission was favoured. However the interference between long and
2.7. HIGH HARMONIC GENERATION

Figure 2.13: a) is a wave vector map of the Gouy phase for a Gaussian beam b) is a wave vector map from the atomic polarisability of the harmonic medium. Figure adapted from [16]

short trajectories encodes information about the generating medium where careful consideration of phase matching is vital [15, 134].
2.8 Attosecond pulse generation

High harmonic generation will occur periodically every half cycle when the laser field has sufficient intensity to distort an atomic or molecular potential. Each half cycle will emit a continuous frequency spectrum, which will interfere with bursts from neighbouring half cycles producing odd harmonics of the driving field. The duration of each of these bursts is limited by half period of the driving field, (1.3fs for 790nm) and therefore of 100s of attoseconds. This will produce an attosecond pulse train [11]. For a many-cycle pulse the intensity of each half cycle in the

Figure 2.14: A vectorial representation of phase matching at different locations across the focus where conditions of equation 2.58 are met.
neighbourhood of the envelope peak is broadly similar, and hence there is little difference in the frequency spectrum from each half cycle event. However for a few-cycle pulse \textit{i.e.} when there is a large difference in intensity between half cycles around the peak of the pulse, neighbouring half cycles will produce different spectra with the highest harmonics orders at the peak of the pulse, where a continuum can be observed\cite{17}.

Attosecond pulse trains contain attosecond pulses separated by $T/2$ \textit{e.g.} 1.3fs for 790nm source. These can be useful for certain applications, but the periodic nature of the burst can lead to confusion and ambiguity in time delay scans which would be removed by using an isolated XUV pulse. There are three mainstream methods to produce isolated attosecond pulses. All either limit or simply select XUV emission from a single half cycle, using either spectral selection, polarisation gating or a single cycle pulse and are discussed below. Other methods have been developed such as Ionisation gating\cite{6} and\cite{102}, 2 colour mixing\cite{135} and a combination of different approaches\cite{133}.

**Spectral selection and single cycle pulse**

The structure of a typical harmonic spectrum consists of three distinct regions. The region of lower order harmonics is called the perturbative region where the XUV energy is lower than the ionisation potential of the parent nuclei. Next is the plateau region containing the majority of the harmonic orders. Harmonics in this regions are contributed from the largest number of half cycle events and will form a train of pulses. The final region with the highest harmonic orders is the cut-off and contains harmonics created by the most intense part of the driving field. For a few-cycle pulse this region will have been emitted from the recombining electrons released in a single half cycle and hence be limited to an
isolated pulse. Selecting just the cut-off harmonics with a spectral filter isolates a single attosecond pulse[50, 49]. This method is commonly used with few-cycle laser systems and allows a large bandwidth of XUV to be isolated.

Isolated attosecond pulses from a single (or near single) cycle IR pulse are produced in a very similar way. With sub 2 cycle IR pulses, the peak intensity of the pulse is highly dependent upon CEP [20] and the CEP can be set to limit nearly all the ionisation in a gas from a single half cycle oscillation, this is shown in figure 2.15a), b) and c). Goulielmakis et al. [48] have recently used a 3.3fs IR pulse to produce an isolated XUV pulse with sufficient bandwidth in the XUV to compress the pulse to 80as.

![Figure 2.15: The use of CEP to limit HHG to one half cycle of the laser field. Isolated production is achieved in a) and c) where only one half cycle is above the threshold for HHG. In the case of b) two half cycles are over this threshold resulting in two attosecond bursts separated by T/2. The arrows refer to the over-threshold regions where electrons producing the highest energy photons are released, the corresponding XUV emission is shown in green.](image)

**Polarisation gating**

High harmonic generation only has a probability of occurring when the returning electron wave packet overlaps with the parent atom/molecule’s nuclear wave packet. If they were to miss the electron would not be reabsorbed and no harmon-
ics produced. Corkum proposed in 1993 that if the electron’s trajectory could be controlled, the subsequent emission of harmonics could also be controlled [25]. By introducing two counter-rotating circular polarised fields, with their polarisation in the e and o axes of a pulse of duration $\tau$, and a time delay $\Delta t$, between the two, the superimposed polarisation will change from circular to linear and back to circular. It has been shown that the intensity of the harmonic emission drops significantly when the ellipticity of the field $\xi$ is greater than 0.2 [12], hence high harmonic emission will be limited to the section of the pulse which is near linearly polarised, this region is typically called the polarisation gate and is given by:

$$\tau_G \approx 0.3 \frac{\tau^2}{\Delta t},$$  \hspace{1cm} (2.59)

where $\tau_G$ is the duration of the polarisation gate [22]. Using a short pulse (6 - 5fs) this gate can be made shorter than 1 cycle and limit high harmonic generation to a single half cycle of emission. While this is a useful technique and has been used to produce an isolated pulse of 130as[109], it still requires a very short driving pulse. This pulse duration limit is set as if the driving pulse was longer, the ground state of the medium would be depleted before the linear part of the pulse reached the target. The short pulse requirement is similar to the requirements to produce an isolated pulse via spectral selection, however polarisation gating is not restricted to producing isolated pulses from the cut-off region of a harmonic spectrum.

A method has been developed to increase this few-cycle limit, opening up the opportunity for many more labs to produce isolated pulses. Mashiko et al. have demonstrated how combining a $2\omega$ field to the collinear counter circular polarised fields, an optical gate is introduced. This reduces the ionisation of the medium by the leading edge of the pulse allowing a longer $\tau$ to be used [91]. This method has allowed isolated 130as pulses to be produced from a 10fs pulse.
Figure 2.16: Polarisation gating to produce an isolated attosecond pulse. Two counter-circulary polarised pulses are produced with a quarts and $\lambda/4$ waveplates. The superposition of these two fields produced a gate where the field ellipticity is less than 0.2, where the returning electron wave packet overlaps with the parent ion, outside this gate the electron wave packet misses the ion. Figure from [116]

2.9 Characterisation of attosecond pulses

Attosecond pulse trains

Paul et al demonstrated that attosecond pulse trains are locked in phase, and through two colour ionisation with IR and XUV fields temporal information about the pulse train can be extracted [98].

With a low IR intensity and an XUV flux of harmonics two-photon ionisation can occur, where an atom or molecule from a gas target is ionised by both a harmonic photon and with an IR photon. In this low intensity regime the ionisation process can be viewed as second order perturbation - in a similar fashion to low order
harmonic generation. Figure 2.17 is a representation of the quantum paths possible in the two-photon ionisation causing a sideband. A key point is that different paths from two different harmonics are involved in the production of a single sideband. Introducing a phase shift by delaying the IR pulse relative to the XUV photons produces an interference in the sideband which can be used to extract temporal information about the attosecond pulses in the pulse train.

Figure 2.17: Sideband production from two-photon ionisation with an XUV and IR photon. A sideband sitting $\omega_{\text{laser}}$ between two harmonic photoelectron emission is produced from neighbouring harmonics (q-1 and q+1) either by absorbing or emitting an IR photon. The insert on the right is a cut from a measured photoelectron spectrum made during this PhD from neon gas showing the sideband between electrons produced by the 23rd and 25th harmonics of an 800 nm 30 fs beam (see section 4.2).

A brief view of the quantum origin of these sidebands shows the source of inter-
ference. If the sideband energy is given by:

\[ E_q = E_0 + q\hbar\omega \]  

(2.60)

the signal will be proportional to:

\[ S = \sum_f |M_{f,q-1}^+ + M_{f,q+1}^-|^2 \]  

(2.61)

where \( f \) are the angular quantum numbers, \( M \) the matrix elements. Each value of \( M_{f,q\pm 1} \) contains the dipole operators \( D^\pm \) which can be expanded to:

\[ D^\pm = D_0 \exp(\pm i\varphi) \]  

(2.62)

then \( S \) can be expanded to include:

\[ A_f \cos(2\varphi_{IR} + \varphi_{q-1} - \varphi_{q+1} + \Delta\varphi_{atomic}) \]  

(2.63)

where:

\[ A_f = 2 |M_{f,q-1}^+||M_{f,q+1}^-| \]  

(2.64)

where \( \varphi_{IR} = \omega_{IR}\tau \) when the IR field is relative to the XUV field. A fuller derivation is found in [98].

Furthermore the emission time \( t_e \) is different for different harmonics representing the different duration spent in the continuum. This spread of emission times produces a natural chirp in harmonic spectra. As a result, without compression, the pulse duration of an attosecond pulse produced from a range of harmonics has a longer duration than the transform limit. The phase difference between neighbouring harmonics can be seen by comparing the phase of the sideband oscillation [89]. Measuring the emission time of each harmonic contributing to a pulse allows
the minimum pulse duration to be calculated. This mapping can be seen in figure 2.18 from [89].

Figure 2.18: The emission time of different harmonics are mapped by the sidebands visible in a photoelectron spectra. The chirp in the emission is from the different times an electron spends in the continuum during HHG to produce a harmonic. Measuring this spread of emission times $\Delta t_e$ allows the minimum pulse duration to be calculated. The thick white line shows the varying emission time compared to the vertical (thin line). Figure taken from [89]

**Isolated attosecond pulse**

As the duration of isolated x-ray pulses has gone below the duration of a cycle of an IR field a new method has been developed to allow a measurement of the duration of chirp of the x-ray pulse. Whereas previous methods have involved the cross correlation of IR and XUV pulses to produce sidebands or looking at the AC Stark shift, these methods either merge or become undetectable when the duration of the XUV pulse is shorter than the fundamental field’s period [57].
The accepted method for measuring such XUV pulses is the atomic steak camera method (ASC). ASC measures the deflection of an electron produced by ionisation from an XUV photon in a strong field of a laser. The strength of the deflection is dependent upon the phase of the laser field and it will be shown that this can be used to measure the chirp and duration of a sub-cycle XUV pulse. This process can be separated into two distinct events: first the ionisation of an atomic medium by an x-ray photon, then its acceleration in a strong laser field. For simplicity the field of the streaking IR laser pulse will just be referred to as simply the field in this section.

The kinetic energy of the electron produced by an XUV photon is given by:

\[
W_0 = \frac{m_e v_0^2}{2} = \hbar \omega_{\text{XUV}} - I_p ,
\]

where \(v_0\) is the initial velocity of the electron and \(\omega_{\text{XUV}}\) is the frequency of the XUV photon and \(I_p\) is the ionisation potential of the atomic medium. Classical mechanics can then be used to model the motion of the electron in the laser field \cite{26} with the electron’s velocity given by:

\[
v(t) = -\frac{e}{m_e} A(t) + v_0 + \frac{e}{m_e} A(t_i) ,
\]

where \(A(t)\) is the vector potential of the field, and \(t_i\) is the time of ionisation of the medium by the XUV photon. After the field is over it can be seen that the final velocity of the electron is:

\[
v_f = v_0 + \frac{e}{m_e} A(t_i) ,
\]

and as \(A(t_i)\) varies according to the phase of the field sub-cycle variation can be measured. A representation of this variation is shown in figures 2.19 and 2.20.
Figure 2.19: The principle of atomic streaking. The brown circle represents the drift velocity \( \mathbf{V} \) distribution of an electron released by ionisation from an XUV photon, the blue is the net final distribution when the laser field is included \( \mathbf{V}_{f,x} \) for different values of \( \mathbf{A}(t) \). The red oscillation represents the laser field. It can be seen that the greatest shift in the electron velocity is at the zero crossings and the least at the turning points of the field. It is important to note that the greatest shift is seen in electrons collected along \( \mathbf{V}_{f,x} \).
By temporally scanning the birth of the electron by the XUV photon across the field the shift in the velocity of the XUV photoelectron will be mapped out. For a linearly polarised field, the width of the photoelectron spectra from XUV photoelectrons, $\Delta E$ contains information about the spread of the births of the photoelectrons caused by the width of the XUV pulse, and the chirp on the XUV pulse [57]. First the angle of collection needs to be considered. Including the angle $\theta$, the angle of observation from $V_{f,x}$ and considering the kinetic energy of the electron [57]:

Figure 2.20: A representation of the atomic streaking principle. A XUV photon ionises an atomic medium releasing an electron (green). This electron is then accelerated by the strong electric field of an IR field. By scanning the delay of the laser pulse and the XUV pulse, the electron experiences a different vector potential of the field $A(t)$. 
2.10. **Theories of Condensed Matter Processes Related to This Thesis**

\[ K = W_0 + 2U_p \cos 2\theta \sin^2 \phi_i \pm \alpha \sqrt{8W_0 U_p \cos \theta \sin \phi_i} , \]  

(2.68)

where:

\[ \alpha = \left[ 1 - \left( \frac{2U_p}{W_0} \right) \sin^2 \theta \sin^2 \phi_i \right]^{1/2} , \]  

(2.69)

\( U_p \) is the ponderomotive potential of the field and \( \phi_i \) is the phase of the field at ionisation. It can be shown that the width of the photoelectron spectrum measured is proportional to the streaking speed \( \delta k/\delta \phi \) and the pulse duration of the XUV pulse \( \tau_{XUV} \). By comparing the width of the photoelectron spectrum where there is no field, \( i.e. \) where the field is not temporally overlapped with the XUV pulse, to a section of overlap at a known phase, the pulse width \( \tau_{XUV} \) and chirp can be extracted using a similar approach to the FROG extraction method (see section 4.3).

This extraction method imposes a limitation on the minimum pulse duration for a given XUV photon energy that can be resolved. Typically for an XUV pulse centred at 100eV a 70as pulse can be measured if \( \theta = 0 \) (electrons are collected along \( V_{f,x} \). This resolution would be less for larger values of \( \theta \).

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2.10 Theory of condensed matter processes related to this thesis

**Photoexcitation and photoemission**

When a photon is absorbed by a solid two processes may occur. The first, photoexcitation is the absorption of a photon which promotes an electron to a higher...
state inside the bulk of a solid. Photoemission describes the process of the emission of an electron from a solid into the vacuum after the absorption of one (or many - multiphoton photoemission) photon. In this case the electron has been given energy equal to or greater than the forces holding it inside the solid. The minimum energy required to release an electron from a solid is called the work function $\phi$ and the kinetic energy of an electron released by a solid is given by:

$$E = \hbar \omega + E_b - \phi,$$

(2.70)

where $\hbar \omega$ is the energy of the photon absorbed and $E_b$ is the binding energy of the electron in the solid.\(^3\) As in the case of atoms and molecules, for a high photon flux electrons can absorb many photons and have energies significantly greater than $\hbar \omega$. This non-linear process is shown in figure 2.21 and the released electron is given by $E = n\hbar \omega + E_b - \phi$ where $n$ is the number of photons absorbed. This multiphoton emission (MPE) process allows electrons to be emitted by irradiation of photons with energies less than $\phi$ for example a photon with 1.5eV (800nm) can ionise a solid with a typical work function of 5eV.

