High harmonic generation from combined femtosecond laser fields

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Abstract

In this thesis I introduce experiments that explore the effect of different combinations of femtosecond laser fields on the high harmonic generation (HHG) process and its applications to probe ultrafast dynamics. Combining a fundamental driving field with a secondary field allows for control over the HHG process in several ways. The ionisation step of the process can be altered significantly by introducing a secondary field. The electron trajectories in the continuum can be controlled and manipulated by the secondary field. Further, the secondary field can be used to drive a population transfer between different states of the cation.

In a first experiment, we used the fundamental pulses in combination with copies of themselves ($\omega + \omega$ experiment) to synthesise a field with a new temporal and spectral structure. Using this synthesised field to drive the HHG process results in a shift of the central frequency of the high-order harmonics. We demonstrated very fine control over the harmonic energy with a setup which is significantly simpler and more cost effective than more commonly used setups, and compatible with very high pulse energy sources.

In a second experiment, the fundamental field is combined with its second harmonic ($\omega + 2\omega$ experiment). The addition of the second frequency results in a harmonic spectrum consisting of odd and even harmonics, as the symmetry of the combined generating field is broken. We observed below- and above-threshold harmonics in Kr and CO$_2$ and investigated the effect of the secondary field on the harmonic generation as a function of the time delay between the fundamental and its second harmonic. We observed harmonics generated by the secondary field only, a delayed onset of some even harmonic orders depending on the delay and interesting modulations of the harmonic yield depending on the delay. This experiment served as a proof of principle for the setup used for the more demanding third experiment.

The third experiment combined the fundamental with its third harmonic ($\omega + 3\omega$ experiment). The idea of this experiment is to drive the HHG process with the fundamental field, whilst the third harmonic drives a population transfer between two cation states in CO$_2$. If the population transfer is timed right, the recombination probability for the short and long trajectory contributions can be controlled separately. Since each trajectory represents a specific ionisation and excursion time, any changes of the state of the system are encoded in the interferences between the contributions of the short and long trajectories. This makes so-called quantum path interferences (QPI), interferences between the short and long trajectory contributions, a useful observable to probe femtosecond and attosecond dynamics.
Declaration of Originality
The work presented in this thesis is my own, unless otherwise stated and referenced.

Konstantin Holzner

Author’s Contributions
All experimental work is done collaboratively. The experiment described in chapter 4 was performed at the CELIA laser facility where the Imperial team had no involvement in the running of the laser. The field synthesis setup described in that chapter was developed by Martin Arnold, Amelle Zaïr and myself in collaboration with the team at CELIA, mainly Ludovic Quintard and Eric Constant. All experimental data presented in that chapter was collected by that group of people, with technical support from Nikita Fedorov and other CELIA technicians and laser engineers. The simulations presented in that chapter were developed by myself.

The work presented in chapters 5 and 6 was done in the Red Dragon lab at Imperial College London. All researchers in that laboratory contribute to the maintenance of the laser and the general running of equipment. The experimental chamber used for the experiments described in those chapters was first installed before my time at Imperial and then developed further by Allan Johnson before I modified the setup inside the chamber for those experiments (with the help of Allan Johnson). The setup for the generation of the UV in both those chapters and the various setups for beam manipulation and separation were designed and developed by myself in discussion with Amelle Zaïr. The data described in those chapters was collected by myself and Amelle Zaïr.

The crosscorrelation setup and various beam characterisation setups used in those experiments were developed by myself. The FROG used to characterise the IR in the Red Dragon lab was designed and developed by Christian Brahms.

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Publications

Steffen Driever, Konstantin B. Holzner, Jean-Christophe Delagnes, Nikita Fedorov, Martin Arnold, Damien Bigourd, Frédéric Burgy, Dominique Descamps, Eric Cormier, Roland Guichard, Eric Constant, and Amelle Zaïr.

**Near infrared few-cycle pulses for high harmonic generation.**

Konstantin B. Holzner, Martin Arnold, Ludovic Quintard, Nikita Fedorov, Eric Cormier, Eric Constant, and Amelle Zaïr.

**Frequency tunable high-order harmonics.**


**High harmonic half-cycle cut-offs beyond the oxygen K-edge.**
In preparation.
In science, if you know what you are doing, you should not be doing it. In engineering, if you do not know what you are doing, you should not be doing it. Of course, you seldom, if ever, see either pure state.

— Richard Hamming in The Art of Doing Science and Engineering
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Chapter 1

Introduction

Since the first implementation of a laser\(^1\) in 1960 by Maiman [1], this technology has truly revolutionised both industry and science. Nowadays, lasers are ubiquitous from manufacturing to cutting edge science in many different fields. Lasers are used extensively in medicine, both in new diagnostics techniques and in treatment. Medical imaging has made huge advances in terms of resolution and what can be imaged in a non-invasive manner thanks to the laser. The manufacture of modern computer chips relies heavily on the capabilities of lasers to enable precision on extremely small length scales. Other areas where lasers are indispensable are quality control, where lasers are used to monitor distances and dimensions with unprecedented precision. Remote sensing is an emerging area that is bringing low cost but powerful optical measurement devices to a huge variety of applications. Recent years have seen the development of more military applications of the laser too, be that in remote sensing, target tracking or in the form of laser cannons that can bring down drones and missiles. In short, it is hard to imagine a modern world without lasers.

One area where the laser has enabled a huge step forward in terms of what is possible is time-resolved measurements. In order to measure an event in time, one needs an even shorter event. In the early days of time-resolved measurements, the aim was to resolve dynamics that are just outside of what the human eye can resolve. In the late 19th century, Eadweard Muybridge famously recorded the gait of a horse with a series of cameras, settling the long discussed question of whether all four feet of a horse leave the ground when trotting and galloping (spoiler: they do). The stroboscope, whose early versions predate Muybridge’s achievements, has been widely used to capture fast motion by seemingly freezing periodic motion in time. However, all those techniques are quite limited in the time resolution they can achieve.

\(^1\)LASER = light amplification by stimulated emission of radiation
Figure 1.1: Top: Plot of 5 different equally spaced frequencies. Bottom: The sum of the frequencies plotted in the top plot. Because the frequencies are mode-locked, i.e. have a fixed phase relationship, they produce a pulse train. The more frequencies are added up, the shorter the resulting pulses.

Once again, the laser comes to the rescue. There are a number of different ways of producing a pulsed laser (e.g. Q-switching [2,3] and pulsed pumping [4]), but the technique that produces by far the shortest pulses is called mode-locking. Mode-locked lasers can achieve pulse durations on the femtosecond timescale. This is only possible because instead of relying on some switching mechanism, be it mechanical or electronic, this technique relies on the underlying physics. As the name suggests, the technique locks the different cavity modes into a fixed phase relationship. The sum of those modes results in a pulse train. Figure 1.1 illustrates that fact. The resulting pulses are shorter the more frequencies are involved, which is why gain media with a broad gain bandwidth (e.g. titanium-doped sapphire) are required to produce the shortest pulses.

In atomic and molecular physics, we are often interested in electron dynamics and charge migration, that is, how electrons move between different energy levels and how electrons reorganise across the different atoms that make up molecules. Ultrashort laser pulses are the shortest controllable events we can create and they enable measurements on the atomic timescale. This is why research in the field, and the research presented in this thesis, uses ultrashort laser pulses.

Another important development in laser technology was so called chirped pulse amplification (CPA) [5] in 1985. Through the CPA technique, laser pulses can now be routinely...
amplified to levels where the laser electric field strength becomes comparable to the electric field experienced by bound electrons. One of the processes made possible by the advancement of laser field strengths to the so called strong field regime is high harmonic generation (HHG). First discovered in the late 1980s (independently by McPherson et al. in the USA and Ferray et al. in France), HHG is now the single most important technique in experiments looking to temporally resolve electron dynamics in atoms and molecules. The strong laser field necessary for HHG frees electrons into the continuum. After the electrons are accelerated back towards the parent ion by the reversed field direction of the passing laser field, the electron can recombine with the parent ion. Upon recollision, photons with energies several odd multiples higher than that of the generating laser are emitted. Interestingly, structural information about the emitting atom or molecule is encoded in the harmonic spectrum. Further, the bandwidth of the emitted harmonics is large enough to support attosecond pulses, and therefore pulses much shorter than the pulse duration of the driving laser. HHG therefore enables access to both structural and dynamic information on the time scale of electron dynamics in atoms and molecules.

Each high harmonic contains contributions from two different electron trajectories that recombine with the same kinetic energy and therefore produce photons at the same energy. These trajectories differ in their excursion time and in the phase they accumulate during their time in the continuum. Because each trajectory represents a specific ionisation and recombination time, any changes of the system on the timescale of the excursion times are encoded in the phase and recombination probability of the different trajectories. This was first observed by means of quantum path interference (QPI), the interference between the short and long trajectory contributions, by Zaïr et al. in Zurich [6].

Adding a secondary laser field at a different central wavelength into the equation gives additional degrees of freedom and control over the HHG process. The ionisation step can be controlled by adding a secondary field that enhances or decreases the field strength of the driving laser field at different points in its optical cycle. The effect of the secondary field on the overall field can be controlled by controlling the phase relationship between the two fields. The secondary field can also be used to control the different trajectories of the electrons in the continuum before recombination, and therefore their phase and recombination probability at recombination. Finally, the secondary field can be chosen such that it provides population control in the cation between the ionisation and recombination processes.

In this thesis I explore how different secondary fields can be used to control and manipulate the HHG process and to gain new insights into the dynamics of the target atom
Chapter 4 introduces an experiment where the laser pulses were combined with copies of themselves to manipulate the spectral and temporal structure of the laser field. This resulted in harmonic spectra with finely tunable and controllable central wavelengths, which is beneficial for a number of spectroscopy applications. The technique used here drastically simplifies the setup requirements compared to other experiments with similar objectives.

In chapter 5 the driving field is combined with its second harmonic, both in parallel and perpendicular relative polarisations, in order to break the symmetry of the total generating field. This leads to the production of even harmonics. We observed below- and above-threshold harmonics in krypton and CO\textsubscript{2} and studied the influence of the second harmonic field as a function of its delay with respect to the pulses of the fundamental field. Importantly, this experiment served as a proof of principle for the setup used for the following experiment, which is experimentally more demanding.

Chapter 6 introduces an experiment that aims to control the population of the cation in between the recombination times of the short and long trajectories. The fundamental field drives the HHG process whilst the secondary field drives a population transfer between the highest occupied molecular orbital (HOMO) and HOMO–2 in CO\textsubscript{2}. Since the population of the HOMO strongly affects the recombination probability of the electrons at recollision, controlling the population over time allows us to control the relative contributions of the short and long trajectories to the overall harmonic yield of a particular harmonic order.
Chapter 2

Background and Theory
2.1 Ultrashort Laser Pulses

In order to fully understand the ultrashort pulses we are using in the experiments, and in order to describe and understand their interaction with matter, we need a mathematical description. Despite the fact that all measurable quantities are real, choosing a complex representation of the pulses is usually more convenient, especially when looking at the propagation of the laser pulses. This section discusses the temporal properties of a linearly polarised laser pulse.

Ultrashort pulses can be described mathematically by the product of an oscillating electric field, known as the carrier, and an envelope function:

\[ E(z,t) = E_0(z,t) e^{i(\omega_0 t - k z + \phi_0)} = E_0(z,t) e^{i\phi(z,t)}, \]

(2.1)

where \( E_0(z,t) \) is the envelope function, \( \omega_0 \) is the carrier frequency, \( k = \omega_0 / c = 2\pi / \lambda_0 \) is the wavenumber (\( \lambda_0 \) is the vacuum wavelength) and \( z \) is the spatial coordinate along the propagation axis. The phase term \( \phi_0 \) is called the carrier-envelope phase (CEP) offset and is a measure for the offset between the peak of the envelope and the peak of the electric field inside the envelope. The CEP is illustrated in figure 2.1, where an ultrashort pulse is plotted (blue solid line) along with its envelope (black dashed line) for three different values of the CEP.

The temporal phase, \( \phi(z,t) \), represents the variation of the carrier wave with time. We can therefore define the instantaneous frequency as:

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

(2.2)

When solving problems that involve the propagation of laser pulses through a medium, it is useful to define two different velocities for the pulse propagation. The first is the phase velocity of light:

\[ v_{ph} = \frac{\omega}{k}. \]

(2.3)

The phase velocity is the velocity at which the phase fronts propagate in a medium. Or in other words, it is the velocity of the carrier wave. In vacuum, the phase velocity is equal to the defined constant speed of light, \( c = 299,792,458 \, \text{m/s} \), and is independent of the carrier frequency.

The other important velocity associated with the propagation of laser pulses is the group velocity:

\[ v_g = \left( \frac{\partial k}{\partial \omega} \right)^{-1}, \]  

(2.4)
Figure 2.1: Plot of a few-cycle pulse (solid blue line) and envelope (dashed black line) for three different values of carrier-envelope phase offset.

which is the velocity at which the envelope moves.

So far we have discussed the temporal profile and phase of laser pulses. In other words, we have described the laser pulses in the temporal domain. There is an equivalent representation in the spectral domain, where the laser pulses are defined by a spectral amplitude function and a spectral phase:

\[ \tilde{E}(z, \omega) = \tilde{E}_0(z, \omega) e^{i\tilde{\phi}(z, \omega)}, \]  

(2.5)

where \( S(\omega) = |\tilde{E}_0(z, \omega)|^2 \) is the spectrum of the pulse. The spectral phase \( \tilde{\phi}(z, \omega) \) describes the relative phase between different parts of the spectrum.

The temporal domain and the spectral domain are connected through Fourier transformation, such that:

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

(2.6)

\[ E(z, t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \tilde{E}(z, \omega) e^{i\omega t} d\omega. \]  

(2.7)

This Fourier relationship leads to a number of interesting features. One of those features which is of concern when trying to produce the shortest pulses possible with a given laser is the time-bandwidth product (TBP). As the name suggests, the TBP is simply the product of the full width at half-maximum (FWHM) of the pulse in the time domain, \( \Delta t \), and the FWHM of the same pulse in the frequency domain, \( \Delta \nu \). The Fourier relationship between the two different domains puts a constraint on the TBP, which depends on the shape of the pulse envelope:

\[ \Delta t \Delta \nu \geq C_{TBP} \]  

(2.8)
Table 2.1: Temporal ($\Delta t$) and spectral ($\Delta \omega$) FWHM intensity profiles and time-bandwidth products for Gaussian and sech$^2$ pulse profiles.

<table>
<thead>
<tr>
<th>pulse shape</th>
<th>temporal intensity profile</th>
<th>spectral intensity profile</th>
<th>$C_{TBP}$</th>
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<tbody>
<tr>
<td>Gaussian</td>
<td>$e^{-\frac{g^2}{\Delta t^2}}$</td>
<td>$e^{-\frac{\ln(\ln(1 + \sqrt{2})t)^2}{\Delta \omega^2}}$</td>
<td>$\ln(\frac{4}{\pi}) = 0.441$</td>
</tr>
<tr>
<td>sech$^2$</td>
<td>$\text{sech} \left( \frac{2\ln(1 + \sqrt{2})t}{\Delta t} \right)^2$</td>
<td>$\text{sech} \left( \frac{2\sinh^{-1}(1)\omega}{\Delta \omega} \right)^2$</td>
<td>$\left( \frac{2\sinh^{-1}(1)}{\pi} \right)^2 = 0.315$</td>
</tr>
</tbody>
</table>

Table 2.1 shows the constrains on $C_{TBP}$ for the most common pulse shapes. As is evident from equation 2.8, the TBP limits the shortest achievable pulse duration for a given spectrum. The shortest pulse possible is called the transform limit, and occurs when the spectral phase $\tilde{\phi}(z, \omega)$ is a linear function of the frequency [7].

If the spectral phase is not a linear function of the frequency, the pulse is said to be chirped. If a pulse is chirped, its instantaneous frequency is time-dependent. Figure 2.2 shows an example of chirped pulses. The pulse shown on the left is not chirped (for reference). The pulse in the centre is positively chirped (i.e. the group velocity of redder frequencies is bigger than that of bluer frequencies) and the pulse on the right is negatively chirped (group velocities of blue frequencies bigger than that of redder frequencies). Both chirped pulses are linearly chirped, i.e. the phase is a quadratic function of time and the resulting variation in frequency is a linear function of time.

Chirp can be quantified in a number of different ways. The rate of change of the instantaneous frequency can be used as a measure for the chirp. For nonlinear chirps, this rate of change is time-dependent and changes throughout the pulse. Another common way to quantify chirp is by specifying the amount of group delay dispersion (GDD, see below) required to compress the pulse to its Fourier limit pulse duration. This measure of
chirp is often expressed in units of fs$^2$. Note that there is no simple connection between these two measures of chirp.

Besides the introduction of chirp, the spectral phase can be responsible for a number of other effects on the pulse, including significant reshaping of the temporal pulse envelope. If the spectral phase is not smooth, introducing structure in the pulse, light-matter interactions and measurements become more complex. Generally, a variation of the phase with frequency is called chromatic dispersion.

It is useful to express the spectral phase in terms of a Taylor expansion, evaluated at the fundamental frequency $\omega_0$:

\[
\tilde{\phi}(\omega) = \tilde{\phi}_0 + \sum_{n=1}^{\infty} \frac{1}{n!} \left. \frac{d^n \tilde{\phi}(\omega)}{d\omega^n} \right|_{\omega_0} (\omega - \omega_0)^n
\]

\[
= \tilde{\phi}_0 + \left. \frac{d\tilde{\phi}(\omega)}{d\omega} \right|_{\omega_0} (\omega - \omega_0) + \frac{1}{2} \left. \frac{d^2 \tilde{\phi}(\omega)}{d\omega^2} \right|_{\omega_0} (\omega - \omega_0)^2 + \ldots
\]  

(2.9)

The first term, $\tilde{\phi}_0$, is the CEP, which is only really important in few-cycle pulses. The second term ($\left. \frac{d\tilde{\phi}(\omega)}{d\omega} \right|_{\omega_0}$) is known as the group delay. For a narrow-band laser pulse, where higher orders can be neglected, the group delay gives the delay the peak of the pulse experiences when propagating through a medium. The group delay per unit length is the inverse of the group velocity introduced earlier.

The first two terms of equation 2.9 do not affect the temporal envelope of the laser pulses. It is the subsequent terms that affect the temporal envelope of the pulse and that play an important role in the control of the pulse duration and structure. The third term ($\left. \frac{d^2 \tilde{\phi}(\omega)}{d\omega^2} \right|_{\omega_0}$) is called the group delay dispersion (GDD) or second-order dispersion. This term usually dominates the overall phase, with the subsequent terms (third-order dispersion (TOD), fourth-order dispersion (FOD) and so on) becoming more important the broader the bandwidth of the pulse (generally the effect of the spectral phase is bigger the bigger the bandwidth). One generally distinguishes between positive (or normal) dispersion, where $\left. \frac{d^2 \tilde{\phi}(\omega)}{d\omega^2} \right|_{\omega_0} > 0$ and longer (redder) wavelengths precede shorter (bluer) wavelengths, and negative (or anomalous) dispersion, where $\left. \frac{d^2 \tilde{\phi}(\omega)}{d\omega^2} \right|_{\omega_0} < 0$.