Emission of electrons from inside a solid also involves transport of the electron to the surface for it to be emitted. Emission is commonly described as a three step process of excitation, transport and escape from the solid over the vacuum boundary. During the second stage, as the electron travels to the surface it will travel through a dense collection of electrons. Electron - electron scattering (e-e) and electron - phonon scattering (e-p) will significantly reduced the kinetic energy of the electron. With reference to figure 2.22 it can be seen that the mean

\(^2\)Multiphoton Emission processes where an electron leaves a surface is also referred to as above threshold photoemission (ATP) akin to ATI in gases

\(^3\)The energy $E_b$ can be also be referred to as the initial energy. In this thesis the value will be with reference to the energy below the fermi level ($E_f$) and therefore will be negative.
2.10. THEORY OF CONDENSED MATTER PROCESSES RELATED TO THIS THESIS

Figure 2.21: *left* schematic of the electronic structure of a metal. *right* Emission mechanism for an electron from the fermi level via a multiphoton process. An electron can absorb many photons and be emitted above the vacuum level with an energy given by $E = n\hbar\omega + E_b - \phi$.

free path of an electron with several 10s of eV is less than 1nm. For electron spectroscopy scattering processes significantly influence the source of electrons observed. Mapping the fermi level of a metal with a work function of 5eV with 60eV photons the highest energy photon detected would be 55eV. The vast majority of these electrons would have been released from only the first couple of layers from the surface. Electrons from deeper in the sample would be detected with a range of lower energies as their kinetic energy is reduced through scattering. The result is a large tail of lower scattered electrons will also be detected below 55eV. As a result electrons collected from a solid are very surface sensitive.

**Surface plasmon**

Electromagnetic waves can couple to the free electrons of a conductor at the interface between it and an insulator [104, 19]. This collective oscillation of the wave
Figure 2.22: The mean free path of an electron in Au for different energies. The different curves refer to the number of electrons per atom used in the calculation. The insert displays the mean free path for energies of interest in for this thesis. Figure from [124]
2.10. THEORY OF CONDENSED MATTER PROCESSES RELATED TO THIS THESIS

is referred to as a surface plasmon polariton and the wave vector $k_{sp}$ is given by:

$$k_{sp} = \frac{\omega}{c} \left( \frac{\epsilon_{di} \epsilon_{con}}{\epsilon_{di} + \epsilon_{con}} \right)^{1/2},$$  \hspace{1cm} (2.71)

where $\epsilon_{di}$ is the dielectric constant of the dielectric and $\epsilon_{con}$ is the dielectric constant of the conductor. The wave vector $k_{sp}$ is greater than for a dielectric and is therefore confined within the 2 dimensions of the surface of the conductor. At the boundaries of this surface the wave will decay away. There is also a mismatch between the wave vector of a free photon, therefore to couple the electromagnetic wave of a laser field to the surface this mismatch must be phased matched, typically by using a prism or grating [56]. Using a prism the photon wave-vector is shifted to $k = k_\sqrt{\epsilon \sin \theta}$ or a grating where the line spacing can be chosen to match $k_{sp}$ where:

$$k_{sp} = k \sin \theta \pm 2\pi a^{-1},$$  \hspace{1cm} (2.72)

for the first order where $a$ is the grating constant. Grating coupling is often applied by coating a suitably spaced grating with a conductor eg with an evaporation of gold [77].

Localised fields can also couple to a small localised area many times smaller than the wavelength of the driving field. These fields are different to surface plasmon polaritons as they are non-propagating and are localised to a three dimensional volume compared to the 2 dimensional travelling nature of a polariton. Localised nano-plasmonic fields can be exited by both s and p polarisations and are attributed to high field enhancement observed from rough surfaces[7, 68] and nanoparticles [122]. It is thought that the field enhancement (up to $10^6$) observed is from the localisation of the field in a small three dimensional area in a similar fashion to lightning conductors [114].
Chapter 3

An attosecond source

Production of high energy,\(^1\) isolated attosecond pulses requires carrier envelope stabilised, few cycle driving fields. This chapter describes the laser system used to produce 30fs IR pulses which are further broadened through self phase modulation and compressed to produced sub 7fs CEP stabilised pulses. The vacuum beamline is presented which is used to produce extreme ultra violet (XUV) radiation through high harmonic generation which contains attosecond temporal dynamics. Spectral and spatial characterisation of the XUV radiation by a XUV spectrometer is described.

3.1 The drive laser - Chirped Pulse Amplification

This section described the CPA laser system used to seed the production of few-cycle laser pulses. The laser is a commercially available CompactPRO Femtopower

\(^1\)High energy refers to photons with energies in the region of 100eV
Titanium:Sapphire CPA system manufactured by Femtolasers. It produces 1mJ pulses of 30fs at 1kHz repetition rate with additional equipment from Menlosystems actively stabilising the carrier envelope phase of the pulses. A description of the key components of the CPA, the oscillator, stretcher, amplifier and compressor follows.

**Oscillator & stretcher**

The oscillator is a highly-doped Titanium:Sapphire laser producing 10fs pulses in a 75Mhz pulse train. The oscillator cavity is pumped by a 4-5W frequency doubled diode pumped Nd:YVO$_4$ Coherent Verdi. The mode-locked output spectrum of the oscillator is centred around 800nm with a FWHM of 100nm with a typical output power of 500mW when mode locked. A typical output spectrum is shown in Figure 3.2. Following the cavity 50% of the output is spilt off to CEP stabilisation apparatus described in section 3.2, while the remainder is temporally stretched in 10cm of SF57 glass to $\sim 20$ps to allow the pulse to be safely amplified without causing damage to optics. A set of broadband chirped mirrors after the oscillator cavity are used to pre-compensate for third order dispersion introduced later as the beam propagates through the amplification and compression stages of the laser. A summary of the oscillator specifications is given in table 3.1

<table>
<thead>
<tr>
<th>Specification</th>
<th>Specification [40]</th>
<th>Typically achieved</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pump laser</td>
<td>4W</td>
<td>4 - 5W</td>
</tr>
<tr>
<td>Mode locked output power</td>
<td>420mW</td>
<td>500mW</td>
</tr>
<tr>
<td>CW output</td>
<td>520mW</td>
<td>540mW</td>
</tr>
<tr>
<td>Rep rate</td>
<td>79.5 MHz</td>
<td>79.5 MHz</td>
</tr>
<tr>
<td>Spectrum</td>
<td>104nm FWHM</td>
<td>104nm FWHM</td>
</tr>
<tr>
<td>Pulse duration</td>
<td>10.4fs</td>
<td>not measured</td>
</tr>
</tbody>
</table>
3.1. THE DRIVE LASER - CHIRPED PULSE AMPLIFICATION

Amplifier

After the pre-compensating mirrors and a Faraday isolator the 20ps pulses from the oscillator make 9 passes through a Titanium:Sapphire crystal where they overlap with a frequency doubled diode pumped Nd:YAG Coherent Corona laser running at 1kHz and 13W. The crystal is housed in a Peltier cooled chamber maintaining the internal environment at -20°C and 20mbar, preventing thermal lensing in the crystal and surface damage from condensation build-up. The Nd:YAG pulse makes 2 passes through the crystal depositing 90% of its energy [40]. The lifetime of the gain is longer than the pump pulse duration meaning any of the pulses in the oscillator pulse train that temporally overlap with the gain will be amplified. The entire pulse train passes through the crystal for the first 4 passes, after which a Pockel’s cell and polariser combination picks the most energetic single pulse before it makes a further 5 passes through the crystal, the pulse picking also sets the repetition rate at 1kHz.

The total gain of the system is approximately $10^6$ with a spectral bandwidth output of $\sim 50\text{nm}$. Figure 3.1 is a schematic of the amplification section of CompactPRO. Following application the 1kHz pulse train passes to the compressor stage of the CPA.

Compressor

The compressor is a four prism system with two prism pairs which are double passed with a folding mirror. It is possible to translate one prism pair allowing optimisation of the compression or to pre-compensate for further dispersion of the beam after the compressor. Prisms are used in place of gratings to reduce pointing fluctuations leading to instability in the CEP of the pulse. The input energy of
the compressor is limited to around 1mJ otherwise the B-intergral in the prism material is $> 1$ with an increased chance of self focusing. For the same reason the minimum pulse duration achievable is $\sim 30$fs even though the bandwidth would support a shorter pulse.

A summary of the specifications typically reached from the laser are shown in table 3.3. The following section describes the active CEP stabilisation systems used to allow the production of an isolated attosecond pulse.

<table>
<thead>
<tr>
<th></th>
<th>Typically achieved</th>
</tr>
</thead>
<tbody>
<tr>
<td>Output power</td>
<td>800mW</td>
</tr>
<tr>
<td>Pulse duration</td>
<td>30fs</td>
</tr>
<tr>
<td>Beam quality</td>
<td>$M^2 = 1.5$</td>
</tr>
<tr>
<td>Spectrum</td>
<td>40nm</td>
</tr>
<tr>
<td>Beam diameter ($1/e^2$)</td>
<td>15mm</td>
</tr>
</tbody>
</table>
3.2 Carrier envelope phase stabilisation

To control the carrier envelope phase (CEP) the CPA system has two systems to correct for drifts from different parts of the laser. A ‘fast loop’ corrects fluctuations in the 75MHz pulse train and a ‘slow loop’ corrects fluctuations in the 1kHz part of the system.

Both systems use interferometry to measure the CEP by measuring the interference of the fundamental spectrum and a broadened doubled spectrum. The value of $\omega_{\text{CEP}}$ can then be measured (see section 2.2). This type of interferometry is referred to as f - 2f interferometry[60]. A CEP stabilisation system has been developed to stabilise the CEP to better than 200mrad rms over many hours. For this to be achieved all parts of the system need to work together with a number of feedback loops. A flow diagram of the full system is shown in figure 3.3.

The fast-loop f-2f uses 50% of the oscillator output to measure the CEP. The spectrum is broadened in a photonic crystal fibre(PCF) to over an octave after which
Figure 3.3: A flow diagram of the CEP stabilisation system used for the Femtopower. 50% of the output from the oscillator is diverted to a f -2f interferometer where \( \omega_{CEP} \) is measured for every fourth pulse. An electronics system in a feedback loop modulates the pump laser power with an acousto-optic modulator (AOM). A further f-2f is used after the amplifier to measure the slow drift in the kHz pulse train. This can feedback to either a prism pair in the compressor or the AOM

The green part of the spectrum is split from the beam via a dichroic beamsplitter while the red is frequency doubled. The two spectra are then temporally and spatially overlapped before being passed into a spectrometer. A photodiode is used to measure \( f_{rep} \) of the input beam with a direct pick-off the broadened pulse out of the PCF. An other photodiode placed in the spectrometer measures \( f_{beat} \). The electronics system then locks the value of \( f_{beat} \) by feedback to an acousto-optic modulator (AOM) in the beam of the oscillator pump laser. By controlling the power of the pump beam the refractive index of the Ti:saph crystal is altered via the nonlinear refractive index \( n_2 \). This results in small adjustments in the group and phase velocities and hence the CEP of the oscillator output.
3.2. CARRIER ENVELOPE PHASE STABILISATION

It was noticed that in the first few hours of operation every morning the CEP stability dropped as the system warmed up with a larger voltage required on the AOM. The AOM has a stable range of operation, outside this range the modulation of the pump beam is more dramatic and can cause the oscillator to stop mode-locking. This problem was rectified by including an active feedback to a course adjustment of the CEP in the form of glass wedges in the cavity of the oscillator. The voltage applied to the AOM is monitored via a PC, when this is greater than a set range \( \omega_{\text{CEP}} \) has changed significantly in the oscillator cavity, the wedges are driven with a picomotor to adjust \( \omega_{\text{CEP}} \) of the cavity back to the linear range of the AOM.

Pulses propagating through the amplifier and compressor pick up slow fluctuations in CEP from variation in the amplifier pump laser altering the refractive index of the Ti:saph, or beam pointing instability through the compressor, or even turbulence in the air path changing the density of air travelled through. This instability is measured with a further f-2f interferometer after the compressor. A few percent of the amplifier output is focused onto a sapphire plate generating over an octave of bandwidth. The spectrum then passes through a BBO crystal generating second harmonic of 1000nm. After the polarisation of both spectra are aligned with a beamsplitter the inherent delay caused by dispersion produces a series of spectral fringes from the interference of the broadened and doubled spectra. By recording this spectrum onto a PC and taking the fourier transform the CEP can be extracted [123]. The slow-loop can then feed back to the AOM or a prism set in the compressor for correction of the CEP. It is also this PC which controls the value of the CEP offset applied allowing the CEP value to be scanned. An interferogram showing stability of the CEP over a 30 second interval, measured in the slow loop f-to-2f is shown in figure 3.4.
The stabilised output of the CPA is then be used to produce few cycle IR pulses after further broadening and compression in a hollowed cored fibre.

### 3.3 Hollow fibre pulse compressor

The output of the CPA is either delivered to the attosecond beamline directly as an unbroadened 30fs pulse, or broadened and compressed further to only several cycles of the laser field. The spectral broadening required for further pulse compression is done in a differentially pumped hollow fibre system [106]. The pulse is focused into the entrance of a 1 meter long glass hollow fibre with a 250 µm inner diameter.
by a 0.9m concave mirror. As described in section 2.4, best coupling into the $\text{EH}_{11}$ mode is achieved when the focal spot diameter is $0.65 \times$ the fibre diameter. The laser then propagates along the fibre along a pressure gradient achieved by differential pumping of the gas medium. Careful alignment of the fibre is required to reduce losses along the fibre and is provided by 2 3-axis manipulators at either end of the fibre support. The fibre itself is housed in a large glass hollow fibre outer for support, with the vacuum seal from o-rings and glue. The laser enters and leaves the fibre through 300 $\mu$m thick AR coated glass windows. Argon and neon are routinely used in the fibres, typical broadened spectra are shown in figure 3.5. As broadening is proportional to the nonlinear refractive index $n_2$[106] which is greater for argon than neon, broader spectra can be obtained in argon, the input power into the fibre has to be limited due to the low ionisation potential (15.8eV) to avoid a plasma forming along the fibre.