Most materials display positive dispersion when interacting with visible and near-infrared laser light. As a result, optical setups that induce negative dispersion are required to com-

---

$^1$fs$^2$ is a measure for the second-order dispersion. Dispersive media are often specified with the second-order dispersion they introduce per length of material (e.g., in fs$^2$/mm).

$^2$Note that the GDD refers the propagation through a given optical element or a given length of material. The GDD per unit length (usually in units of fs$^2$/mm) is called the group velocity dispersion (GVD).
press pulses back to their Fourier limit after propagation through material. In the absence of negatively dispersive materials, this is usually achieved with geometric dispersion (see section 3.2 for a brief introduction to prism compressors that use geometric dispersion).
2.2 Temporal Pulse Characterisation

In order to fully understand the dynamics we induce and probe in the experiments described in this thesis it is necessary to characterise the laser pulses we use. Traditional electronic means of measuring events in time are not capable of reaching the time resolution required to characterise femtosecond laser pulses. New techniques that use the pulses to be measured themselves were therefore developed to measure ultrashort pulses. An early review of these techniques, developed with the emergence of nanosecond and picosecond lasers, can be found in [8]. A number of different pulse characterisation techniques have emerged since, all with different advantages and limitations. The techniques and devices used to determine the pulse durations of the laser pulses used in the experiments described in this thesis are briefly introduced in the following.

2.2.1 Auto- and Cross-correlation

The most straightforward way to measure the spectrum of a laser pulse is with a spectrometer using some kind of dispersive medium or device (e.g. a diffraction grating). However, it is also possible to measure the spectrum in the time domain with a so-called Fourier transform spectrometer. This technique requires a means of introducing and scanning a time delay between two copies of the pulse, e.g. a Michelson interferometer. The integrated intensity of the two overlapped copies of the pulse is then measured as a function of the time delay $\Delta t$. The measured signal is also referred to as the field autocorrelation and is given by [9]:

$$s_{ac}(\Delta t) = |\mathcal{E}(\Delta t)|^2 = \int_{-\infty}^{\infty} \mathcal{E}(t) \mathcal{E}^*(t - \Delta t) dt,$$

(2.10)

where $\mathcal{E}^*$ is the complex conjugate of the electric field $\mathcal{E}$. Taking the Fourier transform of the signal as a function of the time delay, we obtain the spectrum:

$$s_{ac}(\omega) = |\mathcal{E}(\omega)|^2 = FT \left[ s_{ac}(\Delta t) \right] = FT \left[ \int_{-\infty}^{\infty} \mathcal{E}(t) \mathcal{E}^*(t - \Delta t) dt \right].$$

(2.11)

This information is easy to obtain in experiments. Unfortunately, any phase information is lost and it is therefore not possible to reconstruct the pulse from the measured spectrum. This is known as the 1d phase retrieval problem. The problem is that introducing a phase shift to the complex amplitude of the electric field $\mathcal{E}(t)$ does not change the spectrum, hence leading to ambiguity. Akutowicz showed in the 1950s that the spectrum, even together with additional knowledge such as that we are dealing with a pulse of finite
duration\textsuperscript{3}, is not sufficient to retrieve $E(t)$ without ambiguity \textsuperscript{[10,11]}. One way of retrieving more information about the pulse shape and duration is through a so-called field cross-correlation. Here we scan the delay between the pulse we want to measure and a known reference pulse.\textsuperscript{4} The integrated intensity signal measured by the detector becomes:

$$s_{cc}(\Delta t) = \int_{-\infty}^{\infty} [E_1(t) + E_2(t - \Delta t)]^2 dt = 2 \int_{-\infty}^{\infty} E_1(t)E_2^*(t - \Delta t)dt + \text{const.}, \quad (2.12)$$

where $E_1$ and $E_2$ are the known and unknown electric fields. The constant term contains terms that are not dependent on the time delay $\Delta t$ and simply introduces an offset to the recorded signal. The Fourier transform gives:

$$s_{cc}(\omega_1, \omega_2) = FT[s_{cc}(\Delta t)] = FT \left[ \int_{-\infty}^{\infty} E_1(t)E_2^*(t - \Delta t)dt \right]. \quad (2.13)$$

Using the cross-correlation theorem\textsuperscript{5} we obtain:

$$s_{cc}(\omega_1, \omega_2) = FT[E_1(t)] \cdot [FT[E_2(t - \Delta t)]]^*. \quad (2.14)$$

Knowing one of the electric field functions, information about the phase and spectral amplitude of the other can be retrieved.

Cross-correlation has been used to estimate the pulse duration of unknown UV pulses in this thesis. See chapters 5 and 6 for details.

\textbf{2.2.2 Frequency-Resolved Optical Gating}

Since autocorrelations are always symmetric and any phase information is lost, and cross-correlations require a second reference pulse, other self-referencing techniques have been developed that provide both amplitude and phase information. In other words, techniques that retrieve the pulse envelope and the time-dependent phase of the pulse. One of the most successful and widely used techniques to achieve this, frequency-resolved optical gating (FROG), was developed in the early 1990s by Kane and Trebino \textsuperscript{[13, 14]}. Since then, a vast variety of implementations of FROG has been developed for various applications, improving on the retrieval accuracy, sensitivity and practicality of the original setup. Trebino’s book on frequency-resolved optical gating discusses the development and details of the many variations (many of those have their own swamp related acronyms)

\textsuperscript{3}Most pulse shapes are not actually finite and only approach zero asymptotically.

\textsuperscript{4}The reference pulse can be measured using more sophisticated pulse characterisation techniques such as FROG, SPIDER etc., see \textsuperscript{[9,12]}.

\textsuperscript{5}C.f. convolution theorem.
of FROG [9].

The main advantage of the FROG technique over the methods discussed in the previous section is the fact that it operates in a hybrid domain, the time-frequency domain. Measurements in the time-frequency domain are called spectrograms. Essentially, a spectrogram is a two-dimensional map of frequencies versus a time delay. If the spectrogram of $E(t)$ is known, the pulse can be reconstructed completely, bar a small number of ambiguities that are not usually important to optics problems (e.g. absolute phase) [15,16].

The spectrogram can be expressed as:

$$s_g(\omega, \tau) = \left| \int_{-\infty}^{\infty} E(t)g(t-\tau)e^{i\omega t}dt \right|^2 = \left| \int_{-\infty}^{\infty} E(t)E(t-\tau)e^{i\omega t}dt \right|^2,$$

(2.15)

where $\tau$ is the delay and $g(t-\tau)$ is the gate function of the variable delay. The right hand side of equation 2.15 shows the case where the pulse itself is used as the gate function, which is what is used in the FROG technique. Therefore, the only modification we need to make to the second harmonic autocorrelator is to replace the photodetector with a spectrometer. At each delay, the spectrometer records a spectrum. The overall spectrogram is then a set of spectra, where each individual slice is a part of $E(t)$ as the delay $\tau$ is scanned.

However, traditionally the algorithms used to retrieve information from a spectrogram require knowledge of the gate function [16]. The FROG retrieval algorithm therefore has to solve the problem of retrieving the phase and intensity information with an unknown gate. The problem the FROG retrieval algorithm has to solve is known as the 2d phase retrieval problem (cf. the 1d phase retrieval problem mentioned in the previous section). Curiously enough, the 2d phase retrieval problem has been solved within certain constraints and has an essentially unique solution. One such constraint is the requirement for finite support, which demands that the signal is zero outside a finite range, both in the time domain and the frequency domain [17,18]. With finite support, the phase-retrieval problem can be solved with exception of the so called trivial ambiguities, namely the absolute phase factor, translation in time and time reversal. The FROG algorithm iteratively reconstructs the pulse by minimising the error between the recorded FROG trace and the FROG trace calculated from the reconstructed pulse.

FROG measurements have been used to characterise infrared pulses used in experiments presented in this thesis. Details of the results can be found in sections 5.3 and 6.3.

---

6The solution is essentially unique and not strictly unique because there is a small chance that the retrieval algorithm converges to a different solution. However, this can be circumvented by using the separately measured spectrum of the pulse as feedback.
There are, as mentioned above, many variations of the FROG, as well as a number of other pulse characterisation techniques adapted to fit various applications. Some of those techniques are compared in this review article [12]).
2.3 Nonlinear Optics

2.3.1 Sum Frequency Generation and Second Harmonic Generation

For the experiments described in chapters 5 and 6 we need both an IR and a UV field.\(^7\)

One relatively straightforward way to produce UV from the IR (which is readily available in our lab) is to use second harmonic generation and subsequent sum frequency generation in non-linear crystals. The fundamentals of these processes are described below.

The electric field $\mathbf{E}$ of laser radiation interacting with matter exerts a force on the charged particles in the medium. This force, called the Lorentz force, accelerates the charges, which leads to the radiation of new fields \([19]\):

$$
\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B}),
$$

where $\mathbf{B}$ is the magnetic field. Since the electrons are considerably less massive than the ions, they are accelerated more and hence mainly responsible for any new fields generated in the medium. In the following, we will consider electrons moving much slower than the speed of light $c$, in which case the $\mathbf{B}$-field component of the Lorentz force can be neglected, as $|\mathbf{B}| = |\mathbf{E}|/c$ \([19]\). As before in section 2.5, we will now restrict our considerations to linearly polarised fields in the $x$-direction and we can hence work with the scalar rather than the vector quantities. The resulting force on the electrons is:

$$
F_x = -e\mathbf{E}_x.
$$

Driven by the $\mathbf{E}_x$-field, the electron oscillates around its equilibrium position. Using the equation for such an oscillating dipole moment:

$$
d(t) = -e x(t),
$$

where $x(t)$ is the displacement of the electron (dependent on $\mathbf{E}_x$, cf. equ. (2.61)), we can define the polarisation $P$. The polarisation of a medium is a measure for the density of electric dipole moments:

$$
P_x(t) = N d(t) = -N e x(t),
$$

where $N$ is the number density. The electron is bound by an anharmonic potential, which we can write as a Taylor series with respect to the equilibrium position $x = 0$:

$$
U(x) = U(0) + x \frac{\partial U}{\partial x} \bigg|_{x=0} + \frac{x^2}{2!} \frac{\partial^2 U}{\partial x^2} \bigg|_{x=0} + \frac{x^3}{3!} \frac{\partial^3 U}{\partial x^3} \bigg|_{x=0} + ....
$$

\(^7\)Ultraviolet (UV) radiation is divided into a number of wavelength ranges between 10 nm and 400 nm according to ISO-21348. The classification of the different UV ranges is as follows: UVA (315–400 nm), UVB (280–315 nm), UVC (100–280 nm), VUV (10–200 nm) and XUV (10–121 nm).
As the potential has a minimum at \( x = 0 \), the second term evaluates to zero. The resulting force on the electron in the potential, known as the restoring force, is given by:

\[
F_{\text{rest}} = -\frac{\partial U}{\partial x} = -ax - bx^2 - cx^3 - ..., \tag{2.21}
\]

where the values of the parameters \( a, b, c, ... \) are determined on the specific potential. The first term in equation (2.21) is the linear contribution and all following terms are non-linear. If we include this restoring force in the equation of motion for the electron, together with the force due to the \( E_x \)-field (cf. equation (2.17)), we can derive an expression for the electron displacement \( x(t) \) that we can plug into equation (2.19) for the polarisation. Conventionally, the polarisation is given as a function of the electric susceptibility \( \chi \) of the medium [19]:

\[
P_x(t) = \varepsilon_0 (\chi^{(1)} E_x + \chi^{(2)} E_x^2 + \chi^{(3)} E_x^3 + ...), \tag{2.22}
\]

where again the first term corresponds to the linear polarisation and the following terms are the non-linear polarisation. \( \chi^{(n)} \) is the \( n \)th order electric susceptibility with units \([\chi^{(n)}] = m^n V^{1-n} \). The values or equations for \( \chi^{(n)} \) can be looked up in the literature.

Maxwell’s wave equation, which describes the propagation of the electric field \( E \) in a medium, is given by\(^8 \) [9]:

\[
\frac{\partial^2 E_x}{\partial z^2} - \frac{1}{c^2} \frac{\partial^2 E_x}{\partial t^2} = \mu_0 \frac{\partial^2 P_x}{\partial t^2}, \tag{2.23}
\]

where \( \mu_0 \) is the vacuum permeability. The term on the right hand side of the equation is the source term, describing the generation of new fields in the medium (this term is zero in vacuum). Since the polarisation \( P_x \) is proportional to the electron displacement, its second partial derivative with respect to the time \( t \) describes the electron acceleration. This means that a term oscillating at a given frequency in \( P_x \) leads to a new field oscillating at this frequency. This property gives rise to sum frequency generation (SFG) and second harmonic generation (SHG), which are explained in the following.

**Sum Frequency Generation:**

In order to study the implications of equation 2.23, we will now consider an electric field \( E_z \) of the form:

\[
E_z(t) = E_1 \cos(\omega_1 t) + E_2 \cos(\omega_2 t), \tag{2.24}
\]

\(^8\)Assuming propagation along the \( z \)-axis and polarisation along the \( x \)-axis.
with $\omega_1 > \omega_2$. From equation 2.22 we get:

$$P^{(2)} = \varepsilon_0 \chi^{(2)} |\mathcal{E}_1 \cos(\omega_1 t) + \mathcal{E}_2 \cos(\omega_2 t)|^2 = ... \quad (2.25)$$

$$... = \varepsilon_0 \chi^{(2)} \left[ \mathcal{E}_1^2 \cos^2(\omega_1 t) + \mathcal{E}_2^2 \cos^2(\omega_2 t) + 2\mathcal{E}_1\mathcal{E}_2 \cos(\omega_1 t) \cos(\omega_2 t) \right] = ... \quad (2.26)$$

$$... = \varepsilon_0 \chi^{(2)} \left[ \mathcal{E}_1^2 \cos^2(\omega_1 t) + \mathcal{E}_2^2 \cos^2(\omega_2 t) + \mathcal{E}_1\mathcal{E}_2 \left( \cos((\omega_1 - \omega_2)t) + \cos((\omega_1 + \omega_2)t) \right) \right]$$

for the second order polarisation. The second order polarisation now has terms oscillating at the sum and difference frequencies of the original fields. For SFG to be efficient, the process must be phase-matched (cf. section 2.3.2) and the second order non-linear susceptibility $\chi^{(2)}$ has to be sufficiently large.

An alternative way of looking at SFG is the photon picture, illustrated in an energy level diagram in figure 2.3. In the photon picture, SFG corresponds to two photons of the two different frequencies $\omega_1$ and $\omega_2$ adding up to create a new, more energetic photon at the sum frequency $\omega_1 + \omega_2$. Both energy and momentum of the photons involved must be conserved. The energy relation of the process is:

$$\hbar \omega_1 + \hbar \omega_2 = \hbar (\omega_1 + \omega_2) \quad (2.26)$$

and momentum conservation gives: \(^1\)

$$\hbar k(\omega_1) + \hbar k(\omega_2) = \hbar k(\omega_1 + \omega_2), \quad (2.27)$$

where:

$$k(\omega) = \frac{n(\omega)\omega}{c} \quad (2.28)$$

is the so called wave number or spatial frequency.

**Second Harmonic Generation:**

SHG is a special case of SFG. For $\omega_1 = \omega_2 = \omega_0$ and $\mathcal{E}_1 + \mathcal{E}_2 = \mathcal{E}_0$ the original electric field $\mathcal{E}_x$ from equation (2.24) becomes:

$$\mathcal{E}_x(t) = \mathcal{E}_0 \cos(\omega_0 t). \quad (2.29)$$

The last term of equation (2.25) now immediately gives a term oscillating at twice the original frequency. Alternatively, using this field in equation 2.22, the second order

---

\(^9\)Using the identity $\cos(x)\cos(y) = \frac{1}{2}(\cos(x - y) + \cos(x + y))$.

\(^1\)Considering only collinear schemes, this equation can be written in terms of the wave number $k$ rather than the wave vector $\mathbf{k}$, where $k = |\mathbf{k}|$. 

35
Figure 2.3: Energy level diagram illustrating the photon picture. Left: Two photons of different frequencies $\omega_1$ and $\omega_2$ add up to a photon at a frequency equal to the sum of the original frequencies. This is known as sum frequency generation (SFG). Right: Two photons of the fundamental frequency $\omega_0$ add up to one higher energy photon at twice the original frequency. This process is a special case of SFG and is known as second harmonic generation (SHG).

The identity $\cos^2(x) = \frac{1}{2}(1 + \cos(2x))$ was used in the derivation.

### Polarisation

\[
P^{(2)} = \epsilon_0 \chi^{(2)} E^2_x(t) = \frac{1}{2} \epsilon_0 \chi^{(2)} (\mathcal{E}_0 \cos(\omega_0 t))^2 = \frac{1}{2} \epsilon_0 \chi^{(2)} (\mathcal{E}_0^2 + \mathcal{E}_0^2 \cos(2\omega_0 t)) ,
\]

(2.30)

where we get a term oscillating at $2\omega_0$, i.e. the second harmonic of the fundamental frequency. The efficiency of SHG again depends on phase-matching (cf. section 2.3.2) and a large enough $\chi^{(2)}$.

In the photon picture, two photons of the original frequency $\omega_0$ add up to a single photon of twice the original frequency (and energy) inside the non-linear medium:

\[
h\omega_0 + h\omega_0 = h(2\omega_0).
\]

(2.31)

Momentum conservation now gives:

\[
hk(\omega_0) + hk(\omega_0) = hk(2\omega_0).
\]

(2.32)

Note that both SHG and SFG require $\chi^{(2)} \neq 0$. Hence SFG and SHG are not possible in centrosymmetric media (e.g. gases), as in these media all even-order susceptibilities are zero.

### Conversion Efficiency:

An important consideration when converting frequencies is the conversion efficiency. The full derivation of the conversion efficiency $\eta$ is quite cumbersome and outside of the scope of this chapter, but can be looked up in [19,20]. Here we will focus on the main steps and
results for the case of SHG. If we substitute the terms for the (linearly polarised) electric field $E_x$ and the polarisation source terms $P_x$ into Maxwell’s wave equation (equ. (2.23)), we obtain [19]:

$$\frac{\partial E_j}{\partial z} = \frac{-i\omega_j}{2\epsilon_0 cn(\omega_j)} P_j,$$

where $j$ is a placeholder for the frequencies involved. In the case of SHG, where the involved frequencies are $\omega_0$ and $2\omega_0$, we obtain the following coupled equations:

$$\frac{\partial E_{\omega_0}}{\partial z} = \frac{-i\omega_0 \chi^{(2)}}{2cn(\omega_0)} E_{\omega_0}^*(z) E_{2\omega_0}(z) e^{-i\Delta kz},$$

$$\frac{\partial E_{2\omega_0}}{\partial z} = \frac{-i\omega_0 \chi^{(2)}}{2cn(2\omega_0)} E_{\omega_0}^2(z) e^{i\Delta kz},$$

where $\Delta k$ is the wave number mismatch (cf. section 2.3.2 and equation (2.38)). This set of equations has to be solved numerically. However, assuming that the pump (the $\omega_0$ wave) is undepleted ($E_{\omega_0}(z) = \text{const.}$), we can omit equation (2.34). The results obtained from this low depletion approximation are a good approximation for a conversion efficiency $\eta_{SHG}$ of up to 10%.