The material dispersion of the gas medium will add positive chirp to the broadened pulse and is estimated to be $60\text{fs}^2$ for around 3 bar of gas in the fibre [106]. To compress the pulse close to the transform limit and to pre-compensate for further material dispersion up to 8 negatively chirped mirrors (BBCOMP, Femtolasers) can be used. Each mirror produces $-50\text{fs}^2$ of GDD per bounce over the bandwidth of 650-900nm, which is sufficient to support a 6fs pulse. The GDD of each mirror will approximately compensate for the dispersion from 1.25mm of glass or 2m of air allowing a near transform limited pulse with flat phase to be produced.

Fluctuations in the beam pointing into the entrance of the fibre cause significant differences in the transmission, broadening and output mode of the fibre requiring realignment of the fibre after several hours of operation. To compensate for this an active beam pointing system is used. A 1% reflection from the input beam into the fibre is monitored on a CCD. A PC is used to feedback any motion to picomotors.
controlling the pointing of the focusing optic into the fibre. Using this system there is no noticeable fluctuation in the fibre output as a result of beam coupling. An overall schematic of the few cycle system is shown in figure 3.6. To measure the pulse duration of the few cycle pulses the beam can be sent to a SHG FROG located after the chirped mirror set, a description is given in the next section.

3.4 Pulse measurement - FROG

A FROG [127] is used for routine characterisation of the output of the hollow fibre system. The FROG uses second harmonic generation as its non-linear process and
3.4. PULSE MEASUREMENT - FROG

Figure 3.6: Representation of the few cycle source. The 30fs output of the Femtopower is focused into a 1m long differentially pumped hollow cored fibre where the pulse is spectral broadened through self phase modulation. The coupling into the fibre is stabilised with beam-pointing system. A few % of the output is picked off by the CEP stabilisation slow loop. The broadened output of the fibre is compressed with broadband chirped mirror before being delivered to the beamline. A SHG FROG is used to measure the temporal profile of the few cycle pulse.

was adapted from a previous single shot autocorrelator. A schematic of the optical layout is shown in figure 3.7.

Care is taken that none of the optics used in the SHG FROG significantly alter the spectral or temporal profiles of the pulse. Two pulse replicas are created using a thin (0.46mm) ultra broadband beam splitter (Layertec GmbH) with a partially reflective coating on the front surface and anti-reflective coating on the back. This allows 50:50 replicas to be made for s-polarised light between 500-1000nm. The beamsplitter has a low and relatively flat dispersion across the working bandwidth (ranging from -1.5fs$^2$ to 1fs$^2$). The dispersive path through the beamsplitter is matched for the reflected pulse with a 0.46mm fused silica plate (CP in figure 3.7)
Figure 3.7: A schematic of the SHG FROG used to measure the broadband pulses produced by the hollow fibre system. Two pulse replicas of the s polarised IR pulse are created by a beam splitter BS. Broadband silver mirrors and a concave mirror (M1-M5 & CM) are used to overlap the two replicas in a 10μm BBO crystal. The autocorrelation signal is then imaged onto a slit S with lens L1. The signal at the slit is then spectrally resolved onto a CCD with L2 & L3 with a transmission grating G. Aluminium mirrors with a flat spectral response are used after the BBO.
in the reflected arm. A reflection from this plate is also collected by a separate fibre coupled spectrometer to help with the FROG retrieval algorithm and correct for errors in the measured SHG spectrum caused by the spectral response of the optics.

The two replicas are then focused onto a 10µm BBO crystal with a delay stage in one arm used to ensure temporal overlap. A very thin crystal is required to provide the necessary phasematching bandwidth. This also has the advantage of introducing very little dispersion into the replicas. The autocorrelation signal produced in the BBO crystal is imaged onto a slit (S in figure 3.7) and the signal is spectrally resolved onto a CCD in a perpendicular plane to the slit using a UV transmission grating. Again care is taken to use optics with a flat spectral response in the UV after the BBO crystal. However as the temporal information of the pulse is encoded in the width of the autocorrelation trace, dispersive optics such as fused silica lens can be used in imaging the signal.

The FROG ‘trace’ on the CCD is given by:

\[ I_{FROG}^{SHG}(\omega, \tau) = \left[ \int_{-\infty}^{\infty} E(t)E(t-\tau)e^{i\omega t}dt \right]^2 \]  

(3.1)

This information is then passed to a commercially available FROG algorithm (FROG 3 Femtosoft Technologies) which compares an imaginary pulse with a certain spectral phase and intensity of the measured trace. The algorithm works by comparing the error between measured pixels and the FROG trace of the imaginary pulse and iteratively works to reduce this error. The result of a typical FROG trace and the retrieved pulse is shown in figure 3.8. For this trace the retrieved pulse length 6.8fs.

Care is therefore taken to match the same dispersive path into the SHG FROG up
Figure 3.8: A SHG FROG trace and its retrieval by FROG3 algorithm of a 6.8fs pulse. Top left is the image of the trace recorded in the CCD (C in figure 3.7), top right is the FROG trace produced by the algorithm. From the retrieved FROG trace the temporal pulse envelope and its phase is shown in the bottom left while the retrieved spectrum and phase is shown in the bottom right. Also shown in red is the measured spectrum by a spectrometer of the pulse.
to the BBO crystal as the IR beam follows to the HHG focus so that a pulse with the same chirp and duration is measured. Once this is done the SHG FROG offers a relatively simple method of reconstructing the electric field of a broadband pulse. While this is not an online method as the reconstruction algorithm can take several minutes to compute, the online display of the autocorrelation and spectrum of the pulse is very useful in tweaking the dispersion in the chirped mirror compressor and gives a visual check that the full spectrum is being transmitted by the system.

### 3.5 Summary of few-cycle IR light source

The hollow fibre compressor system described in the previous sections, combined with the CPA stage of the Femtopower increased the pulse energy from nJ’s in the oscillator by $10^6$ to 1mJ. These broadband CEP stabilised pulses are then used to produce high harmonics. This stage is described in the following sections. A summary of the output of the few-cycle IR source is presented in table 3.3.

<table>
<thead>
<tr>
<th></th>
<th>Typically achieved</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulse energy at HHG target</td>
<td>350µJ</td>
</tr>
<tr>
<td>Pulse duration FWHM</td>
<td>6.7fs</td>
</tr>
<tr>
<td>Spectral bandwidth FWHM</td>
<td>250nm</td>
</tr>
<tr>
<td>Peak power</td>
<td>60GW</td>
</tr>
<tr>
<td>Beam diameter ($1/e^2$)</td>
<td>15mm</td>
</tr>
</tbody>
</table>

### 3.6 Overview of Beamline

As the short wavelength high harmonics do not propagate more than a few microns in air, experiments producing and using high harmonics have to be carried
out in vacuum. A series of vacuum chambers allowing the production, character-
isation and use of attosecond pulses has been constructed which will be referred
to as the Attosecond beamline or ASB, a schematic of which is shown in figure
3.9. The following sections describe the generation, spectral selection and spectral
measurement of high harmonics followed by spectral selection involved to produce
attosecond pulse trains and isolated pulses.

Figure 3.9: Schematic of the attosecond beamline at Imperial College, High Harmonic
Generating chamber: a variety of continuous flow and pulsed gas targets are used to
produce XUV through High Harmonic generation. Filter chamber: Metallic filters can
be placed in the beam to spectrally select certain harmonics and filter IR. Spectrometer:
a flat-field grating and micro channel plate are used to resolve the harmonics. Attosecond
streak chamber: A two-part delay stage mirror and time of flight electron spectrometer
are used to measure photoelectrons from gas targets. See chapter 4 for details details of
the measurements conducted in this chamber. Surface beamline: a detailed description
of the surface capability is given in chapter 5
3.6. OVERVIEW OF BEAMLINE

Generation

The IR enters the high harmonics generation chamber through a 400μm AR coated glass window and is then focused into a gas target using a spherical mirror. The focal spot diameter is around $\sim 100\mu m$ giving an intensity $\sim 4 \times 10^{14} W/cm^2$ for a 6fs pulse and 350μJ of energy. The focal length of this mirror can be changed to carefully tune the cut-off region of the harmonics to the desired wavelength \textit{i.e.} to match the reflectivity bandwidth of a mirror, or to probe a particular energy band in a metal. At the focus the gas medium where high harmonic generation takes place is supplied by one of two gas targets which have been developed. One is a pulsed valve target (figure 3.10) and the other a continuous flow (CF) (figure 3.11).

The CF target is made from an inner tube surrounded by a larger differentially pumped outer. The inner tube has a small hole drilled for the laser to pass, where it interacts with a gas such as argon or neon, while the outer jacket is differentially pumped reducing the volume of gas escaping into the chamber (Figure 3.11). The interaction length between the laser and gas can be set by changing the diameter of the inner tube.

The pulsed valve was designed around a piezo electric disk to open and close a poppet releasing gas from a reservoir. Using a Physik Instmente P-286.23 piezo a repetition rate of 1kHz can be achieved [42]. To open the valve a slow ramping and decaying signal is applied of about 100 volts. The FWHM of the signal is 250μs, however scanning the timing of the opening shows the effective opening time is $\sim 100\mu s$ \textit{i.e.} the voltage needs to be delayed by $\sim 100\mu s$ for the harmonic signal to disappear. The gas is injected into a small tube, of diameter 800μm and length 6mm with the laser focused through. Using the pulsed valve the harmonic yield can be increased until the gas pressure is so high the reabsorption of the XUV by the gas limits higher yields. This is in contrast to the CF target where figure 3.12
shows that pumping limitations limit higher yields and not reabsorption by the gas. The pumping in the high harmonic generation chamber allows a maximum background pressure of $5 \times 10^{-3}$ mbar.

![Image](image1.png)

Figure 3.10: Pulsed gas valve, a piezo is driven by an electric trigger to open and close a poppet sealed with a rubber o-ring, releasing gas into a small target region below. The valve is capable of running at 1kHz.

![Image](image2.png)

Figure 3.11: Continuous flow target, a inner tube containing gas is surrounded by a differentially pumped outer. The inner tube has a 1.0mm hole drilled through the centre and is sealed at the bottom. The outer hole diameter is 2.0mm

With a short focusing optic of 40cm producing a peak intensity at the focus of $6 \times 10^{14}$ W/cm$^2$ the cut-off to be extended in neon to around 110 - 120eV ($81^{st}$ harmonic, 10nm). These high energy photons are used to probe bands in solids
such as the 4f band in Au. This band has a binding energy of 87eV [4]. With a 120eV photon the released photoelectron will have an energy of 33eV placing it above any IR background photoelectrons which may be present. For the gas phase steaking measurements however, the focal parameters are changed so the cut-off harmonics overlap with the peak intensity of the XUV mirror (93eV)[2]. Large changes in the peak intensity are achieved by changing the focal length of the mirror, while it was found fine adjustment can be made by adjusting an iris before the harmonic chamber. This is not an ideal method of tuning the intensity but is useful as it does not include introducing dispersive elements such as a waveplate and polariser to attenuate the broadband pulse. Figure 3.13 is a plot of the expected cut-off harmonic energies under ideal settings. This irising method allows the cut-off to be tuned by around 10eV without dramatically changing the yield. An example of harmonic spectra where this is used is given in section 3.7.

The harmonic yield of the pulsed valve can be 10 times greater than the CF target as a larger gas density can be used. However the CF target provides a very stable
Figure 3.13: The expected cut-off harmonic energies for different focal length mirrors assuming a 6fs pulse, with 250µJ and a beam size of 6mm on to the focusing optic.

target with the ability to set the interaction length of the laser and gas medium with more certainty.

Spectral selection

After the high harmonic generation chamber the the radiation passes through metallic filters for spectral selection. This process is fundamental to many experiments for example where an isolated attosecond pulse is required. Descriptions of the filtering employed to specific experiments is given in the appropriate sections, but routinely aluminium and zirconium thin (200nm) foils are used. Both filter IR and have different bandwidth selectively for higher order harmonics.
3.6. OVERVIEW OF BEAMLINE

Spectral measurement

To diagnose the high order harmonics a flat-field grating and micro-channel plate (MCP) imaging detector are used, giving both spatial and spectral information. The design of the spectrometer on the ASB is flexible as the MCP is mounted on a sliding plate which is sealed with double o-rings allowing the wavelength range detected to be scanned while maintaining chamber vacuum. Spectrometers using an x-ray CCD often allow the camera to be moved followed by a quick pump-down (the vacuum requirements for a CCD are less stringent than for an MCP), however an MCP has benefits over a CCD. The principle advantage of a MCP for imaging high-order harmonics is its lack of sensitivity to IR photons. The quantum efficiency of the MCP for a 1.5eV 800nm photon is too low to instigate an electron cascade. This allows direct imaging of high-order harmonics without having to

Figure 3.14: a) schematic showing the deign of the flat-field spectrometer used on the ASB. The incident laser is 3° from horizontal and the MCP is mounted on a sliding flange in a vertical plane to the grating. b) A plot displaying the heights different harmonics energies intersect the plane of the MCP. The red dashed lines represent the active area of the MCP.
filter out the IR of the drive laser. A CCD on the other hand is more sensitive to IR than higher energy photons and would be saturated without filtering of the IR.

The geometry of the spectrometer on the ASB follows the design described in [71] utilising a variable line spacing grating and a shallow curved profile to focus the harmonics in a plane perpendicular to the beam. Figure 3.14 shows the arrangement used on the ASB. One can see the requirement for the MCP to move for harmonics from 15 to 140eV to be imaged. A cooled 12-bit CCD (Coolview) camera is used to image the MCP phosphor screen, with single shot harmonic capture possible.

![Graph](image)

Figure 3.15: High order harmonics produced in neon with a sub 10fs IR pulse. The red line is a spectral marginal of the unfiltered beam viewed on the MCP, the blue is with a 200nm Al filter. The black line is the predicted transmission from [2] showing the L-edge in Al at 73eV

The spectrometer was calibrated by looking for a known transmission feature of a metallic filter. The clearest is the L-edge absorption feature in aluminium (Figure 3.15). If one also uses a longer driving field to produce harmonics producing clean discrete harmonics, one can use the edge as a reference point. Combined with the
grating equation it is then possible to calibrate the MCP for different positions.

3.7 High harmonic spectra

The previous sections have described the apparatus required to produce high harmonics from an IR pulse. This section gives examples of typical high harmonic spectra routinely recorded on the ASB for both surface and gas phase investigations and a summary of what experiments each spectra can be used for.

Argon harmonics

High harmonics produced in argon are typically used to produce pulse trains of attosecond pulses. For a 800nm fundamental pulse the yield of argon is greatest between 20 - 50eV. The estimated XUV photon yield in this range is $10^{10}$ photons per pulse with an average energy of 50nJ. A spectrum like that shown in figure 3.16 would typically be used for an experiment requiring an attosecond pulse train [89].

Figure 3.16: High order harmonics produced in argon with a 7fs pulse, intensity $3\times10^{14}\text{W/cm}^2$. A typical spectrum would produce $\approx 50\text{nJ}$ per pulse.
Neon harmonics

Neon harmonics are used when a higher photon energy is required. The higher $I_p$ of neon extends the cut-off for a given intensity compared to argon. Figure 3.17 is a spectrum produced with a 6.7fs pulse. These harmonics will be filtered with a Zr filter to pass wavelengths higher than 70eV. A spectrum like that shown would be used to produce an isolated attosecond pulse (see chapter 4). The estimated XUV photon yield in the cut off and filtering is $3 \times 10^8$ photons per pulse with an average energy of 5nJ.

![Energy vs Spatial Profile](image1)

![Intensity vs Energy](image2)

Figure 3.17: High order harmonics produced in neon with a sub 6.7fs pulse, intensity $4.5 \times 10^{14}$W/cm$^2$. The cut-off harmonics have an estimated 5nJ per pulse.
3.7. **HIGH HARMONIC SPECTRA**

**Single harmonic**

An almost isolated single harmonic can be produced from neon gas. By filtering a harmonic spectrum with both a zirconium and aluminium filter a narrow bandwidth is passed (figure 3.18). Surface spectroscopy is aided when a single harmonic energy is used to investigate a material. This is discussed in chapter 6.

![Spatial profile and intensity plots](image)

Figure 3.18: The bandwidth passed from a neon harmonic spectrum by a combination of a zirconium and aluminium filter, produced with a few-cycle IR pulse. The estimated energy is 0.05nJ per pulse.

**Extended cut-off**

By using a shorter focal length lens to focus the IR beam into the harmonic gas target the cut-off produced in neon gas can be extended. Figure 3.19 is the
spectrum produced with a 7fs IR pulse from neon harmonics. These harmonics would be passed by a zirconium filter and be used in surface spectroscopy work.

Figure 3.19: High order harmonics produced in neon with a 7fs pulse. The cut-off was extended by using a short focal length (0.4m) to focus the beam into the gas target. It is estimated the energy per pulse in the cut of is 5nJ

Tuneable cut-off

The spectra shown in figure 3.20 are produced in neon with a few-cylce pulse. The cut-off harmonic can be tuned by careful closing an iris before the HHG chamber (the irising method described in section 3.6). This subtle effect is most likely to shift the cut-off by changing the focusing arrangements into the gas target. This method is extremely useful in accounting for day-to-day fluctuations in the laser energy in tuning the cut-off harmonics for the bandwidth of the Mo-Si mirror used in the atomic streak-camera experiment (chapter 4).
Figure 3.20: High order harmonics produced in neon with a few-cycle IR pulse. The blue curve is the spectrum without irising the beam. The red and green curves are spectra collected with the beam reduced by 1 and 2mm respectively.

3.8 Summary of light sources produced by the ASB

This chapter has described a robust and versatile system which on a daily basis can produce the following light sources:

1. 30fs IR CEP stabilised, 700μJ, 1kHz
2. sub 7fs IR CEP stabilised, 350μJ, 1kHz
3. 92eV cut-off harmonics to produce an isolated attosecond pulse, 5nJ, 1kHz
4. 30eV - 60eV harmonics as an attosecond pulse train, 50nJ, 1kHz
5. 120 eV cut-off harmonics, 5nJ, 1kHz
6. 71 eV few eV bandwidth harmonics, 0.05nJ, 1kHz
These can be used for a wide range of applications to probe matter details of which are given in the subsequent chapters.
Chapter 4

Attosecond metrology

This chapter describes the apparatus and techniques used to generate and characterise both an isolated attosecond pulse and attosecond pulse trains. The atomic streaking technique \cite{67} is employed using a gas phase atomic medium to measure an isolated pulse of $\sim 270$as duration. To date only a handful of groups around the world have demonstrated this ability.

4.1 Experimental setup

After the spectrometer chamber the XUV and IR beams propagate into the gas phase streaking chamber designed to conduct XUV-IR cross correlation measurements with an isolated XUV pulse. The chamber is a 50cm diameter UHV compatible chamber with a 1000l/s turbo pump to allow the use of a continuous flow gas target. The electron spectrometer is differentially pumped using two 70l/s turbo pumps to allow safe operation of the detection system (section4.1). Figure 4.1 is a plan view of the setup used for the streaking measurement, and figure 4.2
a representation of the geometry of the IR and XUV beams.

![Figure 4.1: A plan view of the TOF chamber. XUV and IR beams enter the chamber and pass through a motorised aperture and two part filter producing an annular IR and XUV inner beam. These map onto a two part mirror with a piezo stage adding a time delay to the inner. Both beams temporally and spatially overlap at a focus in front of the TOF where a gas target is also located. The IR focal spot is re-imaged outside the chamber, while an internal CCD views the alignment in front of the TOF.](image)

Atomic streaking is achieved using a cored two-part molybdenum silicon (MoSi) multilayer circular mirror. Multilayer mirrors are designed to reflect short wavelength photons at the interface between layers at near normal incidence [131]. Each interface is designed to reflect a certain wavelength which is dependent upon the depth between layers. The precise nature of this design restricts the bandwidth that a mirror can reflect, and in this case the MoSi mirror reflects 5eV FWHM centred on 93eV. What may seem as a limitation is exploited in producing isolated attosecond pulses by tuning the cut-off of the high harmonic spectrum to sit within
the bandwidth supported by the mirror (see section 2.8).

The mirror was manufactured from a single quartz substrate (\( f = 100 \text{ mm} \)) with a 4 mm inner cored from the centre (figure 4.2). The OD of the annular outer is 25 mm with the ID 5 mm. The 4mm cored section of the mirror is supported by a P-753 LISA Piezo Nanoautomation stage from PI GmbH which translates the inner mirror ± 12\( \mu\text{m} \) relative to the outer mirror giving a delay of 80 fs (full range) in steps of 0.5 as. The MoSi layers were deposited onto the substrate by NTT -AT nanofabrication.

The high harmonics are phase matched to produce strong on axis harmonics \( ie \) short trajectory harmonics which are selected by placing the HHG gas target before the laser focus. The divergence of these harmonics is measured with the imaging MCP and is typically 2 mrad FWHM, leading to an XUV beam diameter of 3.6 mm at the 2 -part mirror mirror, slightly smaller than the diameter of the inner mirror. The divergence of the IR from the HHG focus is 20 mrad FWHM giving a diameter over filling the two part mirror at 32 mm.

A split 2-part filter is placed upstream of the mirror comprising of a 200nm thin zirconium foil mounted on a 2 \( \mu\text{m} \) nitro-cellulose film to produce an annular outer IR beam and a circular filtered inner XUV beam. A motorised aperture is used to carefully control the IR intensity used as a streaking field, and is placed upstream of the two-part filter (see figure 4.2).

The gas target is delivered through an effusive stainless steel needle, 50mm in length with an ID of 110\( \mu\text{m} \) and OD 300\( \mu\text{m} \). The needle support and housing is grounded to avoid charge build up. The inside of the chamber was tested with a magnetometer to ensure no magnetic fields were present higher than the normal background field (\( \sim 40\mu\text{T} \)). The whole gas target unit is supported on an \( xyz \) stage to position the gas target accurately at the laser focus. Scanning the needle while
measuring an photoelectron flux from XUV ionisation showed a 1mm wide gas target of uniform density (uniform electron counts). Typically the backing pressure to the needle is 300mbar which delivers an estimated target pressure of a few mbar (estimated by monitoring the flow rate of the gas). The background pressure inside the chamber of $3 \times 10^{-4}$mbar when the gas target was used.

As shown in figure 4.1 the focal spot from the two part mirror is reimaged externally on a CCD. This imaging system allows the overlap of the foci from the inner and outer parts of the mirror to be aligned (see section 4.1), and can be used to check the gas target is at the focus of the beam. A further CCD mounted internally is used to check the alignment of the gas target related to the aperture of the time of flight electron spectrometer (TOF).
4.1. EXPERIMENTAL SETUP

Electron spectrometer

The electron spectrometer measures the time of flight of an electron produced at the focus of the two part mirror. The design of the TOF is broadly similar to the TOF designed by Hemmers et al [52], but without the linear motion (see figure 4.3). The TOF has an electrostatic lens system mounted in a front ‘snout’ allowing the initial energy of the electrons to be retarded to 2% of their initial energy before entering a field free drift tube thus increasing the resolution (E/Δ E) of high energy electrons(keV) to $10^4$. However for the streaking measurement in which electrons with $\sim 70$eV are detected, the 440mm field free drift length gives a resolution of 0.15eV which allows streaked electrons to be resolved without requiring retardation [57].

After the drift tube electrons are detected on a ‘Z’-stack MCP where three plates are placed to form a Z shape with the angle of tilt placed on the plates (see insert of figure 4.3). To accelerate electrons from the drift tube to the plates the front plate is connected across a 2.2MΩ resistor to ground. Under normal operation 1kV is applied per plate forming a potential of 600V between the end of the drift tube and the plates. Electron pulses are detected on an anode directly behind the last plate with a typical cascade of electrons producing a pulse of 10mV with a FWHM of 3ns. A high bandwidth $\times 50$ amplifier is used before the pulses are recorded on a time to digital card (TDC) (FAST Comtech P7889) on a PC with a 100ps bin size.

The spectrometer was calibrated by looking at the energy spacing of a known structure, in this case ATI photoelectrons measured with a 30fs IR pulse from neon. First the flight time of the electrons needs to be calculated. A photodiode is used to trigger the TDC, but is an inappropriate method to time the flight time of the photoelectrons from birth to detection. By introducing XUV photons
Figure 4.3: A schematic of the time of flight electron spectrometer used in the experiments reported in this chapter. The TOF has a set of electrostatic lenses placed in front of the drift tube to retard electrons, increasing resolution. However the ~ 0.45m drift tube provides an energy resolution of 0.15eV at 70eV which is sufficient for the measurements described in this chapter. The insert shows the Z arrangement of three micro channel plates used before the anode. The front of the plates was grounded through a resistor producing a short accelerating voltage between the end of the drift tube and MCPs. Figure is adapted from [52]

along with the IR it was found that a sufficient number of photons were scattered from the gas target to produce counts on the MCP, with this peak used as time zero for measurements. The length of the drift tube was calibrated by comparing the calculated peak spacing for an ATI electron spectrum given by absorption of an increasing number of photons to a measured spectrum. The photon energy was calculated by measuring the central wavelength of the laser spectrum. The calculated peak spacing was adjusted to match the measured by changing the value
4.1. EXPERIMENTAL SETUP

of \( d \), the drift tube length in:

\[
E = \frac{m_e d^2}{2l^2}
\]

until there was good agreement (see figure 4.4). The drift tube was found to be 0.445 (± 0.001)m long.

![ATI spectrum](image)

Figure 4.4: An ATI spectrum collected from an Ar target using a 30fs IR pulse to calibrate the electron spectrometer. The blue curve is the collected spectra and the red curve is the region of the spectra used for calibration. The blue dots are calculated positions of the peaks for the measured wavelength of the laser. The length of the drift tube was varied until good agreement was reached between the calculated and measured spectra.

**IR -IR autocorrelation**

A clear stepping stone to measuring an XUV - IR cross correlation is to measure IR - IR correlation first. This is because the alignment of the IR and XUV is broadly similar and IR is easy to image on CCDs to check spatial and temporal overlap.
The two-part mirror is supported by a mount allowing the pointing of each mirror to be individually set, and then both mirrors to be aligned as one to position the combined focus. Initial spatial alignment of the two mirror sections was done by focusing the 30fs IR beam into air to produce a visible plasma, which could be aligned for spatial overlap. Coarse temporal overlap was done in the same way, a visual change in the plasma is observed when the beams from each mirror were temporally overlapped. The video image from the CCD inside the experimental chamber (figure 4.1) was then used to precisely align the overlapped foci from both mirrors in front of the opening of the TOF.

To ensure good spatial and temporal overlap the external CCD was used to image the foci of the two-part mirror. This allowed fine adjustment to be made. An interferogram was produced scanning the inner beam ± 40fs relative to the outer and summing the intensity of the overlapped focal spots. Figure 4.5 shows a good overlap of the beams, with the lower inserts examples of destructive and constructive interference recorded at fixed delays on the CCD.

As can be seen from figure 4.5 temporal overlap was set to be at one end of the stage’s range, to compensate for an extra delay experienced by the the outer beam as it will pass through a kapton or nitro-cellousoe pelical support holding the thin metal filters in the streaking experiments.

4.2 IR and attosecond pulse trains

Sidebands in the photoelectron spectrum caused by two-photon ionisation are readily seen when a low intensity of IR field is mixed with plateau harmonics that constitute an attosecond pulse train [98]. It was observed that the MoSi mirror has residual reflectivity of a few percent for lower order harmonics (∼ 40eV). The
4.2. IR AND ATTOSECOND PULSE TRAINS

Figure 4.5: Interferogram of the outer and inner IR focal spots from the 2-part mirror with a 30fs pulse. The lower inserts are images from fixed delays of the constructive (bottom left) and destructive (bottom right) interference patterns.

typical flux of plateau harmonics produce in argon is approximately 100 times greater than the cut-off harmonics produced in neon. Therefore the photon flux at the gas target in the experimental chamber will be of the same order for Ne or Ar when suitable filtering is used to bandpass the lower order plateau harmonics.