Integrating equation (2.35) from $z = 0$ to $z = L$ (where $L$ is the length of the non-linear medium), the SHG conversion efficiency becomes [9,19]:

$$\eta_{SHG} = \frac{I_{2\omega_0}}{I_{\omega_0}} = \frac{2\pi^2 (\chi^{(2)})^2 I_{\omega_0}(0) L^2 \text{sinc}^2 \left( \frac{\Delta k L}{2} \right)}{\lambda_0^2 \epsilon_0 cn(\omega_0)^2 n(2\omega_0)},$$

where $\lambda_0 = \frac{2\pi c}{\omega_0}$ is the vacuum wavelength of the pump. The efficiency is highest for the phase-matched case (cf. section 2.3.2), where $\Delta k = 0$ and hence the sinc function equals 1.\textsuperscript{12} The Franken experiment [21], the first ever SHG experiment in 1961, achieved an efficiency of around $10^{-8}$ due to very poor phase-matching. Nowadays, conversion efficiencies of around 0.5 and higher can be achieved [22]. Since $\eta_{SHG}$ is proportional to the pump intensity $I_\omega$, increasing the pump intensity leads to an increased conversion efficiency. This is limited by the damage threshold of the non-linear material.

\subsection*{2.3.2 Phase-Matching}

The efficiency of frequency conversion depends on the overlap of the fundamental wave and the generated wave throughout the non-linear medium. As the fundamental wave travels through the medium, photons are transferred from the fundamental to the newly generated wave. Hence, the intensity of the fundamental decreases, whilst the new frequency increases (e.g. the second harmonic). The build-up of intensity in the generated wave is only efficient as long as the two waves maintain a fixed phase relationship. Due\textsuperscript{12}Note that for $\Delta k = 0$ the efficiency quickly exceeds 10% and hence the low depletion approximation is no longer valid.
to chromatic dispersion, however, the two waves generally travel at different velocities through the non-linear medium. Techniques that ensure a constant refractive index, and therefore a constant velocity, for the frequencies involved are called phase matching techniques.

For SHG, for example, we can see from equations (2.28) and (2.32) that:

\[ n(\omega_0) = n(2\omega_0) \]  

(2.37)

is required by momentum conservation. This is called the phase-matching condition for SHG. In general, we require the difference between the wave number of the original wave and the generated wave, the phase-mismatch \( \Delta k \), to be zero [23]:

\[ \Delta k = k_{out} - k_{in} \overset{!}{=} 0. \]  

(2.38)

The most common way of phase-matching exploits the birefringence of many non-linear materials. The birefringence, the fact that waves with different polarisations experience different refractive indices, allows for matching refractive indices at different wavelengths. The polarisation dependence of the refractive index in birefringent materials (crystals) can be visualised with the help of a so called index ellipsoid shown in figure 2.4. We will only consider uniaxial crystals here, i.e. crystals with only one optical axis \( c \). The shaded red area in figure 2.4 is the plane perpendicular to the wave vector \( k \) of the incident light wave. All possible polarisations of the incident beam will lie in this plane. The refractive index any incident polarisation experiences in the crystal is proportional to the distance from the centre of the ellipsoid to its surface along the direction of the given polarisation. From figure 2.4 it is easy to see that incident radiation with its polarisation perpendicular to both the optical axis \( c \) and the wave vector \( k \) experiences a constant refractive index, independent of the angle of incidence \( \theta \). This fixed refractive index is called the ordinary refractive index \( n_o(\omega) \). Any other polarisation will experience a refractive index dependent on \( \theta \) and the polarisation direction. A light wave polarised in the plane containing \( c \) and \( k \) experiences the so called extraordinary refractive index \( n_e(\omega, \theta) \), dependent on \( \theta \). For \( \theta = 0 \), i.e. beams propagating along the optical axis, the difference in refractive indices is zero \( (n_e(\omega, 0) = n_o(\omega)) \). In positive uniaxial crystals \( (n_e(\omega, \theta) \geq n_o(\omega)) \), as depicted in figure 2.4, the extraordinary refractive index increases with an increasing angle of incidence, until it reaches its maximum at \( \theta = 90^\circ \). The maximum value of \( n_e(\omega, \theta) \) is denoted as \( \bar{n}_e(\omega) = n_e(\omega, 90^\circ) \). For many crystals, the values of \( n_o(\omega) \) and \( \bar{n}_e(\omega) \) can be looked up in the literature. Note that the ordinary and extraordinary axes are also often referred to as fast and slow axes, respectively.\(^{13}\)

\(^{13}\)The use of this terminology depends on whether the crystal is positive or negative uniaxial. The axis with the smaller refractive index is referred to as the fast axis.
The extraordinary angle dependent refractive index can be calculated with [23]:

$$n_e(\omega, \theta) = \left[ \frac{\cos^2(\theta)}{n_0^2(\omega)} + \frac{\sin^2(\theta)}{\bar{n}_e^2(\omega)} \right]^{-\frac{1}{2}}. \quad (2.39)$$

The two phase matching schemes based on the birefringence of non-linear crystals are known as type 1 and type 2 phase matching, respectively. These two schemes will be introduced in the following by example of SHG.

**Type 1 phase-matching:**

In the type 1 phase-matching scheme, the fundamental wave is incident with its polarisation along the axis of the ordinary refractive index, whereas the polarisation of the generated second harmonic lies in the plane containing c and k (cf. figure 2.4). As a result, the incident wave experiences $n_o(\omega)$, and is called the o-wave, and the second harmonic experiences $n_e(\omega, \theta)$, and is referred to as the e-wave. In the photon picture, this can be denoted as [23]:

$$o_\omega + o_\omega \rightarrow e_{2\omega}. \quad (2.40)$$

The refractive indices of both the o-wave and the e-wave are dependent on the frequency of the respective waves. Using the angle dependence of $n_e(\omega, \theta)$, the refractive index of
the e-wave can be tuned to match that of the o-wave. For second harmonic generation, equation (2.38) for the phase-mismatch becomes\textsuperscript{14}:

\[
\Delta k_1 = k_e(2\omega, \theta) - 2k_o(\omega) = \frac{2\omega}{c} [n_e(2\omega, \theta) - n_o(\omega)]
\] (2.41)

and the type 1 phase matching condition, as a function of the type 1 phase-matching angle $\theta_1$, gives:

\[
n_e(2\omega, \theta_1) = n_o(\omega).
\] (2.42)

Using this in equation (2.39), an analytical expression for the type 1 phase-matching angle $\theta_1$ can be derived\textsuperscript{23}:

\[
\sin(\theta_1) = \left[ \frac{n_o^{-2}(\omega) - n_o^{-2}(2\omega)}{n_e^{-2}(2\omega) - n_o^{-2}(2\omega)} \right]^{\frac{1}{2}}.
\] (2.43)

Knowing the ordinary refractive index $n_o$ and the maximum extraordinary refractive index $\bar{n}_e$ of a given crystal and the wavelength to be used, this allows to determine $\theta_1$.

**Type 2 phase-matching:**

In contrast to type 1 phase-matching, where the fundamental wave had only one polarisation, type 2 phase-matching involves a combination of an o-wave and an e-wave in the fundamental. The resulting second harmonic can be either an o-wave or an e-wave. As before, in the photon picture, the notation is\textsuperscript{23}:

\[
o_\omega + e_\omega \rightarrow o_{2\omega}
\] (2.44)

or:

\[
o_\omega + e_\omega \rightarrow e_{2\omega}.
\] (2.45)

In the case of equation (2.45), the phase-mismatch becomes:

\[
\Delta k_2 = k_e(2\omega, \theta) - [k_o(\omega) + k_e(\omega, \theta)] = \frac{\omega}{c} [2n_e(2\omega, \theta) - n_o(\omega) - n_e(\omega, \theta)].
\] (2.46)

The type 2 phase-matching condition, as a function of the type 2 phase-matching angle $\theta_2$, therefore is:

\[
n_e(2\omega, \theta_2) = \frac{1}{2} [n_o(\omega) + n_e(\omega, \theta_2)].
\] (2.47)

Unlike for type 1 phase-matching, no analytical solution for $\theta_2$ exists.

Both schemes introduced above are critically angle-dependent and therefore known as critical phase-matching techniques. Non-critical phase-matching can be achieved exploit-
ing the different temperature dependence of the refractive index along the different axes of the crystal. There are a number of things to consider with critical phase-matching schemes. Some of the most common issues are explained in the following.

**Beam walk-off:**

The wave vector $\mathbf{k}$ points in the direction of $\mathbf{E} \times \mathbf{B}$, where $\mathbf{B}$ is the magnetic field. It is therefore perpendicular to planes of equal phase and represents the propagation direction. In isotropic media, the energy flux density, given by the Poynting vector $\mathbf{S}$, is parallel to the wave vector. The Poynting vector is given by [19, 24]:

$$\mathbf{S} = v_{p}^{2} \varepsilon (\mathbf{E} \times \mathbf{B}),$$  

where $\varepsilon$ is the permittivity tensor. In anisotropic media, where the diagonal elements of the permittivity tensor are not all equal\(^{15}\), the Poynting vector and hence the energy flow and the wave vector are not collinear [26]. This leads to an energy walk-off in space between the fundamental frequency and the generated frequency. The decreasing overlap between the two leads to a decrease and eventually termination of the energy exchange.

In order to simplify the above derivations we have made a number of assumptions in the theoretical description of the laser beams (plane wave, monochromatic, c.w.). In the following we will consider more realistic laser sources (focussed beams - curved wavefronts, finite spectral bandwidth) and analyse the impact on the phase-matching conditions.

**Acceptance angle:**

In the preceding derivations we have assumed the wave vector $\mathbf{k}$ to be a clearly defined quantity, incident on the non-linear crystal at a given angle $\theta$\(^{16}\). However, if we consider a divergent (or convergent) beam, different parts of the beam exhibit different wave vectors at different angles. Hence, the phase-matching conditions for the two different phase-matching schemes discussed above can not be fulfilled by all parts of the beam simultaneously, leading to a decrease in conversion efficiency.

The wave vector mismatch $\Delta k$ is a function of the incidence angle $\theta$. We can expand

\(^{15}\)Due to physical considerations (energy conservation and time reversal symmetry), the permittivity tensor is always symmetric and can therefore be diagonalised by a suitable choice of basis vectors (the principal axes of the material) [25]. In isotropic media, all three diagonal elements are the same. In uniaxial anisotropic media two of the diagonal elements (ordinary elements) are the same, a third diagonal element differs from the other two (extraordinary element). In biaxial anisotropic media, all three diagonal tensor elements are different [23].

\(^{16}\)Note that $\theta$ is the angle between the wave vector of the incident radiation and the optical axis of the medium. This can be the angle of incidence if the crystal surface the laser is incident on is perpendicular to the optical axis. Usually, however, the crystal is cut at the appropriate angle $\theta$ with respect to the optical axis so that the angle of incidence of the beam can be perpendicular to the crystal surface.
\( \Delta k(\theta) \) in a Taylor series with respect to the phase-matching angle \( \theta_{PM} \):

\[
\Delta k(\theta) = \Delta k(\theta_{PM}) + \frac{\partial \Delta k}{\partial \theta} \bigg|_{\theta_{PM}} (\theta - \theta_{PM}) + ..., \\
(2.49)
\]

where the first term is zero (per definition). If we substitute the expression for the full angle spread of wave vectors \( \Delta \theta = 2|\theta - \theta_{PM}| \) in the first order expansion (the second term in equ. (2.49)) , we obtain:

\[
\Delta \theta = \frac{2\Delta k(\theta)}{\frac{\partial \Delta k(\theta)}{\partial \theta} \bigg|_{\theta_{PM}}}. \\
(2.50)
\]

Defining the acceptance angle \( \Delta \theta_{acc} \) as the full angle spread of wave vectors within which the conversion efficiency is 50\% or higher, we can derive the following expression\(^{17}\) [23]:

\[
\Delta \theta_{acc} = \frac{4 \times 1.392}{L} \left| \frac{\partial \Delta k(\theta)}{\partial \theta} \bigg|_{\theta_{PM}} \right|. \\
(2.51)
\]

The term \( \left| \frac{\partial \Delta k(\theta)}{\partial \theta} \bigg|_{\theta_{PM}} \right| \) can be derived from equations (2.41) and (2.46) for SHG and SFG, respectively.

**Phase-matching bandwidth:**

Previously, we have considered phase-matching for continuous wave (monochromatic) laser sources. Laser pulses, especially ultrashort pulses, can have huge bandwidths. Only one wavelength is exactly phase-matched. In order to achieve a decent overall conversion efficiency, a wide range of wavelengths have to be approximately phase-matched. This range of wavelengths is known as the phase-matching bandwidth.

In the non-linear crystal, the laser pulses travel at the group velocity \( v_g \):

\[
v_g = \frac{\partial \omega}{\partial k} = \left[ \frac{\partial n(\omega)}{\partial \omega} \frac{\partial \omega}{\partial k} \right]^{-1}. \\
(2.52)
\]

Even with phase-matching, where \( n(\omega) = n(2\omega) \) (in the case of SHG), the derivatives of the refractive indices are in general not equal \( \left( \frac{\partial n(\omega)}{\partial \omega} \neq \frac{\partial n(2\omega)}{\partial \omega} \right) \). Hence, the group velocities of the fundamental and the second harmonic are not the same \( (v_g(\omega) \neq v_g(2\omega)) \). Due to the different velocities, the fundamental and its second harmonic will separate during propagation through the crystal and the energy transfer between them will decrease. This is known as pulse walk-off (cf. beam walk-off above). We can define a separation between

\(^{17}\)From equ. (2.36) we can see that the efficiency drops to half its maximum value for \( |\Delta k| = \frac{2 \times 1.392}{L} \). The factor of 1.392 originates from our definition, where we require 50\% efficiency, and the sinc\(^2\) function of equation 2.36 takes the value of 0.5 when the argument is 1.392.
the two pulses (fundamental and second harmonic) equal to the full-width half-maximum (FWHM) as the criterion for the walk-off. The pulses reach a separation equal to their FWHM after travelling through a non-linear medium of length $L$ if the pulse duration $\tau$ and the pulse separation $\Delta t$ become:

$$\tau = \Delta t = \left| \frac{1}{v_g(2\omega)} - \frac{1}{v_g(\omega)} \right| \cdot L.$$ (2.53)

Since the pulse duration and the bandwidth are related through the time-bandwidth product, we get for the phase-matching bandwidth of a Gaussian pulse [19, 23]:

$$\Delta \nu_{PM} = \frac{0.441 \lambda_0^2}{\left| \frac{1}{v_g(2\omega)} - \frac{1}{v_g(\omega)} \right| cL},$$ (2.54)

where $\lambda_0$ is the central wavelength. We can see that the crystal thickness is a trade-off between phase-matching bandwidth ($\propto \frac{1}{L}$) and the conversion efficiency ($\propto L^2$).

---

18See table 2.1 for details on the time-bandwidth product for a Gaussian pulse, $C_{TBP} = 0.441$. 

43
2.4 Strong Field Physics

Strong field physics is a general research field concerned with light-matter interactions. Again, this is an area of research that would not be possible without the laser. In the strong field regime, the laser-electron interaction becomes comparable in strength to the potential binding the electron. As a result, the atom (or molecule) can be ionised. The following sections discuss a number of different ionisation pathways and discuss useful quantities for strong field physics before section 2.5 introduces an intensely studied strong field phenomenon known as high harmonic generation. High harmonic generation is the main ingredient for all experiments presented in this thesis.

2.4.1 Ionisation

There are several mechanisms or pathways that lead to the ionisation of an electron. Which mechanism dominates is dependent on the incident laser intensity (and therefore field strength) and the wavelength. Together with the laser intensity and wavelength, the so called ionisation potential \( I_p \) of an atom gives a good idea of whether ionisation is possible and which pathway is likely to dominate. The ionisation potential is defined as the energy required to remove the most loosely bound electron (the valence electron) of an isolated atom or molecule to form a cation. Ionisation is also known as a bound state to continuum state transition. If the incident light is of sufficiently high frequency (i.e. sufficiently high photon energy), this is possible with a single-photon transition [27].

However, the most commonly used laser frequency for strong field experiments is 800 nm, which corresponds to a photon energy of 1.55 eV. When comparing this to the ionisation potentials of atoms commonly used for high harmonic generation (cf. section 2.5) shown in table 2.2, it becomes clear that ionisation must be possible with photon energies lower than the target \( I_p \).

Figure 2.5 illustrates the various ionisation pathways, which are described in more detail in the following.

**Single-photon ionisation:** A single photon can ionise and free an electron when its

<table>
<thead>
<tr>
<th>species</th>
<th>( I_p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>15.76 eV</td>
</tr>
<tr>
<td>Kr</td>
<td>14.00 eV</td>
</tr>
<tr>
<td>( \text{N}_2 )</td>
<td>15.58 eV</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>13.78 eV</td>
</tr>
</tbody>
</table>

Table 2.2: Ionisation energies for atoms and molecules commonly used in high harmonic generation. Data from NIST (National Institute of Standards and Technology) database [28].

---

19 Note that single-photon processes are not strictly speaking strong field processes.

20 The unit of electronvolt (eV) is defined as the energy expended to move the fundamental charge (the charge of a single electron) across an electric potential difference of 1 V. 1 eV \( \approx 1.6 \times 10^{-19} \) J. The photon energy and the wavelength of a photon are related by \( E_\gamma = \frac{hc}{\lambda} \).
energy is greater than the ionisation potential, $\hbar \omega > I_p$.

**Multi-photon ionisation:** Ionisation is possible in laser fields of lower frequency (i.e. lower photon energy) via multi-photon ionisation (MPI). MPI requires a high photon flux so that multiple photons can be absorbed to overcome the potential barrier. This was first observed in xenon with a seven-photon transition in 1965 by a Russian team using a ruby laser [29]. Fabre et al. derived the associated ionisation rate in the framework of lowest-order perturbation theory (LOPT) in 1982 [30]. The $n$-photon ionisation rate takes the form:

$$\Gamma_{MPI}^n = \sigma_n I^n,$$  \hspace{1cm} (2.55)

where $\sigma_n$ is the $n$-photon absorption cross-section and $I$ is the intensity of the incident laser light. This power law is valid for intensities below a saturation intensity $I_s$ [31]. Above the saturation intensity, higher order terms contribute significantly and an extension to the LOPT is necessary. This saturation is attributed to population depletion. Note also that despite looking perfectly innocent, equation 2.55 packs a punch. The absorption cross-section is no easy quantity to calculate. For one, $\sigma_n$ decreases rapidly with increasing photon numbers. Near-resonance behaviour leads to further complications [32].

With increasing intensity of the incident laser light, more limitations of the perturbative approach arise. In sufficiently strong laser fields, the field couples to the atomic states and leads to a dynamic shift in energies. They can no longer be treated as unperturbed. This effect is known as the AC-Stark shift [33]. An upper limit to the magnitude of this shift in energy levels (and therefore in ionisation potential) can be estimated by treating the valence electron as a free electron in the oscillating laser field. This is a good approximation for Rydberg states [34,35].

The alternating electric field of the incident laser forces the free electron into an os-
cillatory motion. The cycle averaged quiver energy, called the ponderomotive energy $U_p$, can be derived from the acceleration the free electron experiences in the laser field. In a laser field of the from $\mathcal{E}(t) = \mathcal{E}_0 \sin(\omega t)$, this acceleration is $a(t) = \dot{\mathcal{E}}(t) = \frac{\varepsilon \mathcal{E}(t)}{m_e}$. The ponderomotive energy therefore is:

$$U_p = \frac{1}{2} m_e \langle v^2(t) \rangle = \frac{e^2 \mathcal{E}^2}{4 m_e \omega^2},$$  \hspace{1cm} (2.56)

where $e$ is the charge of the electron and $m_e$ is the mass of the electron. The effective ionisation potential increases by the ponderomotive energy (in this approximation).

**Above-threshold ionisation:** Above-threshold ionisation is a manifestation of strong field MPI. As the name suggests, ATI is MPI by a photon number larger than the minimum number required for ionisation. This was first described by Agostini et al. in 1979 [36]. The additionally absorbed photons add to the kinetic energy of the electron.

**Tunnel ionisation:** Keldysh was the first to introduce a semi-classical non-perturbative treatment for ionisation at higher intensities [37], where the laser field is treated classically and the electron is treated semi-classically. At modest intensities, MPI is the dominating ionisation pathway. However, if the incident field is strong enough and the oscillation frequency low enough (quasi-stationary approximation), the atomic potential is deformed to such an extent that it forms a potential barrier that allows the electron to tunnel through into the continuum (cf. figure 2.5 (d)). The quasi-static approximation is based on the assumption that the tunnelling happens on a time scale where the change of the electric field is negligible. This approximation allows for the ionisation rates in oscillating electric fields to be calculated based on the static ionisation rates (with corrections).

A number of different theories have been developed to calculate the static field ionisation rate. The model introduced by Keldysh [37] ignores the effect of the atomic Coulomb potential (other than for the ground state), an approach known as the strong field approximation (SFA). A year later, in 1966, Perelomov, Popov and Terent’ev developed what is known as PPT theory [38], a theory for the calculation of the ionisation probability that includes a Coulomb correction for the free electron. A mere twenty years later, Ammosov, Delone and Krainov extended PPT theory to the case of more complex atoms and ions [39]. Note that because there are no clear cut boundaries between the different ionisation pathways, great care must be taken when using these models for quantitative predictions [40]. Many more corrections and extensions of the aforementioned models are discussed and compared with experimental results in a study by Larochelle et al. in [40].

\[21U_p[eV] \approx 9.33\lambda_0^2[\mu m]/I_0[10^{14}W/cm^2] \] is a version of equ. 2.56 more useful for experimentalists.
Tunneling ionisation has also been described fully quantum mechanically. In this treatment, there is not a single continuum state for the freed electron, but rather some of the population from the ground state is transferred to a range of continuum states known as Volkov states [41,42]. The electron in the continuum is in a superposition of all possible continuum states, weighted by the transition probability to each one of those states.

However, the classical treatment of the electron in the continuum, with the initial conditions of zero initial momentum and position zero when appearing in the continuum, is surprisingly accurate in its reproduction of experimental results. This is partly due to the fact that once accelerated by the laser field, the centre of the wavepacket in the quantum mechanical treatment quickly approaches the classical trajectory [42].

**Over-the-barrier ionisation:** If the electric field becomes so strong that the potential barrier is lowered to below the level of the ground state, the ground state is no longer bound. This is known as over-the-barrier ionisation (OTBI).

MPI (including ATI) occurs at intensities up to around $10^{14}$ W/cm$^2$, tunnelling ionisation occurs at intensities up to the order of $10^{15}$ W/cm$^2$ and OTBI occurs at intensities beyond $10^{15}$ W/cm$^2$ [43]. Saturation of ionisation occurs when the laser excitation depletes the target atoms of electrons. For a given laser pulse duration and atomic species, the saturation intensity can be found by integrating the ionisation rate over the laser pulse train in time. In order to observe tunnel ionisation or OTBI, ultrashort laser pulses are required. Otherwise, all target atoms are fully ionised before the necessary intensities for tunnel ionisation and OTBI can be reached [44].

Since the boundaries between the different ionisation regimes are not very well defined, the Keldysh parameter was introduced to provide a somewhat quantitative indicator. The Keldysh parameter is defined as [37,42]:

$$\gamma = \sqrt{\frac{I_p}{U_p}} = \omega \tau_t,$$  \hspace{1cm} (2.57)

where $\tau_t$ is the tunnelling time. Often, $\gamma \ll 1$ is taken to be the tunnelling regime, whereas $\gamma \gg 1$ is taken to be the multi-photon ionisation regime. However, Ivanov et al. point out in [42] that $\gamma \ll 1$ simply means that the barrier can be treated as static during the process of tunnelling. This does not mean that tunnelling can’t take place when $\gamma > 1$, but rather that the barrier moves on the time scale of the tunnelling time and that MPI dominates the picture.
2.4.2 Tunnel Ionisation in Molecules

The electronic orbitals of molecules are, unlike those of atoms, not simple spherical distributions. In combination with the nuclear degrees of freedom, molecular ionisation exhibits some additional complications compared to ionisation in atoms. The most important ones are briefly outlined in this section, with references to more comprehensive reviews. Since the molecule used in the experiment described in chapter 6 of this thesis is CO₂, it is used as an example in this section.

Molecular orbitals come in a multitude of symmetries, owing to the underlying nuclear structure. Not only are molecular orbitals non-spherical, but they also show different symmetries for different orbitals. Figure 2.6 shows the highest three occupied molecular orbitals of CO₂. It is somewhat intuitive to think that the tunnel ionisation rate in non-spherical orbitals is anisotropic. This is indeed the case and the molecular ADK model (MO-ADK) [45] reproduces that behaviour by taking the molecular orbital density profile along the axis of polarisation of the incident laser field into account.²² Due to the non-spherical symmetry of molecular orbitals, the ionisation rate depends dramatically on the polarisation of the laser field with respect to the molecular axis [46]. The tunnel ionisation rate decays exponentially with the ionisation potential, so the highest occupied molecular orbital (HOMO) is expected to dominate the overall ionisation rate of a given molecule. However, for a given laser polarisation with respect to the molecular axis, the ionisation rates of certain orbitals can be strongly suppressed due to their symmetry [47,48]. The fact that lower lying orbitals can contribute significantly leads to multichannel ionisation [49–52].

Section 2.5.2 discusses more details related to molecular ionisation effects relevant to high harmonic generation.

²²The agreement between MO-ADK theory and experimental ionisation rates for aligned molecules in general and CO₂ in particular is by no means perfect, as demonstrated in [46].
Figure 2.6: Highest three occupied molecular orbitals of CO$_2$. The different colours of the lobes represent opposite charge signs. Associated energies are those of the final states of the CO$_2^+$ ion from [49]. Molecular orbital renderings from OrbiMol [53].
2.5 High Harmonic Generation

Strong non-linear interactions between laser radiation and matter can lead to a phenomenon known as high harmonic generation (HHG). The result is the emission of photons whose frequencies are odd integer multiples of the generating laser frequency. HHG was first observed in the late 1980s in Chicago [54] and Saclay [55]. The generation of higher-order harmonics, and hence radiation of shorter wavelengths, was the focus of most early work in the field [56, 57]. Nowadays, wavelengths as short as 2.7 nm [58, 59] and even below 1 nm [60] can be generated using HHG. The early 1990s saw the theoretical understanding of HHG develop, with Krause et al. [61] stating the cut-off law (cf. equ. (2.63)) and Corkum [62] and Kulander [63] refining the semi-classical three-step model (see below). Soon after, a fully quantum mechanical description based on the strong field approximation (SFA) was introduced by L’Huillier, Lewenstein and co-workers [64, 65]. Much effort has been put into optimising and improving control of the generated harmonics, leading to more efficiently generated higher frequencies (see [66] for a more comprehensive review and list of publications). Taking advantage of the broad bandwidth of the generated harmonics, attosecond pulses have been realised by Agostini et al. [67] in the form of attosecond pulse trains and Krausz et al. [68] as single attosecond pulses. Attosecond science has since become an important field, enabling better understanding of ultrafast processes such as electronic motion in atoms and molecules with sub-femtosecond temporal resolution and Å spatial resolution [69, 70].

2.5.1 Single-Atom Response

The three-step model provides an intuitive, semi-classical description of the HHG process. The three steps, namely ionisation of an atom, the motion of the released electron after tunnelling and finally the recollision of this electron with the ion, are described in the following and in figure 2.7 (based on [69, 71, 72]). The following description considers a single atom as the target (see further down for macroscopic effects) and a linearly polarised laser field.

**Ionisation:** Strong laser fields can bend the potential well of the atom, where the electron is initially confined, to allow tunnelling. The tunnelling probability is exponentially proportional to the field strength, which is why this process is restricted to a narrow temporal window (on the order of a few hundred attoseconds) around the peak of the laser field. In this window, the force on the electron due to the electric field of the laser becomes comparable to the force due to the Coulomb potential of the atom that binds the electron to the system.
Figure 2.7: Schematic of the three-step model in a 1D atomic potential. (a) The NIR femtosecond pulse (faint red) bends the potential and allows the electron to tunnel through the barrier. (b) The electron starts moving along an approximately classical trajectory. (c) The electron is driven back by the reversed field as the laser pulse passes the atom. (d) When the electron recollides with the parent ion, an attosecond burst of harmonic photons can be emitted on recombination.

**Electron motion after tunnelling:** Whilst in the continuum, the electron is driven freely (i.e. not subject to other forces\(^{23}\)) by the laser field. For a linearly polarised ionising laser field, the electron moves on a trajectory along the polarisation direction of the laser field. As the direction of the passing electric field of the laser changes, the electron is accelerated back towards the ion. The electron trajectories can be approximated using Newton’s classical mechanics.

**Recollision:** The returning electron has a finite probability of recombination with the ion. Successful radiative recombination leads to the emission of photons. The energy of the emitted photon depends on the kinetic energy the electron gained in the continuum (and hence on its trajectory) and the ionisation potential of the atomic species.

This light-matter interaction results in a spectrum that consists of discrete high-order harmonics of the laser frequency.\(^{24}\) After a drop-off in intensity in the so-called perturbative low-energy region, the high harmonics spectrum forms a characteristic plateau with a sudden cut-off at the maximum photon energy (see figure 2.8 for a schematic of a typical high harmonic spectrum). The bandwidths involved, from the VUV to the XUV, are broad enough to support pulses of attosecond duration \([67–70]\).\(^{25}\)

The potential a bound electron is subjected to in the presence of a laser field can be

---

23: This is known as the strong field approximation (SFA), where the influence of the Coulomb potential on the electron in the continuum is neglected.

24: A continuous spectrum can be generated if the contribution of a single maximum of the electric field dominates the harmonic generation.

25: Bandwidth and pulse duration are interconnected through Fourier transformation \([73]\).
written in the form (in the dipole approximation):

\[ V(x, t) = V_C(x) + x\mathcal{E}_x(t), \tag{2.58} \]

where the first term is the Coulomb potential and the second term describes the laser-matter interaction. \( \mathcal{E}_x(t) \) is the electric field, assuming linear polarisation in the \( x \)-direction.

The dipole approximation used here allows us to treat the electric field associated with the laser radiation incident on the target as a function of time only. Spatial dependence of the light-matter interaction due to the laser field is ignored. This is a valid approximation if the length scales of the target (here atom) and the electron trajectory are small compared to the wavelength of the incident light. Note that there is also an upper limit for the validity of the dipole approximation for wavelengths long enough that the interaction between the magnetic field component of the laser field and high energy electrons becomes significant [74].

Once the electron is ionised, and far enough away from the nucleus, the influence of the Coulomb potential becomes negligible and the motion of the electron in the continuum
can be described with Newton’s law:

\[ \ddot{x}(t) = -\frac{eE_0}{m_e} \cos(\omega_0 t), \quad (2.59) \]

where \( e \) is the elementary charge of the electron and \( m_e \) its mass, \( E_0 \) is the electric field amplitude and \( \omega_0 \) is the fundamental laser frequency. Note that in this derivation a continuous wave (cw) laser field has been used for simplicity. An envelope function can be taken into account either by using the slowly varying envelope approximation (SVEA) or by integrating numerically. As the name suggests, the SVEA assumes that the envelope of the forward travelling electric field changes slowly in space and time compared to the wavelength of the carrier wave. For the SVEA to be valid, the spectral width of the field is required to be significantly narrower than the carrier wavelength and therefore breaks down for femtosecond pulses. For simplicity reasons we assume the initial velocity and the position after tunnelling to be zero. Integration gives:

\[ \dot{x}(t) = \int_{t_i}^{t} \ddot{x}(t') dt' = -\frac{eE_0}{\omega_0 m_e} \left[ \sin(\omega_0 t) - \sin(\omega_0 t_i) \right], \quad (2.60) \]

where \( t_i \) is the initial or ionisation time (i.e. the time at which the electron enters the continuum). Further integration leads to an equation for the position of the electron as a function of time:

\[ x(t) = \int_{t_i}^{t} \dot{x}(t') dt' = -\frac{eE_0}{\omega_0 m_e} \left[ \frac{1}{\omega_0} \left( \cos(\omega_0 t) - \cos(\omega_0 t_i) \right) + \sin(\omega_0 t_i)(t - t_i) \right]. \quad (2.61) \]

The path that the electron follows between ionisation and recollision is called a trajectory. The energy of a photon \( E_\gamma \) emitted at the time of recollision \( t_r \) depends on the kinetic energy of the electron at recollision and the ionisation potential of the atom:

\[ E_\gamma(t_r, t_i) = \frac{[\dot{x}(t_r, t_i)]^2 m_e}{2} + I_p. \quad (2.62) \]

As equation 2.62 contains trigonometric functions, its solutions are periodic. It can be shown that only odd multiples of the fundamental laser frequency \( \omega_0 \) contribute to the harmonic spectrum, i.e. the high harmonic spectrum consists only of odd harmonics.

Inserting equation (2.60) and maximising the energy with respect to \( t_i \) under the assumption that \( x(t_r) = 0 \) leads to the well-known equation for the cut-off energy [61]:

\[ E_{\text{max}} = I_p + 3.17U_p, \quad (2.63) \]
where $U_p$ is the ponderomotive energy - the quiver energy of the free electron in the electric field of the laser, averaged over one cycle, as introduced in equation 2.56. From these equations it can be seen that the maximum photon energy is proportional to the laser intensity $I \propto E_0^2$ and $\lambda_0^2$ (with the fundamental wavelength $\lambda_0 \propto (1/\omega_0)$). Consequently, the high harmonic emission and therefore the resulting attosecond pulses can be controlled by means of the parameters of the generating pulse. Note that extending the cut-off by increasing the intensity is limited by a number of factors. Ultimately, depletion of the target atoms by ionisation imposes a limit on intensity scaling. At very high intensities, the B-field component of the laser field becomes significant (due to higher electron velocities, cf. equ. 2.16) and introduces another dimension to the electron trajectories in the continuum, decreasing the recombination probability.

CEP-stabilised few-cycle laser pulses, where ionisation is concentrated around the highest intensity half-cycle, can be used to generate single attosecond pulses (one per generating pulse) [72]. This technique is called ionisation gating [75]. In general, attosecond pulses are emitted each optical half-cycle (resulting in attosecond pulse trains, or APT).

For any given photon energy below $E_{\text{max}}$, there exist two pairs of solutions of ionisation time and recollision time ($t_i, t_r$) for equation 2.62. The two solutions, differing in the so called excursion time $\tau = t_r - t_i$ of the electron, are called short and long trajectories, respectively.

Figure 2.9 shows the different trajectories for a single laser cycle, where the colour map represents the kinetic energy the electron has accumulated along the given trajectory. This figure is the result of simply solving the classical Newton equation of motion for an electron accelerated in the driving laser field. As one can see, each electron kinetic energy below the cut-off occurs twice. Once for the short trajectory and once for the long trajectory. The short and long trajectory contributions to the same energy differ in their ionisation and recombination times. This is illustrated in figure 2.10. The closer the harmonic energy gets to the cutoff energy, the closer the excursion times of the two trajectories contributing to that harmonic order. We can also see that the excursion times of all short trajectories are shorter than that of the cut-off trajectory, and all long trajectory excursion times are longer. Furthermore, the energy of short and long trajectories increases towards the cut-off trajectory. For the short trajectories that means that the energy increases with increasing excursion time, whilst for the long trajectories the energy increases with decreasing excursion time. This phenomenon is known as the so called attosecond chirp (positive chirp for the short trajectories and negative for the long trajectories). Experimentally this attosecond chirp is very useful, as it provides a
Figure 2.9: Classical calculation of electron trajectories and kinetic energies. Only the trajectories for the first half cycle are shown for clarity. The colour map represents the kinetic energy of the electron along the returning trajectories in units of the ponderomotive energy $U_p$. Some trajectories that do not return to the parent ion are shown in grey. The electric field of the laser is shown by the red dotted line.

Figure 2.10: Classical calculation of electron kinetic energies versus the ionisation and recombination times. The black dots are the kinetic energies upon recollision of electrons ionised at that point in time. The blue dots plot the same kinetic energy data, but against the recombination times of the trajectories. The light grey shading highlights the ionisation and recollision times of the short trajectories. The dark grey shading highlights the long trajectories. The electric field of the laser is shown by the red dotted line.
mapping between time and frequency, which means that cation dynamics (time domain) during the HHG process are encoded in the harmonic spectra (frequency domain). For example, with an 800 nm driving laser field, the short trajectories correspond to dynamics approximately between 200 as and 1.7 fs (the cut-off excursion time) into the optical cycle and the long trajectories correspond to dynamics about 1.7 fs to 2.7 fs into the optical cycle. Therefore, harmonic spectra are a useful observable to probe ultrafast dynamics. This is known as HHG spectroscopy [51, 76]. The interferences between the short and long trajectory contributions to the same harmonic order provide an interesting additional observable. Section 2.5.3 below discusses this in more detail and an experimental scheme exploiting this is introduced in chapter 6.