For these measurements a similar experimental arrangement was used as described in section 4.1 with the IR field being reflected from the outer of the two-part mirror and the XUV from the inner. An identical filter arrangement was used with the exception that the zirconium was replaced with a 200 nm aluminium filter to pass the plateau harmonics from argon. To ensure a pulse train was produced with sharp photoelectron peaks the unbroadened output of the 30 fs pulse from the laser was used to produce narrowband harmonics and provide the IR field for the measurement. This IR field was attenuated using the adjustable iris before the two-part filter, and the power transmitted to target was measured with a power meter after the target. The intensity of the IR field at the focus in the neon gas
target was $8 \pm 2 \times 10^{11}$ W/cm$^2$. Photoelectron spectra were collected for 30 seconds (30,000 shots integrated per step) with a scan stepping from 0 to 20fs in steps of 100as.

The oscillation in the intensity of the sideband is clearly visible in figure 4.8, and the chirp between harmonic emission is also apparant. However these data are not suitable to retrieve a pulse duration of the pulses in the train. The MoSi mirror has a very modulated reflectivity in this region, even between neighbouring harmonics ($\pm 50\%$) which is not easily quantifiable leading to large errors an any retrieval.

Figure 4.6: Residual reflectivity of a multilayer MoSi mirror from 30 -50 eV at 83° incidence
Figure 4.7: Photoelectron spectrum collected from plateaux harmonics with an IR field of $8 \times 10^{11}$ W/cm$^2$.

Figure 4.8: Photoelectron spectrum as a function of delay. The sidebands are visible between the photoelectrons detected from harmonics, with the beating of the sideband visible from the interference between the different two photon paths.
4.3 IR and isolated attosecond pulse - Atomic streak camera

For a sub 7fs IR pulse which is more than 2 cycles of the IR field, isolated attosecond pulses can be produced by a combination of spectral filtering and CEP locking to restrict the highest energy XUV photons to a single half cycle of the laser field [67]. The CEP locking system sets the CEP to an arbitrary off-set, and from this value one needs to scan the off-set to cover all ranges. To restrict the highest energy emission the CEP needs to be a ‘±cosine’ pulse ie with CEP $\phi = 0$ or $\pi$, as shown in figures 4.9a) and 4.9c). For these conditions the highest energy harmonic emission is restricted to a single half cycle and forms a continuum at the harmonic cut-off[20].

The continuum is visible in the harmonic spectrum imaged on the XUV spectrometer (figure 4.10). This method is a convenient first step in determining a suitable CEP value for production of an isolated attosecond pulse.

![Figure 4.9: Representation of the CEP influence on isolated XUV pulse production.](image)

Pulses with a 0 or $\pi$ CEP offset result in a single XUV emission at the zero crossing of the IR field. For an offset of $\pi/2$ two half cycles contribute. For the isolated pulse production used in this section one should view the threshold represented by the black dashed line as the band pass of the MoSi mirror. The arrows refer to the over-threshold regions and the corresponding isolated XUV pulse produced by the recombining electron wave-packet is given by 1 or 2.
A more robust test relies on the fact that the highest energy XUV photons will be emitted close to the zero crossing of the IR field. Their emission is synchronised with the highest vector potential of the IR field and therefore an electron produced by these photons will be given the largest streak in momentum from the IR in the direction of the laser polarisation. For a ‘cosine’ pulse ($\phi = 0$) the harmonic emission is synchronised with a positive vector potential and an electron will be streaked to higher energies. Conversely a ‘-cosine’ pulse will produce electrons streaked to negative energies. A ‘sine’ pulse however with two XUV emissions would streak electrons produced by the XUV both up and down corresponding to the two zero crossings of the vector potential separated by $T/2$ of the pulse [67].

By co-propagating the IR and XUV pulses onto the centre of the two-part mirror with no delay and no filtering and collecting photoelectrons from a neon target
this effect was observed. The dependence of the streaking direction with CEP was obtained by scanning the CEP of the laser while recording photoelectron spectra collected. Figures 4.11 and 4.12 display this dependence. It can be seen the pulses with a CEP of $\phi = 0$ and $\phi = \pi$ show a single XUV emission. These have a single emission of XUV in the bandwidth of the two-part mirror - an isolated pulse. Pulses with a CEP of $\phi = \pi/2$ and $\phi = 3\pi/2$ are a ‘sine’ pulse and have two emissions of XUV in the bandwidth of the mirror.

![Figure 4.11: The CEP dependence of streaked photoelectrons produced by XUV emission from few-cycle IR pulses. Pulses with a CEP of $\phi = 0$ and $\phi = \pi$ show a single XUV emission as electrons are streaked in a single direct. Pulses with a CEP of $\phi = \pi/2$ and $\phi = 3\pi/2$ have two XUV emissions separated by T/2 of the laser field. These electrons are streaked up and down.](image)

Once an isolated pulse was verified the CEP is locked at the correct value to produce a ‘cosine’ pulse. The Zr two-part filter was then placed in the beam to
4.3. IR AND ISOLATED ATTOSECOND PULSE - ATOMIC STREAK CAMERA

Figure 4.12: Individual spectra from figure 4.11 a) is a cosine pulse, b) a sine pulse and c) a -cosine pulse

removed lower order harmonics and IR from the centre of the two-part mirror. A motorised iris in the chamber was closed to reduce the intensity of the IR field to $3.5 \times 10^{12} \text{W/cm}^2$ and a sample photoelectron spectrum taken at a delay where the IR and XUV pulses are not overlapped (figure 4.13). The IR pulse and XUV pulse were temporally scanned over a range of 45fs in 200as steps with an integration time of 30 seconds (30,000 shots) at each step. The resulting scan is shown in figure 4.14.

From the figure one can see the distinct oscillation of the photoelectron energy as it is streaked by the electric field of the sub 7fs IR streaking field. The nature of this oscillation suggests that the XUV photons ionising the Ne target were restricted to a single half cycle of emission at the peak of the IR pulse envelope in agreement with the CEP dependence measurement. If another half cycle of the pulse contributed photons in the bandwidth of the MoSi mirror evidence of this would be visible as a secondary out of phase ‘pulse’.
Figure 4.13: The photoelectron spectrum collected from Ne gas when ionised by a 5eV bandwidth of XUV centre at 93eV

Figure 4.14: Spectrogram of streaked photoelectrons produced by 93eV XUV photons. The streaking field was a sub 7fs IR field with an intensity of $3.5 \times 10^{12}$ W/cm$^2$.
Analysis

The spectrogram shown in figure 4.14 produced by the interferometric scan of the IR field and XUV can be described as [76]:

\[
\sigma_A(v, \tau) = \left[ \int_{-\infty}^{\infty} \chi(v, t) G(t - \tau) e^{i(v^2/2) t} dt \right]^2
\]\n(4.2)

where:

\[
G(t - \tau) = e^{i\Theta(t - \tau)}
\]\n(4.3)

Here \(v\) is the final velocity of the streaked photoelectron, \(\tau\) is the time delay between the IR and XUV fields and \(\chi\) describes the quantum mechanical distribution of the electrons released by the XUV pulse [112]. \(G\) describes the gating field, which in this case is a phase-modulating IR field with with phase given by \(\Theta\) [33, 58]. The spectrogram is similar to that of a FROG trace recorded on a CCD allowing the electric field and phase of the pulse to be retrieved in a similar method, but in this case the gate is a phase gate.

A principle component generalised projections algorithm (PCGPA)[61] is used to iteratively converge on a reconstructed electric field amplitude and phase of the IR and XUV pulses used in the measurement\(^1\). This process does not need to use the full oscillation of the trace for reconstruction. If the signal to noise ratio of the centre of the pulse causes a large FROG error the extremities of the IR pulse can also be used. The wings of the IR pulse contain enough information to allow the PCGPA to converge on a reconstructed trace. At the lower intensity wings of the pulse electrons ionised by the XUV are streaked less. As a result there is a higher electron count per time bin. This retrieval technique is commonly referred to as complete reconstruction of attosecond bursts or FROG-CRAB [90].

\(^1\)Work reconstructing the XUV pulse from the spectrogram measurements was carried out by Mr T Witting in the Laser Consortium, Imperial College
An example of this reconstruction is given in figure 4.15. The retrieved XUV pulse duration is $270 \pm 50\text{as}$ with the error estimated by the FROG retrieval error and analysis of the spectrogram resolution. The retrieval also shows a positive chirp. This chirp is the intrinsic chirp of XUV pulses produced by high harmonic generation and is a result of the different times electrons spend in the laser field during HHG [15, 80]. Metallic filters can be used to correct for this chirp or a multilayer chirped mirror could also be used in future work [131]. The pulse duration is close to the transform limited pulse duration of $250\text{as}$ supported by the MoSi mirror.

Figure 4.15: A FROG reconstruction of the XUV pulse from the measurement in figure 4.14. a) The a section of the measured spectrum just to the right of the main body of the IR pulse. b) The reconstruction of the pulse by the algorithm. c) The reconstructed intensity of the XUV pulse showing the FWHM pulse duration to be $272\text{as}$. The reconstruction also shows a positive chirp of the pulse.
4.4 Summary

An isolated XUV pulse with a duration of 270as has been produced from a single intense half cycle of a sub 7fs CEP stabilised IR pulse. The demonstrated ability to control the intensity of individual half cycles of the IR field has allowed a continuum of XUV photons to be emitted at the cut-off (93eV) of a high harmonic spectrum. The CEP can be set to restrict the highest energy photon emission to a single or multiple half cycles of an IR pulse. This control allows electron emission from matter to be turned ‘off’ or ‘on’ on an ultrafast (1.3fs) timescale.
Chapter 5

Surface Beamline

Our motivation in developing a surface science apparatus was to couple the unprecedented temporal resolution offered by isolated attosecond pulses described in chapter 4 to the study of interesting charge behaviour at the boundary of a surface or behaviour influenced by the nanoscale structure on a surface. Just as attosecond science has changed the way scientists think about ‘instantaneous’ events such as photoemission where it has recently been shown there is a delay in photoemission between the 2p and 2s orbitals in Krypton of 21as [111], attosecond pulses have revealed the transit time of electrons from core states in a metal to the surface of 100as.[21, 136]. This ability to directly measure electron emission will allow scientists to refine models of charge dynamics in condensed matter - particularly relevant to the photovoltaic industry.

Plasmonics is an area of physics likely to revolutionise surface devices [36]. Already enhanced resonant plasmons promise to expand an area of science close to the core of this thesis, high harmonic generation [70]. Direct temporal mapping of the field evolution will allow this process to be refined and developed opening up high harmonic generation to a larger number of scientists.
To investigate these areas a surface science apparatus was constructed to allow few cycle IR and copropagating attosecond pulses to probe surfaces in a clean ultra high vacuum condition ($10^{-10} - 10^{-11}\text{mbar}$). Charge dynamics were recorded with an electron spectrometer.

In this chapter I describe the ultra high vacuum system which I designed and constructed during my PhD. Design considerations for the different aspects of the chamber are discussed and a summary of the apparatus capability is presented at the end of the chapter.

The development of the surface science apparatus was divided into two stages. The initial work (Mark 1) was to develop a system to investigate charge and state dynamics resulting from a structured or rough surface, while future work measuring solid state charge and state dynamics was also considered in the design (Mark 2).

The key requirements of the surface system were detailed as:

**Mark 1:**

1. ultra high vacuum conditions - $10^{-10} - 10^{-11}\text{mbar}$
2. ability to present and manipulate a sample in the XUV and IR beams in 5 axes with a reproducibility of less than $10\mu\text{m}$ and resolution better than $10\mu\text{m}$
3. delivery of focused XUV and IR beam onto a sample
4. electron spectrometer
5. multiple samples available for experiments

**Mark 2:**

1. multiple sample preparations techniques
2. surface diagnostics

3. angular resolved electron spectrometer

4. load lock to transfer samples

Mark 1 of the system has been completed (shown in figure 5.1) and design of the system allows a simple upgrade to mark 2 in the future. A description of the surface apparatus and design consideration follows.

Figure 5.1: The surface science apparatus of the Attosecond beamline.
5.1 Initial design criteria

The system requirements were divided into three sections: experimental, preparation and sample transfer with several designs being carefully evaluated. A design incorporating a separate experimental and preparation chamber was favoured with a gate valve between the two. This simplified the pumping requirements and allowed future expansion of the system. Height restrictions in the lab required a horizontal arrangement of the system - this had a knock-on effect for the sample transfer.

The ASB has been constructed to allow re-imaging of the HHG focus with a 2f-2f geometry. Placing the focusing optic in the gas phase time of flight chamber set the laser geometry that was used to build the surface science experimental chambers around.

A gold toroidal mirror (65mm long and 40mm high) is used as the focusing optic with a focal length of 710mm with a $7^\circ$ angle of incidence - shown in figure 5.3. Grazing incidence allows a high reflectivity over a large bandwidth of XUV photons (figure 5.4). However this shallow angle limits the acceptance of the mirror to 6mm. The focal spot at the surface of an IR beam is shown in figure 5.5 with a
1/e² diameter of 500 microns. Surface investigations planned for the chamber all investigate processes occurring at intensities up to the onset of surface ablation ie below $5 \times 10^{11}$ W/cm² [96, 108, 81, 63], typically around $5 \times 10^{10}$ W/cm². Figure 5.6 is a plot of the peak intensities at the focus in relation to the pulse duration and angle of incidence between the surface and beam, where 90° is the sample perpendicular to the beam. The intensities were calculated assuming an IR energy of 120 µJ and using the measured focal spot beam waist of 500 µm 1/e². The plot shows that attenuation will be required for all pulse durations to avoid surface damage, details of relevant attenuation methods are given in chapter 6.

Figure 5.3: Toroidal mirror and mount. The Au coated mirror has a focal length of 710 mm and has a 7° angle of incidence. The mirror is shown in gold and the mount in grey. The red areas are motors allowing the mirror to be translated in 6 axes.

Measurements investigating field enhancement will require careful measurements of the laser intensity. To do this a single shot autocorrelator is installed at the entrance to the ASB to measure the pulse length. The pulse energy is measured by calibrating the IR transmission of the system and recording the input power.
To measure the focal spot size at the surface an imaging system has been built to re image the focal spot onto a CCD mounted externally from the chamber. To give a reference plane for the measurement the transfer arm has been fitted with a small needle allowing the beam to be obscured. This system allows the laser intensity to be routinely measured.

![Graph](image)

Figure 5.4: Reflectivity of the toroidal mirror used to deliver and focus the IR and XUV beams into the surface experimental chamber. Figure shows reflectivity between 35 and 120 eV at 7°. Data from [2]

To reduce the amount of apparatus inside the chambers for UHV considerations, an external manipulator arm was used instead of internal motors and translation stages. Details of the preparation chamber are given in section 5.2 and the experimental chamber in section 5.3 below.

### 5.2 Surface preparation chamber and sample transfer

The surface preparation chamber was built with flexibility in mind while minimising internal surface area. The chamber wall and flanges were constructed from
Figure 5.5: IR focal spot measured at sample surface, with a $1/e^2$ diameter of 500µm

Figure 5.6: The peak intensity at the focal spot of the toroidal mirror as a function of sample angle and pulse duration
electro-polished 316LN stainless steel. A pumping tee was constructed below the chamber for a range of pumps (details in section 5.5) with the pumps situated as close as possible to the chamber. To avoid decreasing effective pumping rates the pumps are connected via CF150 flanges throughout.

In the current phase of development there are no surface preparation methods installed. The next stage of development will be to install an ion sputter gun to produce a tightly focused ion beam able to bombard a surface removing surface contamination. After this process a period of heating the surface or annealing allows a crystalline structure to reorder. The chamber is designed to allow the installation of a low energy electron diffraction diagnostic (LEED) if a well ordered crystalline surface is required [54].

Sample transfer is achieved with a VG Ominax manipulator arm with 1 metre of travel. The arm was modified to reduce coupling of vibrations (see section 5.4) and sits directly onto the optical table. The arm allows the sample to be positioned in front of future surface preparation apparatus inside the preparation chamber and to be transferred into the experimental chamber. A multiple sample head has been built (figure 5.7) to modify the single sample carrier supplied by VG allowing 6 samples to be mounted at once. Translation between samples is via the principle axes of rotation of the arm, and allows measurements to be conducted on different samples under the same conditions. This will be an invaluable tool in studying surface enhancement from different surface roughness values. The design of the sample carrier allows for a simple load-lock\(^1\) to be installed on the chamber at a later date\(^2\).

\(^{1}\)A load-lock is a small chamber allowing new samples to be introduced into the system without letting the whole system up to air

\(^{2}\)The main design of the sample holder was by Thorsten Uphues in consultation with the author.
5.3 Experimental chamber and electron spectrometer

Surface science experiments take place in the experimental chamber which connects directly to the preparation chamber. Here the samples can be transferred on the manipulator arm in front of the IR and XUV beams. The chamber is constructed from 316LN stainless steel and is based around a 400mm diameter vertical cylinder.

A time of flight (TOF) electron spectrometer is used that is identical to the one used in the gas-phase measurements made on the ASB. The TOF uses a z-stack micro channel plate detector to detect electrons. The detector has a similar lens system as [52] to allow electron energies to be reduced to 2 % of their initial energies without effecting transmission, allowing greater energy resolution.

The principal energies of the photoelectrons measured in the apparatus will be 100eV and below. For example using the cut-off harmonics produced in neon at
90eV to measure the Fermi edge of Au will produce photoelectrons of 85eV and below. Probing the 4f band in Au which has a binding energy close to 87eV with 100eV photons would produce photoelectrons with 13eV. For the initial planned work highest energy resolution will be required to measure the streaking of a feature such as the Fermi edge by an IR field. With an XUV bandwidth of several eV an energy resolution of only 1eV would be sufficient to retrieve field information from the trace [57].

In a TOF the energy $E$ corresponding to an arrival time $t$ is given by:

$$E = \frac{1}{2}m_e \left( \frac{d}{t} \right)^2$$

(5.1)

where $d$ is the length of the drift tube and $m_e$ is the mass of an electron. The time to digital convertor (TDC) data acquisition card used has a minimum time bin width of 100ps. Using this the resolution of the electron detector with a field free drift tube is shown in figure 5.8 with a summary in table 5.1. The resolution is given by $E/\Delta E$ and is between to $10^2$ and $10^3$ in the energy range of primary interest (10 - 100eV). This allows features of interest to be resolved without the requirement of applying a retarding voltage to the lens elements.

<table>
<thead>
<tr>
<th>Energy [eV]</th>
<th>Resolution [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.008</td>
</tr>
<tr>
<td>30</td>
<td>0.0413</td>
</tr>
<tr>
<td>50</td>
<td>0.089</td>
</tr>
<tr>
<td>90</td>
<td>0.214</td>
</tr>
</tbody>
</table>

To provide flexibility in electron and ion detection the experimental chamber was designed around several TOF orientations and 5 degrees of freedom on the sample holder. A VG Scientia SH2 series sample holder is used to provide primary and azimuthal axes of rotation. Using the primary axes of rotation as a method of
translating between multiple samples removes the requirement of a load-lock in the first build of the system.

The angle between the sample and solid angle of detection of the TOF is a key factor for electron detection. The initial work will not be looking at crystalline samples with a angular dependence of electron emission, however other factors will come into play. Primarily specular reflection onto the MCP needs to be avoided. Reflecting IR and XUV down the drift tube of the TOF will produce electrons from internal surfaces or direct counts on the detector. These secondary sources of electrons will complicate the time of flight data and are likely to overwhelm the detection system. For these reasons a grazing angle of incidence between the laser
and sample is preferred with the TOF at an angle close to orthogonal.

The relative geometry between the polarisation of the laser and electron collection is a key aspect to measure the time evolution of resonant plasmonic fields. Whereas electric field enhancement from surface roughness is from the random arrangements of gaps and peaks on a surface, ordered structures are designed to resonate for a particular field and polarisation orientation [92]. Referring to figure 5.9 the polarisation of the driving field needs to be in the plane of the structures to enhance a field in the engineered gap. To directly map the momentum shift given to an electron in a streaking field one needs to collect electrons in the plane of the streaking field’s polarisation [35]. It is planned that initial measurements of resonant plasmonics enhancement will be measuring the streaking of electrons mapping the Fermi edge of a dielectric substrate localised in the gap. However it is not possible to collect these electrons released in the plane of the driving field’s polarisation as they will collide with the gold structures. Collecting electrons in an orthogonal plane to the field’s polarisation will allow a projection of the momentum imparted to the electrons to be mapped.

To measure the time dependence of an enhanced plasmonic field, information about the temporal field strength needs to be measured. Collecting electrons perpendicular to the laser polarisation will record a projection of the amplitude of the plasmonic field giving a streak to electrons liberated by a XUV photon. With reference to figure 5.10 it is shown that collecting electrons with a limited solid angle when the vector potential of the streaking field is non-zero results in a downshifting of the momentum of the electron.

By temporally delaying the birth of photoelectrons by delaying the XUV pulse relative to the phase of the plasmonic field there is a shift in the momentum $\Delta p_x$

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3I wonder if anyone will read this footnote. Email me if you do, christopher@imperial.ac.uk
5.4 VIBRATION ISOLATION

Figure 5.9: A representation of nanostructures being excited by an electric field. The structures are only excited with a polarisation in the plane of the substrate. Electrons produced from the gap can not be collected in this plane as they collide with the structure.

of the plasmonic electric field, which as can be seen from figure 5.10 downshifts the momentum of the collected electrons.

It is important to note that with this geometry there is a $\pi/2$ symmetry in the momentum shift relative to the phase of the plasmonic field. This arrangement will provide information about the amplitude of the carrier of a plasmonic field and its envelope. This will be an invaluable stepping stone to developing a technique to fully map the phase of the carrier in future studies.

The experimental chamber is built with an internal breadboard to mount optics that may be required in future studies. Methods to limit coupling of vibrations to the sample and beam optics and described in the next section.

5.4 Vibration isolation

In common with the ASB the surface system has been built to minimise vibrations coupling to any optics used and the sample itself. An identical approach of double
Figure 5.10: A representation of the detected momentum shift of photoelectrons streaked by a plasmonic field when the plane of the electron spectrometer is orthogonal to the streaking field’s polarisation. The black arrows in each figure a) to c) represent the isotropic distribution of electrons emitted by XUV photons with a limiting distribution imposed by a structured surface. When the vector potential is zero and uniform over the electron distribution (figure b)) an unstreaked electron spectrum is detected. If the vector potential is either positive or negative then the projection of the streaked electrons always reduces the momentum of the electrons detected by the TOF.

balanced bellows is used in common with the ASB to decouple the chambers from the internal breadboards. The bellows (figure 5.11) work by maintaining a solid connection between the internal breadboard and the external optical table, while the vacuum chamber is supported by an external frame directly to the lab floor. Any vibrations of the chambers are damped by the flexible bellows connecting the chamber and table supports.

The decoupling was tested using a laser doppler vibrometer (SIOS Lasers GmbH). Mirrors were mounted on the external vacuum chamber wall and on the internal
breadboard. Initially vibrations were measured from both mirrors under normal conditions *ie* all vacuum pumps running (figure 5.12 and 5.13). One can see that even when a strong vibration is coupled to the vacuum chamber this is not transmitted to the internal breadboard.

Extending the approach of isolating all the optics from the chambers, it was decided to also isolate the sample holder from the chamber wall. The market leader for manipulation under vacuum is VG Scienta’s Omniax. Their design was modified to decouple the chamber from the arm by using flexible bellows. In the standard design a short set of bellows connect the translation stages of the manipulator to a solid frame supported by the chamber flange. This directly couples the sample arm to any vibration of the chambers. To avoid this, the bellows were extended to connect directly to the chamber flange without support. The arm was then supported by a solid frame which sat directly onto the optical table. This reduced coupling of vibrations from the chamber to the sample arm. Vibrometer measurements of a mirror mounted on the sample holder showed motion of less than 10 nm when the arm was fully extended into the measurement position. Switching off the mechanical pumps on the chambers had no impact on this small motion, indicating that they were entirely decoupled from the sample head. To the best of the author’s knowledge and with discussion with other researchers in the field this isolation is extraordinary with other systems suffering from coupling from mechanical pumps.

Sources of vibration were also minimised in the design. Magnetic levitation turbo pumps were used to remove mechanical vibration from bearings, and backing lines were sunk into cement blocks to dampen vibrations from backing pumps. Finally a cryo shield was installed, this combined with an ion pump could provide pumping in UHV for the system with only static components.
Figure 5.11: a) A schematic of double balanced bellows. The internal optical table is supported by a solid connection to the external optical table. Flexible metal bellows connect the breadboard support to the vacuum chamber which is supported by and external frame standing directly on the floor. The flexible bellows allow the chamber to move around the optical table b) Vibration isolation from the chambers to the sample is achieved with an extended set of bellows connecting the preparation chamber and the transfer arm. The arm is supported by a metal frame sitting directly onto an optical table, while the chambers are supported by an external frame directly to the lab floor.
5.4. VIBRATION ISOLATION

Figure 5.12: Vibrometer measurements of a mirror mounted on the external wall of vacuum chamber. The blue trace is measured when low frequency (sub 100 Hz) strong vibrations were coupled to the chamber wall, the red trace is measured under normal conditions.

Figure 5.13: Vibrometer measurements of a mirror mounted on the internal breadboard supported by double balanced bellows on a vacuum chamber. The blue trace is when extra vibrations are coupled to the external chamber wall. It is seen very little is coupled from the wall to the internal board.
5.5 Achieving UHV

Reaching and maintaining ultra high vacuum (UHV) conditions - a regime commonly referred to when the pressure is below $10^{-9}$ mbar and lower - involves paying careful attention to every aspect of the chamber design. Ideas of collective motion of particles such as fluid dynamics do not apply at UHV, a point illustrated by examining three values: the particle density, the mean free path of a particle and the particle flux onto a surface.

Particle density: $n = \frac{P}{kT}$
mean free path: $\lambda = \frac{kT}{1.414P\sigma}$
particle flux: $\Phi = \frac{P}{\sqrt{2\pi mkT}}$

where $P$ is the pressure in units of [Nm$^{-2}$], $k$ is the Boltzmann constant, $T$ is the temperature in Kelvin, $\sigma$ is the collision cross section and $m$ is the molecular mass of the species of interest. From these equations the minimum time for a monolayer of particles to form on a clean surface $ie$ how long it takes for a clean surface to become dirty, can be calculated. Typical values are shown in table 5.2.

<table>
<thead>
<tr>
<th>Pressure [mbar]</th>
<th>Particle density [$m^{-3}$]</th>
<th>Mean free path [m]</th>
<th>Time for a monolayer [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>$10^{25}$</td>
<td>$7 \times 10^{-8}$</td>
<td>$10^{-9}$</td>
</tr>
<tr>
<td>$10^{-6}$</td>
<td>$10^{16}$</td>
<td>50</td>
<td>1</td>
</tr>
<tr>
<td>$10^{-10}$</td>
<td>$10^{12}$</td>
<td>$5 \times 10^5$</td>
<td>$10^4$</td>
</tr>
</tbody>
</table>

The importance of UHV can be seen in the minimum time taken to produce a monolayer. Unless the background pressure is $10^{-10}$ mbar or less it really is not possible to perform experiments on a clean surface without surface contamination. The mean free path of a particle in UHV is of the order of km’s meaning particles
interact with the surface walls far more than each other, furthermore the particle density is 13 orders lower than when at atmosphere.

These values influence the design of a UHV system. The lower particle density at UHV highlights the problems of trapped volumes or outgassing from dirt leaking into the vacuum. For example oil from a fingerprint outgasses at a rate of about $10^{-5}$ mbar/sec [3], to maintain a pressure of $10^{-10}$ mbar would require a 10000l/s pump for this contamination alone. Outgassing of gaseous molecules desorbing from chamber walls and other materials can cause problems in pumping down [1]. For this reason materials used to manufacture the chamber and internal components were chosen for low outgassing rates and low magnetic permeability such as stainless steel 316LN, oxygen free copper and titanium. Electro-polishing of the chamber walls decreases the surface area significantly reducing the number of particles stuck to the walls. For particles that remain the chambers were fitted with welded heating wires allowing the surfaces to be heated or baked. The heating increases the desorption rate and reducing the pump down time.