The semi-classical picture presented above is somewhat limited in the accuracy of the predictions that can be achieved. A commonly used quantum mechanical theory, the Lewenstein model, is based on a strong-field approximation (SFA) and the single active electron approximation (SAE). Generally, the challenge is to find the time-dependent wave function that fully describes the atom. This is extremely difficult and theorists usually describe the atom as an effective potential interacting with only one active electron. The single active electron (SAE) then interacts with the laser field. The SAE approximation is readily applicable to systems where the valence electron is outside a closed shell (e.g. alkali metal atoms and negative ions). For systems where the valence electrons sit inside a filled shell, the SAE approximation is still valid if the energy of the ionising photons is much smaller than the energy needed to remove an electron from the atom, i.e. in the multi-photon ionisation (MPI) regime [77, 78].

A number of assumptions are necessary for the SFA model to be valid [64, 65, 79]. It is assumed that only the ground state (initial state) and the states in the continuum play a significant role and that bound states can be neglected. Further, in the continuum, the effects of the Coulomb potential are assumed to be negligible. The approximate solution of the time-dependent Schrödinger equation (TDSE) obtained in the SFA framework is valid if $\hbar \omega_0 \ll I_p \ll U_p$. Comprehensive derivations of the quantum mechanical description of HHG can be found in [64, 65, 80].

Even though SFA based models underestimate the ionisation rate in the intermediate ionisation regime (where the Keldysh parameter is $\gamma \approx 1$), it is still a useful model to describe HHG as the motion of the free electron in the continuum can easily be included.\footnote{Cf. the study by Larochelle et al. [40] comparing different ionisation rate models to experimental results in rare gases with 800 nm pulses.}

In contrast to the generation of lower-order harmonics in crystals (cf. 2.3.1), HHG is
largely restricted to gases, as it is extremely difficult in solid-state materials. There are no solid-state materials that are transparent over a wide range of frequencies in the XUV region, which makes simple collinear set-ups impossible. However, HHG experiments in solids, plasma plumes, liquids and surfaces are under way in a number of groups [81–84].

2.5.2 High Harmonic Generation in Molecules

So far we have looked at HHG from the point of view of a single atom. There are a number of key differences when generating harmonics in molecules. These differences, and how they can affect experimental results and their interpretation are discussed in this section.

The general sequence of HHG in molecules is the same as in atoms, i.e. ionisation, propagation in the continuum, and recombination. The ionisation and recombination steps are where the molecular orbital structure and the potential of the molecular ion play a significant role.

The harmonic yield is highest when the generating laser field is polarised along the direction of the highest electron density of the highest occupied orbital. If that is the case, the ionisation and recombination probabilities are at their maximum [45]. In molecules, the electron density of the highest occupied molecular orbital (HOMO) depends on the orbital structure and symmetry (cf. figure 2.6 for the orbital structure of CO$_2$). Because the harmonic yield depends on the orientation of the molecule with respect to the laser polarisation, it is possible to retrieve the structure of the HOMO by recording the change in harmonic yield versus a change in alignment of the molecular axis with respect to the polarisation of the laser. This was first achieved in N$_2$ by Itatani et al. [85]. Pavičić et al. [46] measured the angular dependence of ionisation for N$_2$, O$_2$, and most relevant to this thesis, CO$_2$. They found a sharp maximum of ionisation in CO$_2$ at 45°, with very little ionisation at 0° and 90°.

After ionisation, the molecular ion reorganises and the internuclear distance changes. This leads to a decrease in harmonic yield depending on the time scale of the nuclear motion after ionisation. Baker et al. [76] showed that the signal is higher for molecules with slower nuclear motion, because the molecular structure at recombination is closer to that at ionisation. The structural rearrangement effects are encoded in the harmonic spectrum as different harmonic orders are affected differently due to the different excursion times of the contributing trajectories, and hence recombination at different stages in the structural rearrangement.
Structural interferences are another interesting phenomenon of high harmonic generation in molecules. Lein et al. [86] presented a comprehensive theoretical investigation of structural interferences in two-centre molecules. They found that changing the angle between the laser polarisation and the molecular alignment resulted in a minimum in harmonic yield moving through the spectrum. They observed the minimum moving to higher orders with an increasing angle. Interestingly, their calculations place the minima at the same positions in the spectrum irrespective of the intensity or the wavelength of the generating laser field. Investigating a different molecule, the minima are found at different harmonic orders for identical angles. Therefore, the location of the minima is species dependent. Lein et al. further investigated the evolution of the harmonic phase versus the alignment angle and found that it evolves slowly before and after the critical angle where the minimum occurs. At the critical angle, however, there is a sudden phase jump with a value close to $\pi$. This implies that in an ensemble of randomly oriented molecules the contributions from angles below the critical angle interfere destructively with contributions at angles above the critical angle. The harmonic yield can therefore be greatly enhanced by aligning the molecules, as was observed in e.g. [87].

2.5.3 Quantum Path Interference

As discussed in section 2.5, each photon energy in the plateau of the high harmonic spectrum contains contributions from two different trajectories. Since the phase of the emitted photons depends on the excursion time of the electrons in the continuum and the intensity profile they are subjected to, the short and long trajectories accumulate a different phase. Interference between the short and long trajectories leads to a modulation of the amplitude in the harmonic spectrum. The phenomenon is known as quantum path interference (QPI).

This was first observed in an experiment in 2008 at ETH Zurich [6]. QPI is hard to observe in experiments due to the strong intensity dependence of the relative phase of the two trajectories and the intensity instabilities of most laser sources. The intensity fluctuations cause the fringes to average out. Zaïr et al. avoided temporal and spatial averaging by means of sophisticated filtering and detection techniques [6].

The signature of QPI is usually detected by recording the harmonic yield whilst scanning the intensity of the driving laser field. The changing intensity causes the relative phase between the contributions from the different trajectories to change. As a result, the interference between the two contributions leads to a change in the harmonic yield. The recorded signal versus intensity then shows modulations. QPI can also be observed in a wavelength scan [88], although this is experimentally more difficult (and has not been
Each trajectory represents a specific ionisation and excursion time. Any changes of the state of the system on timescales on the order of the excursion times of the short and long trajectories, e.g. by means of a perturbative or coupling laser field, will be encoded in the QPI. Hence, QPI can be used as an observable to probe femtosecond and attosecond dynamics.

In [89], Zaïr et al. investigate how the interferences between the short and long trajectory contributions to the overall harmonic yield provide access to information on intramolecular dynamics. They show for the first time experimentally that QPI in molecules is capable of resolving ultrafast nuclear motion after ionisation. In their study, they find that in the case of unaligned molecules, the long trajectories show a stronger dependence on the molecular species than the short trajectory contributions to the overall yield. Based on theoretical studies similar to those presented in section 6.1, they further investigate how electronic motion is encoded in the characteristic quantum path interferences in aligned molecules.

Note that the phase-matching conditions (cf. section 2.5.4) have to be chosen in such a way that both the short and long trajectories contribute sufficiently to the overall signal for the QPI signature to be detectable. A more comprehensive and quantitative description of QPI can be found in [6,90].

Figure 2.11: Time-frequency mapping for a range of intensities of the driving laser field at 800 nm. Figure from [89].
2.5.4 Macroscopic Effects

So far we have looked at HHG from a microscopic point of view, i.e. a single atom or molecule interacting with a laser field. In order to make use of HHG in experiments, macroscopic effects have to be considered. In practice, the laser field interacts with multiple atoms and under certain conditions the individual atoms all contribute to the macroscopic harmonic emission spectrum shown in figure 2.8. Since HHG is a coherent process, the generating laser field determines the phase of the photons emitted at recollision [80]. Phase-matching, i.e. ensuring equal phase velocity of the generating field and the high harmonic radiation, is required for an efficient build-up of macroscopic high harmonic emission.\(^{27}\) The laser intensity, the focussing geometry and the target density and ionisation rate are among the factors influencing phase-matching [80, 91]. Balancing the contributions to the overall phase mismatch by varying the experimentally accessible parameters is important to achieve sufficient harmonic yield.

As before with lower order harmonic generation (cf. section 2.3.2), efficient energy transfer from the fundamental laser field to the generated harmonic fields requires these fields to propagate with the same phase velocity. Otherwise, destructive interferences between waves emitted at different positions within the interaction volume inhibit the overall growth of the harmonic fields.

The phase mismatch (or wave vector mismatch) for the case of high harmonic generation can be written as:

\[
\Delta k = q k_0 - k_q + \Delta k_{\text{correction}},
\]

where \(k_0\) is the wave vector of the fundamental field and \(k_q\) is the wave vector of the \(q\)-th harmonic and \(\Delta k_{\text{correction}}\) is a correction term arising from different material and geometric properties discussed in more detail below. Perfect phase-matching requires \(\Delta k = 0\). In that case, the harmonic signal adds up coherently until the fundamental beam is depleted (or until the phase-matching changes due to changing parameters along the propagation axis). For \(\Delta k \neq 0\) the harmonics are travelling at different phase velocities to the fundamental beam and the harmonic fields interfere constructively and destructively as the fields propagate through the medium. In the case of a non-zero wave vector mismatch, the harmonic field grows only over a limited interaction length known as the coherence length:

\[
L_{\text{coh}} = \frac{\pi}{\Delta k},
\]

\(^{27}\)Due to the fact that dispersion in gases is isotropic, phase-matching schemes for HHG differ from those for lower order harmonic generation, cf. section 2.3.2.
The phase-mismatch correction term $\Delta k_{\text{correction}}$ has three main contributions, namely material dispersion, geometric phase and the dipole phase of the target, that are discussed in the following.

**Material dispersion:**
The interaction of the strong laser field with the target medium influences the dispersion properties of the medium. Ionisation of the medium leads to free electrons and ions in addition to the neutral atoms or molecules. The dispersion caused by the ions is usually neglected due to their reduced polarisability. The dispersion due to free electrons, however, is important as soon as there is a significant amount of ionisation.

The two remaining contributions to the material dispersion are then the atomic dispersion and the electronic dispersion. The atomic dispersion contribution is usually small (unless the target density is very high). The mismatch due to atomic dispersion can be approximated to [80]:

$$\Delta k_{\text{atomic}} \approx n_a \left( \pi \alpha_1 \frac{q}{\lambda_0} + r_e f_r \frac{\lambda_0}{q} \right) \hat{z},$$  \hspace{1cm} (2.66)

where $n_a$ is the atomic density, $\alpha_1$ is the static polarisability, $q$ is the harmonic order, $\lambda_0$ the wavelength of the fundamental, $r_e$ is the electron radius, $f_r$ is the real part of the atomic scattering factor and $\hat{z}$ is a unit vector in the $z$-direction.

The electronic dispersion, due to the free electrons in the continuum, is given by [80]:

$$\Delta k_e = r_e \lambda_0 n_e \left(-q + \frac{1}{q}\right) \hat{z},$$  \hspace{1cm} (2.67)

where $n_e$ is the density of free electrons.

It is easy to see that since the material dispersion depends on the density of the target, its contribution to the overall phase mismatch can be controlled by changing the target geometry and the applied backing pressure (cf. section 3.3).

**Geometric phase:**
The focussing of a Gaussian beam leads to a geometric phase shift as the beam passes through the focus. This is due to the change in wavefront curvature. This phase is known as the Gouy phase and along the propagation axis it can be expressed as [92]:

$$\phi_{\text{Gouy}}(z) = -\arctan \left( \frac{z}{z_R} \right),$$  \hspace{1cm} (2.68)
where $z_R$ is the Rayleigh length, the distance from the focus where the cross-sectional area of the beam doubles, and $z$ is the distance along the $z$-axis from the focus.

In general terms (not confined to points along the propagation axis), the Gouy phase can be written in cylindrical coordinates as [91]:

$$
\phi_{\text{Gouy}}(r, z) = \text{arg} \left( \frac{1}{2z_R + 2iz} \exp \left( -\frac{k_0r^2}{2z_R + 2iz} \right) \right),
$$

where $r$ is the distance from the propagation axis and $k_0$ is the fundamental wave vector.

The phase-mismatch due to the Gouy phase can be expressed as [80, 91]:

$$
\Delta k_{\text{geometric}} \approx q \nabla \phi_{\text{Gouy}},
$$

where $\nabla$ is the Nabla operator.

For $r = 0$, so points along the propagation axis, the Gouy phase undergoes a phase flip of $\pi$ as the beam passes through the focus. From equation (2.68) it is obvious that tight focussing setups with a small Rayleigh length result in a steeper phase gradient around the focal spot, resulting in a larger phase-mismatch.

**Dipole phase:**

The dipole phase for each trajectory is a combination of the phase due to the time delay between the recombination time $t_r$ of that trajectory and the reference point of the optical cycle of the fundamental and the phase acquired by the electron in the continuum. The dipole phase is given by [91]:

$$
\phi_{\text{dipole}} = q\omega_0 t_r - \frac{1}{\hbar} S(p_{\text{stat}}, t_i, t_r),
$$

where $\omega_0$ is the angular frequency of the fundamental, $t_i$ is the ionisation time and $S(p_{\text{stat}}, t_i, t_r)$ is the semiclassical action along the stationary point with canonical momentum $p_{\text{st}}$.

The dipole phase can be approximated to $\phi_{\text{dipole}} \approx -U_p \tau \approx \theta I_0$, where $U_p$ is the ponderomotive energy, $\tau$ is the excursion time of the trajectory and $I_0$ is the laser intensity. The factor $\theta$ is a function of the recombination time and is weakly dependent on the intensity and the harmonic order. At the cut-off, there is only one trajectory contributing to the harmonic yield. For the plateau harmonics, the values of $\theta$ and therefore the dipole phase are different for the short and long trajectories. As a result, efficient phase-matching for
the short and long trajectories requires different conditions. In fact, the long trajectories are usually more efficiently phase-matched off-axis, which results in the typical rings of the long trajectory contributions around the short trajectory contributions on-axis [80].

The phase-mismatch due to the dipole phase can therefore be written as:

\[ \Delta k_{dipole} = \nabla \phi_{dipole}. \] (2.72)

In order to achieve efficient build-up of harmonic radiation, the right balance of all these contributions to the overall phase-mismatch has to be found by changing the relevant laser parameters and the target geometry. The geometric and electronic contributions have an opposite sign to the atomic contribution. The sign of the dipole phase is determined by the location in the interaction volume. Finding the right phase-matching conditions can be an art in itself, as the interplay between different parameters and the different contributions to the overall phase-mismatch is complex. A change in gas density, either by changing the backing pressure or the gas jet or the relative position of gas jet and focus, changes the atomic and electronic contributions. A change in the laser intensity changes the ionisation rate and therefore the electronic contribution, as well as the dipole phase factor. Changes in the focussing setup change the geometric contribution, and changing the position of the gas jet with respect to the focus also changes the gradient of the dipole phase.
2.6 Rabi Oscillations

For the experiment described in chapter 6 we need a population transfer between different orbitals in CO$_2$ that is fast enough to affect the trajectories in HHG. This can be achieved with a resonant transition known as Rabi oscillations. These transitions can be driven by a (near-) resonant laser field (e.g. in CO$_2$ by the third harmonic of a Ti:Sa, cf. chapter 6). The Rabi frequency is the frequency at which the population oscillates between the two energy levels involved in the transition when subject to the laser field. It is therefore a measure for the coupling strength between the atomic transition and the incident laser field. The following section will give a brief introduction to the key aspects of the Rabi frequency. More comprehensive derivations can be found in [93–95].

If we consider a two-level system with the two states $|\psi_a\rangle$ and $|\psi_b\rangle$ as the ground and excited states, respectively, we can define the transition frequency $\omega_t$ as:

$$\omega_t = \frac{|E_b - E_a|}{\hbar} = \omega_b - \omega_a,$$

(2.73)

where $E_a$ and $E_b$ are the energies of the two states and $\omega_a$ and $\omega_b$ are the corresponding frequencies given by $E_i = \hbar \omega_i$. This system and its evolution can be described by the following expansion:

$$|\psi(t)\rangle = a(t) |\psi_a\rangle + b(t)e^{-i\omega t} |\psi_b\rangle,$$

(2.74)

where the amplitude coefficients $a(t)$ and $b(t)$ are related to the population of the respective states and in a closed two-level system constrained to:

$$|a(t)|^2 + |b(t)|^2 = 1.$$  

(2.75)

The interaction between the two-level system and an incident laser field, the light-matter interaction, is described by the interaction Hamiltonian:

$$\hat{H}_I = -\hat{D}\mathcal{E},$$

(2.76)

where the electric dipole operator $\hat{D}$ is:

$$\hat{D} = q\hat{r},$$

(2.77)

where $q$ is the charge and $\hat{r}$ is the operator describing the separation between the atomic nucleus and the valence electrons. If we assume a linearly polarised electric field with an amplitude $\mathcal{E}_0$, the component of $\hat{D}$ in the direction of the electric field is denoted as $d$. The light-matter interaction between the two states can then be written as:

$$\hbar\Omega = -d\mathcal{E}_0,$$

(2.78)
where we have defined the frequency \( \Omega \). With an electric field \( \mathcal{E} = \mathcal{E}_0 \cos(\omega_0 t + \phi) \), the Hamilton operator of this system is:

\[
\hat{H} = \hat{H}_0 + \hat{H}_I = \hbar \begin{pmatrix} 0 & \Omega \cos(\omega_0 t + \phi) \\ \Omega \cos(\omega_0 t + \phi) & \omega_t \end{pmatrix},
\]

(2.79)

where \( \omega_0 \) is the frequency of the incident laser field, \( \hat{H}_0 \) is the atomic Hamiltonian and \( \hat{H}_I \) is the electric dipole (or coupling) interaction Hamiltonian.

Using the Hamiltonian \( \hat{H} \) in the time-dependent Schrödinger equation:

\[
i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H} |\psi(t)\rangle
\]

(2.80)

we obtain the following equations for the evolution of the amplitude coefficients \( a(t) \) and \( b(t) \):\(^{28}\)

\[
i \dot{a}(t) = \frac{\Omega e^{i\phi}}{2} e^{i(\omega_0 - \omega_t)t} b(t) + \frac{\Omega e^{-i\phi}}{2} e^{-i(\omega_0 + \omega_t)t} b(t),
\]

(2.81)

\[
i \dot{b}(t) = \frac{\Omega e^{i\phi}}{2} e^{i(\omega_0 + \omega_t)t} a(t) + \frac{\Omega e^{-i\phi}}{2} e^{-i(\omega_0 - \omega_t)t} a(t),
\]

(2.82)

where \( \dot{a}(t) = \frac{\partial a(t)}{\partial t} \).