The pumping system is designed to achieve a lower pressure in the preparation chamber ($10^{-11}$ mbar) to allow clean surfaces to be prepared and stored in an environment to minimise surface contamination. The primary pumps are 300 l/s turbo pumps with magnetic bearings (Oerlikon MAG W 300IP) and a 70l/s turbo (Varian V-70) on the output to improve the efficiency. This is then backed by a 300l/s scroll pump (Oerlikon SC 30D). The chambers are baked with surface welded heating wires to maintain the chamber wall to 200°C typically for two weeks. After this a 300l/s ion pump (Varian VacIon Plus 300) with titanium sublimation pump (Varian) is used to pump smaller molecules and atoms such as water and hydrogen. The pumping cycle is typically 4 days to reach $10^{-4}$ mbar and two weeks to $10^{-11}$ mbar. The experimental chamber is pumped by similar
turbo pumps and heating wires, while a 70l/s turbo is used on the electron time of flight tube.

An open connection to the ASB is required for transmission of few cycle IR and XUV pulses. To maintain $10^{-10}$ mbar conditions in the surface experimental chamber a differential pumped aperture was constructed. As shown in table 5.2 the mean free path of particles is many kms at UHV. An effective pressure differential can therefore be achieved by limiting the direct path of a particle with a small apperature. Two 70l/s turbo pumps (Varian V-70) pump two small chambers ($\sim 100cm^3$) separated by a aperture with a further aperture at the entrance and exit of the unit. This device maintains a differential of 3 orders of magnitude between the surface chambers and the ASB allowing true UHV measurements to take place. A schematic of the pumping system is shown in 5.14.

5.6 Summary

The requirements set for the surface apparatus in mark 1 of the design have been met. I have designed and built a system that can reach UHV conditions($< 10^{-10}$mbar). The modifications to the sample manipulator arm have provide 5 axes of sample manipulation with a resolution of $5\mu m$ and $0.1^\circ$ while provided exceptional vibrational decoupling. No source of mechanical vibration were observed to couple into the arm with only 10nm of motion of the arm detected.

Experiments demonstrating the capability of the apparatus to measure electron dynamics on surfaces are described in chapter 6.
Figure 5.14: The pumping system used to maintain UHV conditions in the surface science apparatus. The preparation and experimental chamber are separated by a gate valve and a differential pumping unit connects the apparatus to the ASB. An ion and titanium sublimation pump complement turbo pumps in the preparation chamber to achieve $\sim 10^{-11}$ mbar. A cyro unit is also installed to substitute for mechanical pumps if vibrations are a problem.
Chapter 6

Surface investigations

This chapter describes experiments conducted with silver and gold surfaces which have demonstrated the capability of the apparatus presented in chapter 5 to measure electron dynamics of a surface. IR fields were used to excite localised nano plasmons on a rough silver surface enhancing the electric field of the laser by more than a factor of 40. High harmonics were used to map the Fermi energy, and it was found a narrow bandwidth of harmonics was not required to observe the edge. Electron temporal dynamics of hot electrons were measured with a two photon emission experiment from a gold surface. The thermalisation process was found to be dominated by electron - electron scattering.

6.1 Photoelectron spectra from a rough silver surface

The photoelectron emission from a 50 nm thick evaporation of Ag onto a fused silica substrate was investigated using a 10fs IR pulse at intensities ranging from
Experimental method

A broadened pulse from the hollow core fibre was attenuated using a combination of a broadband $\lambda/2$ waveplate and polariser, allowing the energy of the pulse delivered to the sample to be varied from 50nJ to 100µJ. The polariser was set to transmit $p$-polarised light, which is in the plane of the TOF drift tube. A 50nm thick sample of rough silver on a fused silica substrate was mounted on the sample arm and maintained under UHV conditions ($10^{-10}$mbar) (see figure 6.1). This was presented in front of the TOF at 75° to the perpendicular to the TOF drift tube, a geometry which stopped any specular reflection of IR photons being detected by the TOF.

Calibration of the TOF was conducted by producing photoelectrons from a gas target with a known harmonic spectrum produced with the unbroadened 30fs pulse. This method provided a ‘time-zero’ as the TOF detected scattered XUV photons from the gas target. The length of the drift tube was calibrated by measuring the central wavelength of the unbroadened 30fs pulse with a spectrometer (Ocean Optics) and then setting the drift tube length to match the observed harmonic spacing of $2 \times h\omega$. The drift tube length was found to be 0.470 ($\pm 0.001$)m. Ideally an ATI spectrum would be produced with the IR beam for this purpose, however the loose focusing used limits the highest intensity achievable to $\sim 3.0 \times 10^{12}$W/cm² on the sample, which is below the multiphoton ionisation threshold in a gas [100].

Photoelectron spectra were collected for 2 minutes (120,000 shots) at 14 different intensities. Figure 6.2 is a plot of 4 different intensities ranging from the lowest value to the highest.
It is clear from the figure that multiphoton emission (MPE) processes are occurring because the photoelectron spectrum extends to an energy of 35eV when the target is irradiated with 1.5eV photons. A power law relationship was fitted to the integrated yield of photoelectrons in different energy bands with the non-linearity extracted for each. The non-linearity for electrons with 4.5eV was 2.7, 10.5eV was 4.1 and 18.0eV was 7.1. For each energy band the non-linearity is higher than would be expected if a purely perturbative model of MPE was assumed. To explain the difference between the observed energies and a multi-photon model we must consider alternative mechanisms that could boost the electron energies.
Figure 6.2: Photoelectron spectra measured for a range of IR laser intensities from $7.5 \times 10^9 \text{W/cm}^2$ to $4.2 \times 10^{10} \text{W/cm}^2$ from an Ag surface irradiated with a IR pulse.

Coupling of surface plasmon polaritons to the metallic surface can be ruled out as a source of the enhancement for two well documented reasons. First the plane of the surface is perpendicular to the polarisation of the laser field, which stops coupling [88]. Secondly, for coupling, the momentum mismatch between the wave-vector of the plane wave and the surface plasmon needs to be matched. A regular feature in the surface could achieve this by matching the difference between the IR photon momentum:

$$k_{IR} = \frac{\omega_o}{c} \sin \theta + 2\pi a^{-1}$$  \hspace{1cm} (6.1)

and the wave-vector of a coupled surface plasmon:

$$k_{sp} = \frac{\omega}{c} \sqrt{\frac{\epsilon}{1 + \epsilon}}$$  \hspace{1cm} (6.2)

Where $a$ is the grating constant, $\epsilon$ is the dielectric constant of silver. From [104]
Figure 6.3: A plot of the log of the total electrons in different energy bands (width $\hbar \omega_0$) vs log of the laser intensity. Data shown for photoelectrons with energies of 4.5, 10.5 and 18.0eV

$\epsilon = -22.3$ for IR and with the angle between the TOF axis and sample as 75°, the surface would require a regular spacing of 14\(\mu\)m for $k_{IR}$ and $k_{sp}$ to be matched. Atomic force microscope images were taken of Au samples manufactured in similar conditions to the Ag sample used in this measurement\(^1\). It has previously been reported that an evaporation of Ag would produce a surface with a similar roughness to Au [104]. It is therefore a valid assumption that the surface of the Au sample will exhibit a similar roughness to the Ag sample used. The image (figure 6.4) displays a rough surface of the metal with a variation of up to 4nm between the top and base of features. However there is no indication of a feature with a regular spacing of 14\(\mu\)m required for coupling.

Thermal effects caused by heating of the electron population from the surface by the laser pulse can also be discounted for the large enhancement observed. With

\(^1\)Image supplied by Mr D Lei, PhD student Experimental Solid State group, Imperial College
an increasing temperature the Fermi-Dirac distribution of states around the Fermi level is shifted to higher energies, where the distribution is $\propto e^{-E/kT}$ (E is the energy of the state, T is the temperature and k is the Boltzmann constant). Fitting this distribution to the curves in figure 6.2 would suggest an electron temperature of 10’s of thousand of Kelvin, which is several orders of magnitude higher than a typical value of 700K [7].

Experimentally it is shown that thermal effects do not shift the measured electron energies to the extent observed. The plots in figure 6.5 are photoelectron spectra collected from a smooth gold target produced under conditions to minimise surface roughness. The spectra are produced by high harmonics with a cut-off at 80eV (blue curve) and with the addition of a synchronised IR field with an intensity of $1\times10^{11}$W/cm². In these higher intensity conditions, electrons are observed typically with an energy 1eV greater in the presence of the IR field than in its absence. The thermal effect can be ruled out for causing the enhancements observed.

The roughness imaged in figure 6.4 explains the enhanced energies of photoelectrons observed from the Ag sample. The sub-wavelength rough features are the
6.1. PHOTOELECTRON SPECTRA - ROUGH SILVER SURFACE

Figure 6.5: Photoelectrons collected from a smooth gold target. The blue curve corresponds to photoelectrons collected for an harmonic spectra with a cut-off at 80eV irradiating the target. The red curve is obtained under the same conditions as for the blue but with an additional IR field of $1 \times 10^{11}$W/cm$^2$.

sites of localised nanoplasmonic fields stimulated by the IR field. The nanometer scale of the structures enhance the electric field by many orders of magnitude ($10^{-3}$[115]).

A plasmon propagation length can be calculated by examining the ratio of the real part of the relative permittivity of a metal and the imaginary part and is shown in figure 6.6 [18]. The plot shows that:

$$\delta_p \gg \lambda_p$$  \hspace{1cm} (6.3)

where $\delta_p$ is the propagation distance of a plasmon and $\lambda_p$ is the plasmon wavelength. The nanoscale localisation of plasmons to rough features on a surface means the characteristic wavelength of a localised plasmon will be very small.
The penetration length $b$ of the plasmonic field out of the surface is given by [78, 18]:

$$b = \left[ k_p^2 - \frac{\omega^2}{c^2} \right]^{-1/2}$$  \hfill (6.4)

where $b$ would be of the order of 1 - 3nm for the size of structures imaged in figure 6.4 [120]. An electron leaving the surface with a kinetic energy of 20eV would have a $v_e$ given by $v_e = \sqrt{2 \times 20 \times e/m_e} = 2.6 \times 10^6$ms$^{-1}$ where $e$ is the electron charge and $m_e$ the electron mass. This electron would then only spend 380as in a 1nm field penetrating from the surface. As this time is much less than $T/2$ of the driving IR field, the plasmonic field ‘seen’ by an emitted electron can be viewed as electrostatic.

Following a similar approach to [119, 78] the maximum instantaneous electrostatic field potential, $\phi_i$, of the localised nano-plasmonic field is given by:

$$\phi_i = \frac{eU_p}{\eta^2}$$  \hfill (6.5)

where $U_p$ is the ponderomotive potential of the IR field, $e$ is the charge of an electron and $\eta^2$ is given by:
\[ \eta^2 = \left( \frac{E_{\text{plasmon}}}{E_0} \right)^2 \] (6.6)

If one equates \( \phi_i \) to the difference between the electron energy expected from a perturbative MPE model and that actually measured \( i.e. \) 4.5eV for electrons detected with 10.5eV (figure 6.3) then the ratio \( \eta \) can be calculated. With an IR intensity of \( 4.2 \times 10^{10} \text{W/cm}^2 \) giving \( U_0 = 2.4 \times 10^{-3} \text{eV} \), \( \eta = 43 \), or in other words that plasmonic electric field is 43 times greater than the electric field of the laser. An enhancement of this order is consistent with other measurements [115, 66].

6.2 Photoelectron spectra from a gold surface with XUV

Photoelectron spectra collected from gold targets irradiated with high harmonics have a continuum of electron energies from 0eV to the photoelectrons emitted close to the Fermi energy. The continuum is produced by a convolution of the large bandwidth of the high harmonic spectrum and electron scattering as an electron travels to the surface. However photoelectron emission from states close to the Fermi energy from the highest XUV photon energies is visible in the measured spectra. Such a structure in the spectrum may be used as a source of electrons to be streaked in a surface IR-XUV pump-probe streaking measurement.

This section describes measurements with different high harmonic spectra and the collected photoelectrons. Photoelectrons were collected from a 100nm evaporation of Au onto a fused silica substrate mounted in an identical geometry to figure 6.1.
Irradiation with high harmonics from Ar and Ne

Photoelectron spectra were collected from targets irradiated with high harmonics produced in Ar and Ne. An aluminium filter was used to pass harmonics up to the L-edge 71eV. The spectra were collected for 20 minutes ($1.2 \times 10^6$ shots) and are shown in figure 6.7.

![Photoelectron spectra](image)

**Figure 6.7:** Photoelectron spectra measured from a 100nm evaporation of Au on fused silica. The blue curve are photoelectrons collected from an XUV spectra produced in Ne, the red curve is from XUV produced in Ar. The black curve is an overlay of the XUV spectra from Ne as a reference. The red arrows point to local peaks observed separated by $\bar{\hbar}\omega_0$.

Both spectra show characteristics of their high harmonic counterparts. The red curve collected from high harmonics produced in Ar displays the reducing harmonic yield as the Cooper minimum is approached [129]. The neon curve is more uniform representing the plateau region of a high harmonic spectra produced from neon. This continues up to the L-edge of the aluminium filter which filters out

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2 The Cooper minimum in an harmonic spectrum is an observed localised minimum around 48eV caused by a zero dipole moment between the $p$ ground state wavefunction and the $d$ wavefunction of the electron.
harmonics above 71eV[2]. To help with the interpretation of this plot the neon high harmonic spectra is overlaid with its energy axis shifted by 5eV to account for the Fermi level.

The red plot displays local peaks (highlighted by the red arrows in figure 6.7) separated by $\hbar \omega_0$ of the fundamental laser field. These peaks are caused by electrons emitted close to the Fermi energy by each harmonic. This feature however is unclear in the blue curve. The mean free path of electrons in a solid is the cause of this ‘smearing’ to lower energies via scattering processes reducing the energy of an electron as it leaves the surface. Electrons with binding energies lower than $E_{Fermi}$ will also contribute to this band, obscuring the structure of individual harmonics from the plateau region of the spectrum. In the case of Ar harmonics the decreasing yield from neighbouring harmonics reduces this lower electron population allowing the peak photoelectrons from each harmonic to be observed.

An important conclusion from these spectra is that the L-edge of the Al filter produces a uniform high harmonic spectrum from Ne which in turn improves the clarity of the Fermi edge in the photoelectron spectra. Furthermore there is evidence of the argon harmonic structure remaining visible in the photoelectron spectra.

Irradiation with high harmonics from Ne with a reduced bandwidth

A narrow bandwidth of 5eV FWHM centred at 70eV of harmonics was produced by filtering with both Zr and Al filters (shown in figure 3.18). A comparison of the photoelectron spectra obtained with only Al filtering is shown in figure 6.8. A distinct plateau is seen for the photoelectrons collected using a narrow
bandwidth. As the Zr filter removes the lower order harmonics there are fewer lower energy electrons produced that would to contribute to the bulk observed for a large bandwidth of harmonics.

Scaling the photoelectron spectra from figure 6.8a) by accounting for the transmission of the Zr filter measured by the XUV spectrometer and the integration time of the photoelectron spectra reveals a marked similarity for electron emission close to the Fermi level. This is shown in figure 6.9.

The significance of this result is that for mapping the Fermi edge, a narrow spectrum is not required. This removes the requirement for extra filtering and thus increases the photon flux on target.

Figure 6.8: a) photoelectron spectra collected from Au produced by an Al filtered high harmonic spectra produced from Ne (equivalent to the spectrum displayed in 6.7, spectra integrated over 15 seconds) b) Photoelectron spectra collected under same conditions as a) with the addition of a Zr filter limiting the high harmonic spectra to a bandwidth of 5eV (figure 3.18).
6.3 \textit{Two-photon emission from a gold surface}

This section describes the measurement of the lifetime of occupied states above the Fermi level of gold. An electron occupying a state below the Fermi level can absorb a photon with energy $\hbar \omega_0$, if $\hbar \omega_0 < \phi$, where $\phi$ is the work function of the metal, and move to a state above the Fermi level \cite{110, 38}. This redistribution of states is not in equilibrium and 'hot' electrons above the Fermi level will redistribute or 'thermalise' via scattering processes. Electrons redistribute predominately via electron-electron (e-e) scattering or electron-phonon (e-p) scattering on a characteristic time scale \cite{101}.

Using a two-photon emission process with an IR pump and delayed XUV probe this time scale can be measured. An IR photon with 1.5eV of energy can be absorbed by an electron promoting it above the Fermi level (figure 6.10). An XUV probe photon may then be absorbed by the electron in this new state, with subsequent emission of the electron above the vacuum level. Other XUV photons

Figure 6.9: Photoelectron spectra measured with high harmonics filtered with Al (red) and Al and Zr (blue) filters. The red curve has been scaled for a reduced integration time and reduced transmission through the Zr filter.
will ionise electrons from levels below the Fermi level as well, but in the measured photoelectron spectrum there will be a population of electrons with higher energy than an electron emitted from the Fermi level. A pump-probe measurement where the XUV is scanned from before to after the IR pump allows the lifetime of the hot electron population to be measured.

Figure 6.10: Representation of the two-photon ionisation process. An IR photon, $\hbar \omega_0$, is absorbed by an electron occupying a state below the Fermi level and is promoted to a state above the Fermi level but below the vacuum level. This electron can then absorb an XUV photon, $q \hbar \omega_0$, and be emitted from the metal. Emission of electrons from below the Fermi level can also occur with a single XUV photon.
Experimental setup

An evaporation of Au onto a smooth (structures <1nm high) sapphire substrate housed in UHV conditions was used as the target. The pump to create the hot electron population in gold was a 10fs IR pulse, and the probe was a high harmonic spectrum produced from Ne. Preliminary measurements of photoelectron spectra collected with an attenuated IR pulse were used to select a suitable intensity of the IR pump and was found to be $9 \times 10^9 \text{W/cm}^2$.

An interferometer was built that allowed an annular outer beam to be delayed with respect to a small diameter inner beam, figure 6.11. The delay was introduced by translating a piezo stage (PI GmbH LISA) which has a range of 260fs in 0.5as steps. The interferometer was installed before the high harmonic generation chamber and 3mm holes were cored from the centre of two mirrors to pass 20mW of IR required to produce an intensity of $9 \times 10^9 \text{W/cm}^2$ at the focus on the gold target. The annular reflection of the beam was used to produce high harmonics for the probe pulse. After the interferometer both beams travelled collinearly to the Au sample. A 40cm focal length mirror was used to focus the IR beams into the harmonic gas target which was placed before the laser focus to select on-axis harmonic emission (see section 2.7). The XUV producing IR beam had an intensity of $4 \times 10^{14} \text{W/cm}^2$ with the cut-off of the harmonics at 95eV (figure 6.13). The divergence of XUV was 2mrad FWHM, measured at the XUV spectrometer. No harmonics were produced from the inner beam as the intensity was too low. A schematic of the beam arrangement is given in figure 6.12.

The beamsize of the harmonics at the toroidal mirror was measured to be 5mm by monitoring the photoelectron yield while closing a motorised aperture before the mirror. When this motorised iris was set to 5mm the divergence of the annular
outer XUV generating IR beam resulted in none of the outer IR being reflected from the toroidal mirror. This removed the requirement of filtering with metallic filters to remove the IR photons from the probe arm.

The focus of the toroidal mirror in the experimental surface chamber is reimaged onto a CCD behind the chamber. Opening the iris to more than 5mm before the toroidal mirror allowed IR from the annular outer to focus in the chamber. The interference of the outer and inner IR beams was monitored on the CCD and used to set zero delay between the two at the centre of the piezo stage range.

The Au sample was translated into the focus, with the same geometry as used for the Ag measurements described at the beginning of the chapter (figure 6.1), the laser polarisation was horizontal (perpendicular to the sample surface). The iris before the toroidal mirror was closed to block IR from the outer and the inner
6.3. TWO-PHOTON EMISSION FROM A GOLD SURFACE

IR pump pulse was blocked before the HHG chamber. A sample photoelectron spectrum was then collected with only the probe XUV pulse irradiating the target and is shown in figure 6.14.

To increase the detected electron rate 20V was applied to the electrostatic lens at the entrance of the TOF drift tube allowing an average of 1 electron per second to be detected. The IR inner pulse was stepped for the full range of 260fs in 30 8.7fs steps. At each delay a spectrum was recorded for 2 minutes (120,000 shots). The recorded scan is shown in figure 6.15.

The large modulation observed at zero delay is caused by the IR pump and the

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3 This voltage changed the calibration of the TOF. A SIMION model was used to model electron flight times of electrons emitted close to the Fermi level.
Figure 6.13: High harmonics produced in neon by the outer beam

Figure 6.14: Photoelectron spectra collected from Au target with high harmonics generated in Ne
XUV generating IR beams interfering in the focus of the harmonic gas jet, modulating the harmonic yield and cut-off energy. At delays from -100fs up to the large modulation one can see an increasing flux of the earliest (highest energy) electrons. As the delay between the IR pump and XUV probe decreases this flux increases. It should be noted that enhancement from localised surface plasmons can be discounted as IR intensity scans did not measure high energy electrons from the smooth Au surface as previously observed from the rough silver sample discussed at the beginning of the chapter.

The sum of the total electron flux between the two dashed red lines in figure 6.15 is shown in figure 6.16. The position of the lines are at flight times given by SIMION to correspond to electrons with energies 10eV above and 5eV below the predicted Fermi level.
Figure 6.16: The integrated yield of the highest energy electrons measured in the range between the red lines in figure 6.15. The black curve is a fit of an exponential decay of the feature seen before zero delay.

The trend shown in 6.16 is caused by a hot electron population produced by the IR pump. At -100fs delay the hot electron population is thermalising with a decreased population of hot electrons when probed by the XUV. At delays closer to zero, fewer hot electrons have thermalised. It is clear for positive delays, when the XUV probe arrives before the pump, that there is no significant hot electron population.

The black curve in figure 6.16 is a fit of an exponential decay to the plot. Extrapolating the curve to an electron flux equal to the thermalised population for positive delays measures the average lifetime of the hot electron population. The summed total electron flux for an energy band centred at the Fermi energy was used to extrapolate a lifetime of the hot electron population as 400±50 fs.

The thermalisation of the hot electron population by e–e scattering can be modelled by the use of Fermi-liquid theory. This predicts that the lifetime of an electron above the Fermi level is $\propto (E - E_F)^{-2}$ where $E_F$ is the Fermi energy [103, 46].
lifetime $\tau$ can be written as [39]:

$$\tau = \tau_0 \left( \frac{E_f}{\delta E} \right)^2$$  \hspace{1cm} (6.7)

where $\delta E$ is the difference between the energy of the electron and the Fermi level. $\tau_0$ is given by [34]:

$$\tau_0 = \frac{512}{\pi^2} \frac{1}{\sqrt{3} \omega_p}$$  \hspace{1cm} (6.8)

where $\omega_p$ is the plasma frequency (8eV for Au). This expression for $\tau_0$ agrees with measured thermalisation time for hot electrons [38]. Using equations 6.8 and 6.7 the calculated lifetime for electrons which are 0.5eV above the Fermi energy (5eV) is 200fs. The agreement of the data to the theory suggest that the dominate process in the thermalisation of hot electrons is e-e scattering.

### 6.4 Summary

The experiments detailed in this chapter have demonstrated the capability of the apparatus built to measure electron dynamics on a surface. The experiments show that surfaces can be precisely positioned at the IR and XUV foci, with a suitable interaction geometry for photoelectrons to be detected without specular reflection adding noise to the collected signal.

The investigation of a rough silver surface demonstrated both the large laser field enhancement caused by coupled plasmons, and the ability for samples to be prepared and mounted in the apparatus without contamination obscuring surface structure.

Photoelectron spectra produced with XUV radiation highlight the Fermi edge as a suitable candidate to be probed in an XUV-IR pump-probe experiment. Impor-
tantly, a narrow bandwidth of harmonics is not necessarily required for the XUV probe, allowing a large photon flux to be used. Evidence of harmonic structure visible in measured photoelectron spectra produced by Ar harmonics is an interesting observation. With further investigation it may be possible to use this feature to calibrate the TOF. It might also be possible to use a two-photon emission process with XUV and IR akin to the measurement of attosecond pulse trains described in section 4.2.

The temporal dynamics of electrons measured from Au displays the capability of the apparatus to cross correlate IR and XUV pulses on a surface. The temporal overlap of the two beams at the high harmonic gas target that causes modulation in the harmonic yield can be avoided in future work. Inserting a thin glass plate in one beam before the gas target and a plate of the same thickness in the other beam after the target will avoid temporal overlap in the gas. This experiment also highlights the redistribution of the electrons states in a surface in the presence of an IR field. This effect will have to be taken into consideration in future investigations.

The proven abilities of the surface apparatus mentioned, coupled with an isolated attosecond pulse will allow surface processes to be probed in UHV conditions on a revolutionary time scale. This capability has only been achieved by a couple of groups around the world.
Chapter 7

Summary

The work presented in this thesis describes a system that has been developed to allow the ultrafast dynamics of electrons to be probed in gases and on surfaces.

In summary I have achieved the following:

- production of sub 7fs CEP stabilised intense IR pulses with an energy of 350\(\mu\)J
- the ability to produce high harmonics up to 120eV from different gas targets
- the use of high harmonic generation to produce an isolated burst of continuum radiation centred at 90eV
- measurement of an isolated 270as XUV pulse with an atomic streak camera measurement
- designed and constructed a UHV system for surface investigations
- demonstrated the surface apparatus ability to measure field enhancement from localised plasmonic field
• demonstrated a 2 photon emission XUV-IR cross correlation to measure the
temporal dynamics of electrons in a surface

My PhD work has given the Attosecond laboratory at Imperial College the capa-
bility to use attosecond pulses to investigate electron dynamics on surfaces. The
next section describes the direction of our future research to use this capability to
temporally resolve enhanced plasmonic fields.

**Future work**

In the introduction I stated the work of Kim *et al* [69] was a motivating force
behind the construction of the surface apparatus. Harnessing field enhancement
for high harmonic generation from an incident laser intensity of $\sim 10^{11}$W/cm$^2$
where plasmonic enhancement of the field at the tips of the nano structures allowed
high harmonic generation to take place using a laser oscillator as a drive laser in
a background of argon (figure 7.1).

Generation of the up to the 17th harmonic was observed with an estimated en-
hancement of 100 in the intensity. Future development of this technique could lead
to extremely compact, allow almost CW (100s of MHz), coherent XUV sources.

The results presented in [69] raise many questions about the fundamental process
occurring at the site of HHG. In this thesis I have described the phase matching
conditions required over a coherence length of many millimetres in contrast to the
enhanced region of a few nanometers in the structures used by Kim.

A fundamental unknown is the precise nature of the field enhancement driving
HHG. Our aim is to conduct an XUV-IR pump-probe measurement in which the
streaking field is provided by the nanoplasmonically enhanced field. The IR field
from the laser will be coupled to the structure causing field enhancement at the
High harmonic generation by enhanced plasmonic fields was achieved by using an array of nanostructures. The output of an oscillator with an intensity of $\sim 10^{11}\text{Wcm}^{-2}$ was enhanced by a factor of 100 in localised regions of a ‘bow-tie’ structure where high generation in a background gas occurred. Figure from [69]

tips, and an isolated attosecond probe will emit an electron from a region of the enhanced field. This electron will travel through the enhanced plasmonic field receiving a time dependent shift of momentum or a streak. Delaying the birth of this electron by scanning the XUV probe to before and after the driving IR pulse and measuring the energy of electron will allow the time dependent plasmon electric field to be recorded.

A similar experiment has been proposed by [120] to measure the time dependence of localised plasmonic fields using a photoelectron emission microscope (PEEM) [84] to resolve electron emission from a surface both spatially and in energy. It is proposed for our experiment to use the TOF described in this thesis which
resolves only energy. Conducting the pump-probe measurement on similar structures used by Kim would detect photoemission from the Au structures with the electron emission from enhanced region indistinguishable in the large background signal. Manufacturing the structure with either a material suppressing emission for the unenhanced regions, or by placing a material in the enhanced regions with a distinct photoelectron spectra will allow photoelectron emission for regions of enhancement to be detected.

The next stage of this research will examine photoelectron spectra from a range of dielectrics and metals produced by XUV radiation to identify suitable materials to construct the targets.

Work conducted in my PhD will be the foundation for this project. A measurement of the enhanced field will require the measurement of photoelectrons emitted from a cross correlation of an isolated attosecond pulse and IR field on a sample in UHV conditions. I have developed and demonstrated the key elements for this experiment during my PhD.
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