If we only consider the interaction with laser fields close to resonance, we can neglect the terms oscillating at \( |\omega_0 + \omega_t| \) as they oscillate very rapidly compared to the terms at \( |\omega_0 - \omega_t| \). Hence, their average contribution (when integrating) will be very small in comparison. The simplified equations become:

\[
i \dot{a}(t) = \frac{\Omega e^{i\phi}}{2} e^{i(\omega_0 - \omega_t)t} b(t) = \frac{\Omega e^{i\phi}}{2} e^{i\delta t} b(t),
\]

(2.83)

\[
i \dot{b}(t) = \frac{\Omega e^{-i\phi}}{2} e^{-i(\omega_0 + \omega_t)t} a(t) = \frac{\Omega e^{-i\phi}}{2} e^{-i\delta t} a(t),
\]

(2.84)

where we have introduced the detuning \( \delta \). In order to solve these coupled equations we now make a change of variables:

\[
a(t) \equiv \alpha e^{i\frac{\delta t}{2}} e^{-i\frac{\omega_0 t}{2}},
\]

(2.85)

\[
b(t) \equiv \beta e^{-i\frac{\delta t}{2}} e^{i\frac{\omega_0 t}{2}},
\]

(2.86)

where \( \alpha \) and \( \beta \) are constants. Solving equations (2.83) and (2.84) for \( \lambda \) we obtain:

\[
\lambda^2 = \Omega_R^2 = \Omega^2 + \delta^2.
\]

(2.87)

\(^{28}\)Using the identity \( \cos(x) = \frac{e^{ix} + e^{-ix}}{2} \).
Figure 2.12: Red solid line: Rabi oscillations at resonance ($\delta = 0$). Green dashed line: $\delta = \Omega$. Blue dotted line: $\delta = 2\Omega$.

$\Omega_R$ is the Rabi frequency. Note that at resonance ($\delta = 0$) the Rabi frequency $\Omega_R$ is equal to the reduced Rabi frequency $\Omega$.

Solving for $b(t)$ (derivation in [93]), we can obtain an expression for the probability that the system has evolved from state $|\psi_a\rangle$ to state $|\psi_b\rangle$ in the time $t$:

$$P_{ab}(t) = |b(t)|^2 = \frac{\Omega^2}{\Omega^2 + \delta^2} \sin^2 \left( \frac{\Omega_R t}{2} \right).$$  \hfill (2.88)

This probability is illustrated in figure 2.12. At time $t = 0$ all population is in state $|\psi_a\rangle$ and hence the probability for it to be in state $|\psi_b\rangle$ is zero. For the resonant case (red solid line), the maximum probability is equal to one and a complete transfer of the population to state $|\psi_b\rangle$ is possible. Increasing the detuning from resonance, we observe an increasing Rabi frequency and a decreasing maximum probability for the population transfer.
Chapter 3

Experimental Methods, Techniques and Apparatuses

This chapter is meant to give a brief general overview of experimental methods, techniques and setups that were used in a number of the experiments presented in this thesis. Modifications or differing implementations are detailed in the setup sections of the individual experimental chapter.
3.1 Lasers for Strong Field Physics

This section first discusses general laser requirements for high harmonic generation and then briefly introduces the KMLabs Red Dragon laser system used in the laboratory at Imperial College London where the experiments discussed in chapters 5 and 6 were conducted.

3.1.1 Laser Requirements

There are a number of laser parameters that influence the high harmonic generation process. As discussed in section 2.5.1, the cut-off harmonic energy (the highest photon energy produced) is given by \( E_{\text{max}} = I_p + 3.17U_p \), where the ponderomotive energy \( U_p \) scales with \( I\lambda_0^2 \). Here \( I \) is the peak intensity of the laser and \( \lambda_0 \) is the central wavelength.

This immediately suggests two different options to extend the cut-off to higher harmonic energies. One can either increase the intensity or increase the wavelength of the driving laser field to increase the cut-off energy. However, both methods come with practical limitations.

High harmonic generation is a strong field ionisation effect and relies on a field whose influence on the target is strong in comparison with that of the ionisation potential \( I_p \) of the target itself. For ionisation processes, the field is considered to be strong when the potential due to the laser field becomes comparable to the ionisation potential \( I_p \) of the target. This constitutes the lower limit of the intensity for HHG. The upper limit is determined by the ionisation saturation of the target. The saturation intensity is the intensity at which the sample of atoms or molecules in the interaction area is mostly ionised. This is not a precise definition and in fact a number of different definitions are used in the literature. Calculating the saturation intensity is considerably more difficult in molecules for a number of reasons. For example, ionisation can be very sensitive to the alignment of the molecule relative to the polarisation of the ionising laser field. Hankin et al. present a simple way to experimentally determine the saturation intensity in [96]. The saturation intensity of CO\(_2\) is reported to be around \( 2.4 \times 10^{14} \) W/cm\(^2\) [97,98].

The second approach for extending the cut-off is to increase the wavelength. Unfortunately the \( \lambda_0^2 \) scaling of the cut-off energy comes with a very unfavourable scaling of conversion efficiency from the generating field to harmonic yield. Shiner at al. and Frolov et al. reported conversion efficiencies of \( \eta(\lambda) \propto \lambda^{-x} \) where \( x \) is in the range of 5 to 6 [99,100].

Another important factor is that of pulse duration. Shorter XUV pulses improve the
achievable time resolution, which is especially important for experiments aiming to re-
solve nuclear dynamics [101]. Further, shorter drive pulses that approach the single cycle
limit avoid early depletion of the ground state and can therefore extend the cut-off further
than longer pulses. Brabec and Krausz compare harmonic spectra recorded with 800 nm
pulses with a pulse duration of 30 fs and 7 fs in [66]. The harmonic spectrum produced
with the 30 fs pulse shows clear discrete harmonics, characteristic of HHG. The spectrum
produced with the 7 fs pulse however merges into a continuum towards the cut-off, be-
because the highest order harmonics near the cut-off are produced from a single electron
trajectory originating from the only cycle near the peak intensity of the pulse. The reason
why few-cycle pulses allow for an extension of the cut-off is that in the intensity regime
where the ground state is already depleted by the rising edge of the pulse, no electrons are
ionised near the peak intensity of the pulse. Few-cycle pulses, in contrast, do not deplete
the target before the peak of the pulse reaches the interaction volume. The electrons
ionised near the peak of the few-cycle pulse therefore experience a stronger field than the
ones ionised earlier on in a longer pulse with the same peak intensity.

The repetition rate of the laser has an impact on the amount of data that can be collected
in a reasonable amount of time, and therefore ultimately on the data statistics. There
is considerable ongoing effort in developing laser systems at higher repetition rates with
sufficient average power such that the pulse energy is sufficient for HHG.

3.1.2 KMLabs Red Dragon Laser System

The Red Dragon by KMLabs is a commercially available laser system that consists of an
oscillator (called Griffin) and a chirped pulse amplification (CPA) system. The original
design of the laser has been heavily modified in our lab to improve the reliability and
performance of the laser system. For example, a host of beam and pointing monitoring
with active stabilisation has been added.

Griffin oscillator
The Griffin oscillator is a laser based on a titanium doped sapphire crystal (Ti:Sapphire)
as the gain medium. The crystal is optically pumped by a commercial diode-pumped
frequency-doubled continuous wave Nd:YAG laser (Verdi V6, Coherent) at 532 nm with
an output power of 5.2 W. Ti:Sapphire is a very popular gain medium for short pulse,
high peak power laser systems due to its large gain bandwidth and the readily available
optical pump lasers. See [102] for a detailed discussion of Ti:Sapphire as a gain medium.

The Griffin oscillator is passively mode-locked by exploiting the optical Kerr effect. The
overlap of the pump with the cavity modes is optimised for pulses undergoing Kerr-
Figure 3.1: Schematic of chirped pulse amplification. The short but weak pulse out of the oscillator is stretched and then amplified before the amplified but stretched pulse is re-compressed.

Chirped Pulse Amplification

Figure 3.1 shows a schematic of the chirped pulse amplification (CPA) technique. The short but weak pulse from the oscillator is stretched in a stretcher (see figure 3.2) by adding large amounts of GDD. The stretched pulse is then amplified in the amplification stages of the Red Dragon and the amplified but stretched pulse is then compressed in the compressor by adding the opposite sign of GDD. CPA is a powerful technique that allows for the amplification of laser pulses well past the damage threshold intensity of transmissive optical elements such as the gain medium itself.

Stretcher

A schematic of the Red Dragon stretcher is shown in figure 3.2. The input pulse (dark red) enters the stretcher setup from the bottom left. The input beam is then dispersed by the grating. For clarity purposes only the reddest and the bluest rays are shown. The dispersed beam then travels to the curved mirror, a flat mirror and back to the curved mirror. From there it is reflected off the grating for a second time before the retro-reflector sends the beam back through the same path. The beam is aligned such that the output beam travels in a slight downward direction compared to the input beam. The output
beam is then picked off by a pick-off mirror underneath the input beam. The stretched pulse typically has a duration of 150–200 ps. Because the retro-reflector sends the beam back via the same path, each optic is used four times. This makes this single grating stretcher equivalent to a regular stretcher with two gratings, but at significantly reduced cost and allowing for a more compact setup.

**Amplification stages**
After the stretcher, the repetition rate of the pulse train is reduced down to 1 kHz by a Pockels cell and polariser assembly. After the Pockels cell, the pulses are first amplified in a twelve-pass amplifier that increases the pulse energy to around 3 mJ. The gain medium is another Ti:Sapphire crystal, cryogenically cooled to around 40 K to avoid issues of thermal lensing. The crystal is kept under vacuum to avoid condensation and freezing on the crystal. This first stage of the amplifier is pumped by a pulsed nanosecond frequency-doubled Nd:YAG laser (Photonic Industries) operating at 40 W.

After the first amplification stage, a second Pockels cell and polariser assembly selects only the amplified main pulses to be passed on to the second amplification stage and rejects any pre- or post-pulses and peaks originating from amplified spontaneous emission (ASE).

The second amplification stage is a two-pass bow-tie amplifier pumped by two counter-propagating pumps operating at up to 40 W each. The second amplification stage usually brings the pulses up to 11 mJ pulse energy, which corresponds to 8 mJ after the compressor.
Figure 3.3: Schematic of the Red Dragon compressor. The input beam enters the setup from the left. It is then dispersed by the first grating (only reddest and bluest rays shown for clarity). After the second grating the beam is sent back through the assembly by a retro-reflector that returns the beam at a slightly lower height, but parallel to the input beam. The output beam is then picked off underneath the input beam.

**Compressor**

After the second and final amplification stage, the pulses are compressed back down. This is the last step in the CPA system. The compressor setup is shown in figure 3.3. The stretched but amplified input beam enters the setup from the left. The beam is then dispersed by the first grating (only reddest and bluest rays shown for clarity). After the second grating the beam is returned by the retro-reflector at a slightly lower height to the input beam, but otherwise perfectly parallel to the input beam. The compressed output is then picked off underneath the input beam. From there, the beam is sent to the experiment.
3.2 Prism Compressors

As mentioned in section 2.1, most materials are positively dispersive in the visible and near-infrared region of the electromagnetic spectrum. In order to compress pulses back down towards their transform limit after propagation through dispersive optical elements, some way of introducing negative dispersion has to be found. There are a number of ways to achieve this.

So-called chirped mirrors are multi-layered dielectric mirrors that introduce negative dispersion upon reflection (they can also be designed for positive dispersion). Different frequency components of the incident laser pulses are reflected by different layers, and therefore from different depths inside the multi-layer coating, which leads to a delay between the different frequencies. Chirped mirrors can be designed to meet specific requirements, although this can get expensive, especially when looking to compensate GDD over broad bandwidths [103].

Another way to achieve negative dispersion is geometrical dispersion. This is usually done using angularly dispersive optical elements such as prisms [104] and gratings [105]. Gratings have bigger angular dispersion and can therefore compensate larger amounts of GDD, at the cost of significant losses. Since a prism compressor was used for the experiments in this thesis, the focus of this section is on prism compressors. The principles are transferable to grating compressors.

Prism compressors take advantage of the fact that different frequency components of incident pulses are refracted at different angles. This leads to a frequency-dependent time delay when propagating the beam after passing through a prism. This is illustrated in figure 3.4. The beam enters from the left and is refracted by the first prism. The shorter wavelength components are refracted more than the longer wavelength components. The angle $\beta(\lambda)$ denotes the angle between a given wavelength and the line between the apices of the prisms. After the second prism all wavelength components are propagating in parallel but spread out in space (i.e. the beam is spatially chirped) and the different wavelength components are delayed with respect to each other (leading to wavefront tilt). Prisms two and three recombine all wavelength components to be collinear again. Note that alignment of this setup is critical to ensure the recombined beam is not spatially chirped, i.e. that the spectrum does not change across the lateral beam profile. The apex separation is usually used for coarse GDD tuning (larger apex separation leads to more negative chirp) and the prism insertion is used to fine tune the GDD (more prism insertion leads to more positive chirp).¹ Often a prism compressor is built with only two

¹Note that prism insertion and apex separation have different third- and higher-order dispersion effects.
Figure 3.4: The beam enters from the left and is refracted by the first prism. Shorter wavelength components of the incident beam are refracted at a steeper angle than the longer wavelength components. All parts of the beam travel in parallel between the second and the third prism. The third and fourth prisms recombine all wavelength components again to propagate collinearly. The different wavelength components travel different distances in air and in prisms two and three. By adjusting the insertion of prisms two and three and by changing the apex separation $L$ (also that between prisms two and three) the overall dispersion of the setup can be adjusted. The angle $\beta$ is the angle between a given wavelength component and the line that connects the apices of the prisms.

In that case a mirror between prism two and three reflects the beam back (either at a small angle or through a retro-reflection). The beam then passes back through the first two prisms and is picked off after recombination. The return journey doubles the relative delay between the wavelength components and removes the spatial chirp (exactly like prism three and four in the four prism setup). Trebino et al. also introduced a setup using only one prism in combination with two retro-reflectors [106].

It is easy to see that the relative delay between different wavelength components depends on the apex separation $L$ and the insertion of the prisms. The geometric dispersion affected by the apex separation is usually much larger than the group delay dispersion (cf. section 2.1) due to propagation through the prism material. The accumulated spectral phase after the prism compressor due to geometrical dispersion is:

$$\tilde{\phi}_{geo}(z, \omega) = kd(\omega) = \frac{2\omega L}{c} \cos(\beta)$$

(3.1)

for a given frequency component $\omega$, where $d(\omega) = 2L \cos(\beta)$ is the path length of that frequency component. Note that depending on the exact design, prism insertion and apex separation, these prism setups can act as stretchers too.
3.3 Gas Jets for High Harmonic Generation

All experiments presented in this thesis generate high harmonics in gas targets. Gas jets are used to deliver the target gas to the interaction region for high harmonic generation. The geometry, backing pressure and type of gas jet determine the target density and density profile. All gas jet geometries have in common that the target gas enters the vacuum chamber through a small aperture. This results in rapid expansion into the vacuum [107].

All gas jets used in the experiments presented in this thesis used round nozzles, resulting in gas jets that are symmetrical around the axis of the gas jet. Upon exiting the nozzle, the gas abruptly expands, which leads to a rapid drop in density and temperature with distance from the nozzle and the axis of the gas jet [107]. This rapid expansion also results in a gas target with very low internal energies (i.e. low excitation of rotational and vibrational states in molecules) [107, 108]. The flow regime of the gas exiting the nozzle and expanding into the vacuum is determined by the relationship between the nozzle diameter $d_n$ and the mean free path $\lambda_m$, where:

$$\lambda_m = \frac{1}{\sqrt{2\pi d_t^2 N}}, \quad (3.2)$$

with the target atomic or molecular diameter $d_t$ and the number density $N$.

If $\lambda_m > d_n$, the flow regime is that of effusive expansion. In this flow regime, the number of collisions a target atom or molecule experiences is very small, and approaches zero for $\lambda_m$ that are very large compared to the nozzle diameter. An effusive beam is exhibits a velocity distribution of [109]:

$$P(v)dv = \frac{m^2}{2(RT_0)^2} v^3 \exp \left[ -\frac{mv^2}{2RT_0} \right] dv, \quad (3.3)$$

where $m$ is the molar mass of the atom or molecule, $R$ is the gas constant, and $T_0$ is the temperature of the gas in the reservoir. Interestingly, this velocity distribution is independent of the pressure inside the reservoir, often referred to as the backing pressure.

If $\lambda_m < d_n$, the expansion is supersonic and the target atoms or molecules experience many collisions in the gas jet. Therefore, close to the nozzle, the atoms or molecules exhibit a narrow velocity distribution [108, 109]. At high backing pressures, the impact of the gas viscosity and heat transfer on the flow can be neglected [109]. This adiabatic assumption allows us to express the maximum flow velocity as [109]:

$$v_{\text{max}} = \sqrt{\frac{2H(T_0)}{m}} = \sqrt{\frac{2C_p T_0}{m}}, \quad (3.4)$$
where $H(T_0)$ is the molar enthalpy of the gas at the reservoir temperature $T_0$, which equals $C_p T_0$ for gases with a constant-pressure molar heat capacity $C_p$ that is independent of temperature. For an ideal atomic gas, $C_p = \frac{5}{2} R$, so for a reservoir temperature of 300 K, the maximum velocity for krypton is 386 m/s. The velocities predicted with the adiabatic assumption are readily achieved in experiments and the assumption was justified by measurements of local temperatures in an expanding gas jet at various distances from the nozzle [110].

The density distribution throughout the gas jet can be derived to be (see [109] for details):

$$\frac{\rho(x)}{\rho_0} = c_1 \left( \frac{x - c_2}{d_n} \right)^2,$$

(3.5)

where $\rho_0$ is the reservoir density, $\rho(x)$ is the density at distance $x$ from the nozzle and $c_1$ and $c_2$ are constants depending on the atomic or molecular species. The ratio of densities $\frac{\rho(x)}{\rho_0}$ displays an inverse-square law decrease where the atoms or molecules expand along straight but diverging lines [109].

For more details on the different flow regimes, and for a discussion of more realistic models (departures from the idealised model presented here), see for example the comprehensive discussions in [107,109].

The backing pressure that can be used with a given gas jet is ultimately limited by the ambient pressure the vacuum pumps and the detection system in the target chamber can tolerate. Therefore, in applications where higher backing pressures (i.e. high target densities) are required, pulsed gas jets are often used. These can be operated by a solenoid valve (electromechanically operated valve, limited in achievable operating frequency) or a piezo controlled valve (faster operating frequency). Note that piezo controlled valves are limited in the maximum pressure they can handle. However, pulsed targets have to be synchronised with the incident laser pulses and continuous gas jets are therefore used whenever possible. Backing pressures can be somewhat increased with continuous jets if a differential pumping jacket is fitted around the gas jet (cf. section 6.2 and figure 6.10).

For continuous gas jets, hypodermic needles with very small diameters or custom made nozzles are often used. In the experiments described in chapters 5 and 6 a custom continuous flow jet was used. The design of this jet is shown in figure 3.5. The left of the figure shows photographs of the modified Swagelok end plug. The right side of the figure shows a schematic with dimensions of the customised end plug. The final exit hole has a diameter of 200 µm.
Figure 3.5: Left: photos of the Swagelok end plug customised to become a gas jet. Right: schematic with dimensions of the customised end plug.
3.4 Microchannel Plate Detectors

Microchannel plate detectors are the most commonly used type of detector in high harmonic generation experiments. These detectors usually consist of two microchannel plates (MCP) and a phosphor screen. An MCP is typically a piece of lead glass with an array of miniature electron multipliers [111]. Other options include aluminium oxide membranes with Al coated nanopores [112]. These electron multipliers are small channels (usually 10–100 µm in diameter) through the lead glass plate. These plates usually have a channel density of up to 10,000 channels/mm². The channels are either perpendicular to the plate’s surface or at a slight bias angle. The purpose of this small angle is to avoid incident photons (or electrons) from passing through the channels without colliding with the channel walls. Also considering spatial resolution and detection efficiency, the bias angle is usually between 5° and 15° [113]. Typical ratios of channel length to channel diameter are in the range of 40–100 [111,113].

An x-ray photon incident on the MCP frees an electron from the channel wall via photoelectric emission. A potential voltage difference applied across the MCP (usually on the order of 1500 V) accelerates the freed electron, which then triggers an electron avalanche when it collides with the channel walls. This leads to an amplification of up to $10^8$ electrons/photon. The lead glass plate material allows for charge replenishment from the connected voltage supply, so this amplification process can keep happening with very small recharge times. The second adjacent plate serves the purpose of further amplification. The electron avalanche is then incident on a phosphor screen, which fluoresces. Two stage MCP detectors can achieve a resolution of around 80–100 µm [113]. A camera and objective is then used to image the phosphor screen.

Over the years, many different improvements of MCP detectors have emerged. For example, funnel shaped channel entrances can significantly increase the open area ratio (ratio of surface area of MCP to area of all channels put together) to increase detection efficiency [113].

Note that different readout options are available, some of which allow the position of the incident particle to be measured precisely, others are specialised in double-incidence detection and provide very high time resolution. Highly specialised (and very expensive) x-ray CCD cameras also exist (e.g. the Andor camera) as an alternative to MCP detectors. However, none of these options or alternatives have been used for any of the experiments described in this thesis.
Figure 3.6: Schematic of a microchannel plate (MCP). The left shows a cut-out of an MCP, a lead glass plate with microchannels. The right shows an expanded view of an individual channel. An incident x-ray photon (or electron) frees an electron when it hits the wall of a channel (via photoelectric emission). This electron then triggers an avalanche of electrons as it is accelerated through the channel by an applied voltage across the MCP plate. Figure adapted from [113].
Chapter 4

Frequency Tunable High-Order Harmonics
4.1 Background

Wavelength-tunable laser sources are of great importance for many spectroscopy measurements. One such measurement is that of photo-ionisation time delays. Photo-ionisation can occur if the energy $E_\gamma$ of a photon interacting with an atom or molecule exceeds the ionisation potential $I_p$ of that species. The resulting photo-electron has a kinetic energy of $E_{\text{kin}} = E_\gamma - I_p$. Whilst the phenomenon of the production of the photo-electron and the remaining ion is well known, it is not yet well understood. A whole range of fundamental questions remains unanswered. For example, little is known about the mechanism and time scale of reorganisation of the remaining electrons after ionisation. Interesting questions arise when considering a second photon interacting with the same atom or molecule before the reorganisation is complete. One of the experiments trying to answer these questions was performed by M. Kotur et al. and the results are published in [114,115]. In order to retrieve the full temporal dynamics, they use frequency-tunable attosecond pulses in order to be able to measure the phase as well as the photo-ionisation amplitude as a function of the photon energy. To achieve the tunable attosecond pulses, they used a sophisticated laser system with two acousto-optical dispersive elements (dazzler by Fastlite) to tune the frequency of the fundamental laser used to generate the attosecond pulses through high harmonic generation.

Angle-resolved photoemission spectroscopy (ARPES) is another experimental technique that relies heavily on tunable XUV sources. For example, Dakovski et al. [116] used visible probe and XUV pump pulses to study ultrafast electron dynamics in semiconductors. They argue that the use of HHG as a light source for time-resolved studies has a number of advantages over more traditional UV light sources. For one, the higher photon energies allow access to deeper levels, sometimes even core-electron levels. Further, HHG typically covers a very broad range of photon energies. Selecting suitable harmonics from the harmonic spectrum enables access to information on specific orbitals. In order to use HHG as a source for such spectroscopy experiments, individual harmonic orders have to be selected from the harmonic spectrum. In order to maintain the time resolution capabilities, this selection should ideally preserve the pulse duration whilst also providing a high throughput efficiency. A design for a time-delay compensated monochromator (TDCM) has been developed and tested by Poletto et al. in [117,118].

In this chapter we demonstrate an alternative, simple and cost-effective way of achieving tunable high harmonic frequencies. In principle the method presented below is transferable to the generation of single attosecond pulses, although this is not implemented here. The major advantage, however, of our approach is its compatibility with very high energy laser systems as the setup can be placed before the compressor but after the amplification.
stage.
Our approach is based on the fundamental connection between the spectrum and the
time-dependent electric field of a laser pulse. This connection is mathematically ex-
pressed through Fourier transformation (cf. section 2.1). As a result, any changes in the
structure of the electric field manifest themselves in the spectrum (and vice versa).

Therefore, in order to achieve changes in the spectrum, we alter the temporal struc-
ture of the electric field of the laser pulses. This can be achieved in many different ways.
One way is to create two copies of the laser pulse (e.g. by means of a beam splitter) and
then interfere the two copies with each other after applying a time delay between the two
copies.
Some elaborate schemes have been conceived to achieve this, e.g. [119], although so far in
the literature the main aim was that of temporal pulse shaping and the generation of pulse
trains from a single pulse. Simpler, collinear setups have been used much earlier, where
birefringent crystals have been used to generate the two copies of the pulse [120,121].

For stability, simplicity and cost reasons, we implemented a collinear setup similar to
that used by Bates et al. in [120]. Our experimental setup and both theoretical and
experimental results are discussed in the following sections.
4.2 Experimental Setup and Methods

This experiment was carried out as part of a collaboration with CELIA (centre lasers intenses et applications) in Bordeaux and funded by Laserlab Europe. We were given access to the Eclipse laser facility. Eclipse is a titanium-doped sapphire laser, operating at a repetition rate of 10 Hz at around 800 nm. It provides a total pulse energy of 200 mJ, which is split between two laboratories, each receiving 100 mJ. To avoid non-linear effects when propagating through air, the beam arrives in the laboratories uncompressed and is then compressed down to 30–40 fs in each lab individually. The compressor and all beam paths thereafter are under vacuum to avoid ionisation in air and other nonlinearities. Figure 4.1 shows a schematic of the setup used at CELIA.

After the beam enters the lab, there is an option to attenuate the remaining 100 mJ of IR using a waveplate and a polariser. The beam then propagates through the key setup of this experiment, which has been added to the usual beamline in this laboratory. This assembly for temporal field synthesis is described in more detail later on in this section.

Following the field synthesis setup, the pulses enter the standard setup of the laboratory at CELIA, which is entirely under vacuum. First, the pulses are compressed to between 30 fs and 40 fs, depending on the input and the compressor grating settings. The compressor gratings are gold coated and the compressor has a transmission efficiency of 65%.

After exiting the compressor, the beam is sent to a custom deformable mirror. The mirror setup has been developed by engineers at Imagine Optic and ISP System in collaboration with CELIA. It was designed specifically for the high power, low repetition rate laser system in use. The reflective dielectric coating for the membrane has a bandwidth of 215 nm and a damage threshold of 170 mJ/cm². The setup works in conjunction with a Shack-Hartmann wavefront analyser (HASO by Imagine Optic), which receives a small proportion of the beam transmitted by a beamsplitter. After analysing the current wavefront, the software provides the settings for the 47 step motors that change the surface of the deformable mirror, and therefore the wavefront. Note that this feedback is too slow for real-time feedback and the wavefront was usually only analysed and set once a day. The corrected wavefront allows for a better focus.

The majority of the beam is reflected by the beamsplitter and sent towards the high harmonic generation setup. The beam first passes through a motorised iris before being focussed by a spherical mirror with a focal length of 2 m. The gas jet used for this experiment was 100 µm in diameter, which was mounted on a 3-axis motorised translation
Figure 4.1: Schematic of the laboratory at the Eclipse laser facility. A 10 Hz, 200 mJ Ti:Sapph laser provides 100 mJ pulses to two separate experiments. A waveplate (WP) and a polariser are used to control the power into the experimental setup. A pair of quartz wedges, two quartz plates and another polariser are used for field synthesis (described in more detail in fig. 4.3). The compressor and everything thereafter operates under vacuum. The deformable mirror is used to change the wavefront of the beam based on feedback from the wavefront analyser (described in more detail in the body of this section). The beam is then focussed into a gas jet and imaged by a spherical grating into the detector assembly. The imaging setup is shown in more detail in fig. 4.2.

Stage in order to be able to optimise the harmonic generation.

After the gas jet, both the fundamental IR beam and the harmonic beam pass through a 500 µm slit. The harmonics are then imaged into the plane of a micro-channel plate (MCP) detector assembly by an XUV flat-field grating (Hitachi). The gold-coated grating has 1200 lines/mm and was designed for an angle of incidence of 87° (grazing-incidence angle 3°). Figure 4.2 shows the XUV spectrometer setup in more detail.

The assembly for temporal field synthesis (depicted in detail in figure 4.3) consists of a pair of quartz wedges, two quartz plates and a polariser. Since quartz is a birefringent

Figure 4.2: Schematic of the XUV spectrometer. The IR beam is shown in red, the harmonic beam is shown in purple. After the gas jet, the beams pass through a 500 µm slit. After reflection off a gold mirror, the harmonic beam is imaged onto the plane of a micro-channel plate (MCP). The phosphor screen, adjacent to the MCP, is then imaged onto a camera (not shown). The fundamental IR is blocked by a zero-order block.
material, the refractive index seen by any incident radiation depends on the polarisation relative to the axes of the crystal. This property is used here to achieve the temporal field synthesis mentioned in the background section of this chapter (section 4.1). The quartz wedges and plates are oriented with their axes at 45° with respect to the incoming laser polarisation. As a result, the incident laser pulses are projected onto the two axes of the quartz crystals. The two copies, one travelling along the ordinary axis, the other travelling along the extraordinary axis, therefore experience a different refractive index. This difference in refractive index leads to a temporal delay between the two copies. The polariser at the end of the setup projects both copies onto the same axis again, resulting in a synthesised field. The two quartz plates were chosen for the coarse adjustment of the time delay between the two copies. The quartz wedges were used to fine tune the phase difference between the two copies by changing the insertion, and therefore the total length of quartz the pulse travels through.

The two quartz plates used in this experiment had a thickness of $L_1 = 1.01 \text{ mm}$ and $L_2 = 0.48 \text{ mm}$, respectively. Each of the quartz wedges varies in thickness from $L_{tn} = 0.50 \text{ mm}$ on the thin side to $L_{tk} = 1.50 \text{ mm}$ on the thick side. All quartz crystals used had a cut angle of $\Theta = 90^\circ$. The refractive indices of quartz at a central wavelength of 800 nm are $n_o(800 \text{ nm}) = 1.5383$ for the ordinary axis and $n_e(800 \text{ nm}, 90^\circ) = 1.5472$ for the extraordinary axis, giving group velocities of $v_g(o) = c/1.5544$ and $v_g(e) = c/1.5639$, where the denominators are the so called group indices. Using the following equation for the induced time delay between pulses propagating along the ordinary and the extraordinary axes:

$$\Delta t = L \left( \frac{1}{v_g(e)} - \frac{1}{v_g(o)} \right),$$

(4.1)
we get a time delay of approximately 31.6 fs per mm of quartz. Note that depending on
the relative alignment of the ordinary and extraordinary axes of the quartz plates and
the wedges, the delays introduced by each element either add up or subtract. As a result,
a number of different coarse delays are possible, depending on the exact configuration of
the quartz plates and quartz wedges.
A change in phase delay of $\pi$ between the two copies is achieved by a change in beam
path length through quartz of 43.5 $\mu$m, which corresponds to a change in wedge insertion
of around 2.2 mm. Note that in the experiment (as opposed to computer simulations) it
is not possible to change the phase delay independently of the group delay. The amount
of additional quartz required to shift the phase delay by $\pi$ introduces a group delay of
1.4 fs.
4.3 Experimental Results and Discussion

In this section I present the results obtained with the setup described in the previous section and compare the experimental results with simple simulations. The results are presented in three sub-sections for three different values of pulse duration compared to the time delay introduced between the two copies of the pulse in the field synthesis setup. The first section presents the results where the delay $\Delta t$ is smaller than the pulse duration $\tau$. The second section looks at the case where $\Delta t > \tau$ and the third section looks at the case where the delay $\Delta t$ is equal to the pulse duration $\tau$.

The simulations are based on a simple code that generates two pulses at a set FWHM pulse duration and then simulates the field synthesis setup presented in section 4.2. The changing wedge insertion is simulated by changing both the relative phase between the two pulses inside their respective envelopes and the group delay between the envelopes based on calculations of the real changes caused by the changing quartz wedge insertion. The group delays stated in the following refer to the group delay at the centre of the wedge scan (in the plots at $\Delta \phi = 0$). The spectra are obtained by Fourier transformation of the synthesised fields.

Note that higher order effects such as group delay dispersion in the optical elements of the setup have not been taken into account in the simulations. These could easily be taken into account in future implementations of the code. However, the simulation results presented here agree very well with the experimental results, suggesting that the higher order effects play only a small role overall. The model calculates the effects on-axis only and does not take into account any off-axis intensity or spatial distributions. In the setup used here with a very long confocal parameter, this is a good approximation. Again, the code could easily be modified in future iterations to include off-axis effects.

4.3.1 Time Delay Smaller Than Pulse Duration ($\Delta t < \tau$)

This section discusses the results where the delay introduced between the two copies of the pulse in the field synthesis setup is smaller than the duration of the pulses. This was achieved by placing the quartz plate with a thickness of 1.01 mm and the quartz wedges in the field synthesis setup with opposing axes. The quartz plate introduces a group delay of 31.9 fs and the wedges, with the axes opposite, introduce a group delay in the opposite direction of 54.9 fs. The resulting group delay between the two copies of the pulse is therefore $52.4 \text{ fs} - 31.9 \text{ fs} = 20.5 \text{ fs}$. These numbers were first calculated based on the nominal thickness of the quartz plate and the wedges together with measurements of their insertion and then adjusted by comparing the results of the simulation and the
experiment. The small adjustments on the order of 1 fs were based on the comparison of the evolution of the centroid of the IR spectrum in the simulation and the experiment. The oscillation period of the centroid evolution is fixed at $2\pi$, but the oscillation amplitude depends on the group delay between the envelopes of the two copies of the pulse (cf. figure 4.6). The slope of the change in modulations of the IR spectrum in the simulation and the experimental data was also compared and are in good agreement for the group delay of 20.5 fs.

Figure 4.4 shows the results of the simulation for a 35.0 fs input pulse with a group delay of 20.5 fs. The central wavelength was set at 810.3 nm, in agreement with the experimental data. The left panel shows the evolution of the synthesised electric field amplitude with changing relative phase. As one can see, the temporal profile of the pulses changes significantly. This is even more evident in the centre panel, where the field envelope amplitude is shown. Depending on the phase delay, the synthesised pulse actually turns into a double pulse (e.g. around $\Delta \phi = 0$). At other phase delays, the resulting intensity profile is relatively constant. These ‘flattop’ pulses were later used for high harmonic generation, which is discussed in Martin Arnold’s PhD thesis.

The panel on the right in figure 4.4 shows the simulated evolution of the IR spectrum of the synthesised pulses.

Note that even though the patterns in all three plots repeat with a periodicity of $2\pi$, successive patterns are not identical due to the fact that a change in wedge insertion changes not only the phase difference, but also the group delay. This becomes more obvious when plotting the evolution of the three quantities shown in figure 4.4 over a much bigger range of phase values. Here the range of phase values has been limited to the range available in the experiment.

Figure 4.5 shows the measured IR spectra plotted against the change in relative phase (calibrated from the change in wedge insertion).

A comparison between the centroid evolution in the measured IR spectra after the field synthesis and the simulation is shown in figure 4.6. The experimental results are shown in blue (with the data points marked by a star) and the results from the simulation are shown in orange. The oscillation amplitude of the centroid evolution changes throughout the scan as the group delay changes with the wedge insertion. Towards the right of the figure (increasing phase difference values), the modulation depth decreases as the sensitivity to the phase change decreases with increasing group delay. This is due to

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1The spectral centroid is calculated as the weighted mean of the wavelengths present in the spectrum, weighted by their relative amplitudes.
Figure 4.4: This figure shows the results of the simulation for the case where $\Delta t < \tau$. The group delay $\Delta t$ was set to 20.5 fs at the centre of the scan (where $\Delta \phi = 0$), and the pulse duration used in the simulation was 35 fs. The parameters have been tuned to match the experimental results presented in figure 4.5. Left: This panel shows the evolution of the field amplitude and the spectral density as a function of the phase difference. Centre: This panel shows how the field envelope changes as a function of the phase difference. Right: This panel shows how the spectrum changes as a function of the phase difference.
the fact that the overlap between the two copies of the pulse decreases with increasing group delay. As a result, the impact of the interferences between the two copies of the pulse on the overall temporal pulse shape (and therefore also its spectrum) decreases.

Figure 4.7 shows the harmonic yield when using the synthesised field presented above in the HHG setup described in section 4.2. The IR input pulse energy for this measurement was 38 mJ, which was measured after the field synthesis setup but before the compressor (cf. figure 4.1). With a compressor efficiency of 65% and an estimated efficiency of the remaining setup (taking into account the reflectivity of the mirrors and the iris at a size of 10.5 mm) before the interaction area this corresponds to a pulse energy of 20 mJ delivered to the target. With a measured \(1/e^2\) spot size of 147 µm and a pulse duration of 38 fs this corresponds to a maximum intensity on target of approximately \(1.55 \times 10^{15} \text{ W/cm}^2\) (in the focus). The gas used was argon with a backing pressure of 1 bar. The presented yield was integrated in the direction of divergence over an integration box that includes signal above the noise level and was averaged over 5 shots. A background spectrum with the laser blocked was subtracted in data processing.

As expected, the energy of the harmonics shifts as the wedge insertion (and therefore the phase difference) changes. The wedge insertion determines both the temporal profile of the generating pulses and the IR spectrum. As the wedge position is scanned (in the
figures calibrated as the phase difference $\Delta \phi$), the central wavelength of the generating IR pulses changes and therefore the wavelength of the harmonics is shifted accordingly. Because the temporal profile also changes, the intensity in the interaction volume changes too. This is evident from the wedge scan shown in figure 4.7, where for certain ranges of $\Delta \phi$ there is no high harmonic generation. This can be explained by comparing those ranges of $\Delta \phi$ with the results of the simulation presented in figure 4.4. For example in the range where $\Delta \phi$ is between 0 and $\pi$, the harmonics disappear. The left and centre panels of figure 4.4 reveal that in that particular range the synthesised pulse is split into a double pulse (albeit with a varying depth of the ‘valley’ in between the two peaks). This means that the peak intensity at the target drops below the necessary threshold for HHG.

The centroid of the generating IR field changes by 17.4 nm in the range of $\Delta \phi$ from $-3\pi$ to $-2\pi$, where the change is at its biggest (cf. figure 4.6). Figure 4.8 shows the change in the centroid of the harmonic energy for all six harmonics shown in figure 4.7 on the left $y$-axis (blue curves, data points marked by circle). The right $y$-axis shows the centroid evolution of the generating IR field over the same range of $\Delta \phi$ (orange curve, data points marked by star). Figure 4.9 shows the variation in energy of each harmonic order around its average value. As expected, the harmonic energy drops with an increasing wavelength of the generating field. The shift in harmonic energy of these six harmonics varies between 0.3 eV for the lowest order harmonic and 0.58 eV for some of the higher order harmonics. The energy shift in percentage of the harmonic energy varies...
Figure 4.7: The harmonic yield from high harmonic generation in argon with the synthesised field presented above (for setup cf. section 4.2). The harmonics shift in energy as the wedge insertion and therefore the phase difference changes. IR input power: 38 mJ; iris diameter: 10.5 mm; backing pressure: 1 bar. Signal integrated in direction of divergence over range that includes signal above noise level and averaged over 5 shots. Background subtracted.
Figure 4.8: The left y-axis shows harmonic energy. The centroid energy for each harmonic shown in figure 4.7 is plotted versus the change in phase delay. The right y-axis shows the centroid of the IR spectrum versus the same change in phase delay along the x-axis. As expected, the harmonic energy decreases with an increasing IR centroid wavelength.

between 1% for the lowest and highest order harmonic shown and goes up to 1.67% for the harmonic around 35 eV. In terms of spectral coverage, i.e. how much of the spectrum we can cover between harmonics (separated by approximately 3 eV), this corresponds to 10% – 20%.

If the central wavelength of the generating pulses was changing without a change in the temporal profile, we would expect a direct mapping from the change in central wavelength to the change in wavelength of each harmonic order ($\lambda \rightarrow \lambda/q$, with harmonic order $q$). Here, however, we have to deal with the challenge that the temporal profile of the synthesised pulses changes. Particularly at phase delays where the synthesised pulse is a double pulse, this can be problematic as we measure the spectrum (and therefore the centroid) of the entire synthesised pulse, but the harmonics may be generated primarily by the part of the pulse arriving first. In our case, the intensities in the target area are low enough that we do not generate harmonics around the phase delays where the ‘valley’ in between the two components is too deep. This suggests that we are not hugely
affected by this problem, because we are not generating harmonics at the phase delays where the synthesised pulses become double pulses. However, looking at the mapping from the change in central wavelength of the synthesised pulses to the change in harmonic energy, we find that the lower order harmonics (harmonic 19 to 23, cf. figure 4.9) display an almost perfect direct mapping, whereas the higher order harmonics (harmonics 25 to 29) do not. In fact, looking at the harmonics in figure 4.7, the higher orders are affected more by the double pulse nature of the synthesised field because they are more sensitive to the peak intensity. This is evident in the fact that the harmonic yield for these higher order harmonics disappears earlier when moving towards phase delays where a ‘valley’ appears between the two component pulses.

In the case discussed later in section 4.3.2, where $\Delta t > \tau$, the overall pulse envelope does not change as much, and a meaningful definition of a central wavelength is not possible due to the highly modulated nature of the spectrum, making a meaningful discussion of the mapping more difficult.

4.3.2 Time Delay Larger Than Pulse Duration ($\Delta t > \tau$)

We now look at the results where the introduced time delay is larger than the pulse duration. In this regime, the temporal pulse envelope depends less strongly on the phase
difference between the two copies of the pulse. This is due to the fact that the bigger overall delay already introduces a strong modulation in the area where the two pulses overlap temporally. Additionally, the pulses only overlap in the wings of the pulses, where the impact of phase changes on the local pulse shape is small compared to the overall pulse shape.

The group delay larger than the pulse duration was achieved by using both the quartz plate with a thickness of 1.01 mm (introducing a group delay of 31.9 fs) and the quartz plate with a thickness of 0.47 mm (group delay of 15.3 fs) together with the quartz wedges. At the insertion used for this wedge scan, the wedges introduced an additional group delay of 61.8 fs at the centre of the wedge scan, resulting in an overall group delay of 109 fs. As before, these numbers were first calculated based on the measured insertion of the wedges and then adjusted by comparing the experimental results with those of the simulation. Previously (cf. section 4.3.1), the evolution of the centroid of the IR spectrum versus phase delay was extracted. Here however, with the delay significantly larger than the pulse duration, the spectrum is heavily modulated and therefore the definition of a single centroid is not useful. Therefore, the adjustments on the order of 1 fs were based on the comparison of the slopes of the spectral modulations (cf. figure 4.11 for the experimental data and the right panel in figure 4.10 for the simulation).

Figure 4.10 shows the results of the simulation for a 55 fs input pulse and a group delay of 109 fs. The centroid wavelength was set to 806.55 nm in accordance with the measured centroid of the input pulses. As before, the left panel shows the evolution of the synthesised electric field amplitude with the changing phase difference between the two pulses. The centre panel shows the evolution of the field envelope over the same range of phase change. The overall pulse envelope does not change as significantly as it did for the case where $\Delta t < \tau$, as discussed in the previous section. The depth of the ‘valley’ between the two pulses does change, but the overall envelope remains that of a double pulse over the entire range of phase difference. As the group delay increases slowly with increasing phase difference, the two pulses separate more and more.

The right panel in figure 4.10 shows the evolution of the IR spectrum of the synthesised pulses. The spectrum is heavily modulated across the entire range of the wedge scan. Figure 4.11 shows the evolution of the IR spectrum measured in the experiment. The change in relative phase was calibrated from the measured change in wedge insertion.

The harmonics generated with these synthesised pulses are shown in figure 4.12. The IR input power (measured before the compressor) was 32 mJ, which corresponds to ap-
Figure 4.10: This figure shows the results of the simulation for the case where $\Delta t > \tau$. The group delay $\Delta t$ was set to 100 fs at the centre of the scan (where $\Delta \phi = 0$) and the pulse duration used in the simulation was 55 fs. The parameters have been tuned to match the experimental results presented in figure 4.11. Left: This panel shows the evolution of the field amplitude as a function of the phase difference. Centre: This panel shows the evolution of the field envelope as a function of the phase difference. Right: This panel shows how the spectrum changes as a function of the phase difference.
proximately 17 mJ delivered to the target once the compressor efficiency, the reflectivity of various optics and the iris of 10.5 mm diameter have been taken into account. With a measured 1/e² spot size of 147 µm the intensity in the focal spot was approximately $1.32 \times 10^{15}$ W/cm². The harmonics were generated in argon with 1 bar backing pressure. The presented yield was integrated over an integration box that includes signal above noise level. The signal has been averaged over 5 shots. The background was subtracted in data processing.

The harmonic yield is lower here than it was for the harmonics presented in section 4.3.1. This is due to two factors. Firstly, the pulse duration is longer due to the fact that the input pulse travelled through more quartz, which spreads the slightly lower input pulse energy over a longer pulse, decreasing the intensity. Secondly, the spectrum is heavily modulated, which is likely to negatively affect harmonic yield.

Comparing figures 4.7 ($\Delta t < \tau$) and 4.12 ($\Delta t > \tau$) it becomes obvious that the tunability of the harmonic energy has greatly reduced in the case of $\Delta t > \tau$. For the longer delay, the harmonics even split for certain phase delays (cf. figure 4.12, $\Delta \phi$ around $-3\pi$, $-\pi$, $+\pi$ and $+3\pi$).
Figure 4.12: The harmonic yield from high harmonic generation in argon with the synthesised field presented above (for setup cf. section 4.2). The harmonics shift in energy as the wedge insertion and therefore the phase difference changes. IR input power: 32 mJ; iris diameter: 10.5 mm; backing pressure: 1 bar; gas: argon. Signal integrated in direction of divergence over range that includes signal above noise level and averaged over 5 shots. Background subtracted.
In the case of $\Delta t > \tau$, the shift in harmonic energy with changing phase difference between the two copies of the pulse is marginal.

Note that in principle ionisation blue-shifting due to intensity fluctuations could be responsible for the shifts in harmonic energy. However, we observed both red and blue shifts in the experiments presented here, without any obvious exaggeration of the shift towards the blue. Additionally, the shifts in harmonic energy observed here are very much periodic with the changing wedge insertion, ruling out random fluctuations on short time scales. We also did not observe any shifts in harmonic energy when operating at lower input powers, further suggesting that ionisation blue-shifting did not play a significant role here.

The marginal shift in centroid energy of the harmonics is shown in figure 4.13. Because the vertical scale of the plot showing all harmonic orders around their energy suppresses the variation of each individual harmonic around its average value, figure 4.14 shows the variation in energy for each harmonic order shown in figure 4.13.

4.3.3 Time Delay Equal to Pulse Duration ($\Delta t = \tau$)

In this section, the results for the case where the time delay between the copies of the pulse is comparable to the pulse duration are discussed. We do not have any measure-
ments where the pulse duration measured by autocorrelation (cf. section 2.2.1) matches the group delay introduced by the quartz plates and wedges closely. In this section I therefore present a comparison of results of the simulation for the case where $\Delta t = \tau$ for the two pulse durations of the previous two sections. The central wavelength was set to 806.55 nm.

Figure 4.15 shows the results of the simulation for an input pulse duration of 35 fs and a group delay between the two copies of the pulse at the centre of the simulated wedge scan of also 35 fs. This pulse duration corresponds to the pulse duration of the results presented in section 4.3.1, but this time with a delay equal to the pulse duration. The overall length of the temporal envelope of the synthesised field is now longer due to the longer delay. In the case of $\Delta t = \tau$ the range of phase difference where the field envelope is relatively flat (‘flattop’ field envelope) is bigger than in the case of $\Delta t < \tau$.

Figure 4.16 shows the same simulation, but for the case where $\Delta t = \tau = 55$ fs. The differences between this case and the case where $\Delta t > \tau$ presented in section 4.3.2 (cf. figure 4.10) are significant. In the case of figure 4.10, where $\Delta t = 109$ fs $> \tau = 55$ fs, the spectrum is heavily modulated across the entire wedge scan and a meaningful definition of a central wavelength is not possible. In the case presented in figure 4.16, where $\Delta t = \tau = 55$ fs, the central wavelength is well-defined and the changes in the spectrum

Figure 4.14: Shown is the variation of the harmonic energy around the average harmonic energy for each harmonic order shown in figure 4.13. The numbering in the legend refers to the harmonic order, from harmonic 19 (around 29.0 eV) to harmonic 29 (around 43.9 eV).
Figure 4.15: This figure shows the results of the simulation for the case where $\Delta t = \tau$. The group delay $\Delta t$ was set to 35 fs at the centre of the scan (where $\Delta \phi = 0$) and the pulse duration used in the simulation was 35 fs. Left: This panel shows the evolution of the field amplitude as a function of the phase difference between the two copies of the pulse. Centre: This panel shows the evolution of the field envelope as a function of the phase difference. Right: This panel shows how the spectrum changes as a function of the phase difference.
throughout the wedge scan translate into a meaningful tunability of the central wavelength. In both cases the input pulse length is identical. The stark differences in the results are caused by the very different group delay introduced between the two copies of the input pulses. Where the delay between the copies of the pulses is very large compared to the pulse duration, the spectrum is heavily modulated but any changes in wedge insertion (i.e. relative phase difference) translate into spectral changes only slowly (this can be seen from the slope of the spectral features).

Interestingly, looking at the centroid evolution for the two cases presented in this section ($\Delta t = \tau = 35\,\text{fs}$ and $\Delta t = \tau = 55\,\text{fs}$) shown in figure 4.17, the oscillation amplitude is bigger for the shorter pulse, even though the ratio of pulse duration to group delay is the same in both cases.
Figure 4.16: This figure shows the results of the simulation for the case where $\Delta t = \tau$. The group delay $\Delta t$ was set to 55 fs at the centre of the scan (where $\Delta \phi = 0$). The pulse duration was 55 fs. Left: This panel shows the evolution of the field amplitude as a function of the phase difference between the two copies of the pulse. Centre: This panel shows the evolution of the field envelope as a function of the phase difference. Right: This panel shows how the spectrum changes as a function of the phase difference.
Figure 4.17: Comparison of the oscillation amplitudes of the centroid evolution for the cases $\Delta t = \tau = 35$ fs (blue curve) and $\Delta t = \tau = 55$ fs (orange curve).
4.4 Conclusion and Outlook

In the previous sections we have introduced a very simple and cost effective setup that allows for reliable and repeatable tuning of the central wavelength of the input pulses into the field synthesis setup. The synthesised pulses were successfully used for high harmonic generation and a shift in harmonic energy was observed. In [115], M. Kotur et al. used a harmonic tunable between 26.4 eV and 26.9 eV for their measurements of the intensity and phase variation of the photo-ionisation amplitude. The results presented in section 4.3.1 demonstrate a tunability over a comparable range of harmonic energies. The results presented in that section do not cover the same photon energy around 26.5 eV, but the technique presented here is easily extendable to harmonic orders other than those shown. The results shown in section 4.3.1 prove that our simple setup can compete with more sophisticated and expensive systems such as the one used in [115]. The major advantage of our setup over the previously mentioned alternatives is the fact that it is compatible with very high power systems as the field synthesis setup is placed before the compressor and can easily be taken into account when designing the compressor.

The range of tunability demonstrated with our simple field synthesis setup can easily be extended both to other harmonic energies and to a bigger range of tunability. In fact, the above sections showed that both a shorter pulse duration and a smaller group delay between the copies of the pulses lead to a bigger change in the central wavelength of the generating field and therefore a larger tunability range of the resulting harmonics. If a maximum shift in harmonic energy was the goal, shorter input pulses and a group delay short compared to the pulse duration would be the ideal choice. For example, a 25 fs input pulse with a group delay of 10 fs results in a central wavelength range of almost 35 nm around 800 nm input pulses (based on simulation).

The good agreement between the experimental results and the simulations presented in the previous sections shows that even the simple code used adequately describes the physics behind the experiments. However, there are a number of ways in which the work presented here can be improved upon. For example, using a more sophisticated pulse characterisation technique than autocorrelation would allow us to extract phase information of the input pulses, which could quite easily be included in the simulations. The phase information could potentially also be used to better compress the pulses to compensate for the propagation through the quartz plates and wedges.

When using this setup in applications such as the ones presented in section 4.1, it would be interesting to study the effect of the changing temporal profile of the pulses on those measurements in comparison with the techniques used there that shift the wavelength.
whilst leaving the temporal profile largely unchanged.
Chapter 5

Below- and Above-Threshold Harmonics in Two-Colour Fields
5.1 Background

So far we have looked at high harmonic generation with driving laser fields of a single centre wavelength. However, the combination of different wavelengths allows for some interesting phenomena to arise and provides control over the generation process that is not possible with a single generating field.

In the case of two-colour fields, additional harmonic peaks, other than the expected odd harmonics, appear in the harmonic spectrum [122]. In the most common case, where the second field is the second harmonic of the fundamental, the additional harmonics are even harmonics of the fundamental field. The second field breaks the symmetry, and the resulting total field repeats itself only every full cycle, not every half cycle as is the case with a single field. Figure 5.1 illustrates this point. The fundamental is shown in red, the second harmonic in blue (at 0.3 times the field amplitude of the fundamental), and the resulting total field is shown in black. Note that in practice the second harmonic field is usually considerably smaller than 30% of the fundamental. This higher value has been chosen here for clarity as the effect on the total field is more pronounced with a stronger secondary field.

In the earlier days of experimentation with secondary fields, both fields were usually polarised in the same direction [123, 124], although some experimented with perpendicular and even circular polarisation [125]. The main aim of these early studies was to enhance the conversion efficiency, which is possible for certain phase relationships between the two fields.

The use of perpendicularly polarised fields was first proposed by Ivanov et al. in [126]. Perpendicularly polarised fields allow for advanced control over the trajectories of the electrons in the continuum.

Kitzler and Lezius [127] proposed to use perpendicularly polarised two-colour laser pulses to steer electrons in the continuum with attosecond precision around the ionic core. They demonstrated numerically that the angle at which the electron enters the continuum, the angle at recollision, and the energy at recollision can be controlled without the need for CEP stabilisation. In their proposal they argue that this technique might even be used as an alternative to aligning molecules with respect to the laser polarisation.

Shafir et al. [128] were the first to use perpendicularly polarised fields experimentally to manipulate the recollision process in order to resolve the symmetry of the atomic wavefunction of neon, which unlike molecular systems cannot be aligned for tomographic reconstruction of orbitals.
Since the interplay of the two fields affects the electron trajectories and the time spent in the continuum, the chirp of the emitted attosecond pulses is also affected. Zheng et al. [129] first introduced this scheme for chirp compensation of the harmonic attosecond pulses. The intrinsic chirp can be controlled by varying the relative time delay between the two pulses of different wavelength. Zheng et al. achieved compensation of the negative chirp in the harmonic emission and produced almost transform-limited attosecond pulse trains.

Perpendicular fields can further be used for trajectory selection. The dominant contribution to the overall harmonic signal can be switched between the short and long trajectories simply by changing the relative phase between the fundamental field and its second harmonic. This application of the secondary field was first proposed by Kim and Nam in [130]. This was later demonstrated experimentally by Brugnera et al. in [131].

Studies involving high harmonic generation further usually focus on harmonic orders with photon energies well above the ionisation potential of the target atomic or molecular species. However, there is still significant interest in the so called below-threshold harmonics, with photon energies below the target’s ionisation potential. Below-threshold harmonics have so far not been studied extensively. These lower order harmonics could however lead to new advances towards megahertz repetition rates and high average power vacuum ultraviolet (VUV) sources [132]. Since below-threshold harmonics can be generated with comparatively low driving laser intensities on the order of $1 \times 10^{13} \text{W/cm}^2$ and their conversion efficiency is much higher, their production at high repetition rates puts less stringent demands on the pulse energy of the generating laser. Yost et al. [133]
studied various properties of below-threshold harmonics both experimentally and theoretically and found that the low-order harmonics showed pulse-to-pulse coherence. Although the generation of below-threshold harmonics is not compatible with the three-step model of HHG introduced in section 2.5.1 due to the non-negligible influence of the atomic or molecular potential, certain aspects of the generation process are similar. For example, Yost et al. showed that laser-driven electron dynamics in the continuum are still a major factor in their generation. In particular, they found that the intensity-dependence of the phase accumulated in the continuum is larger for below-threshold harmonics than it is for above-threshold harmonics. This can be explained by the larger influence of the atomic or molecular potential on the generation process of these below-threshold harmonics. Further, Yost et al. demonstrated both experimentally and theoretically that different generation pathways (similar to the short and long trajectories in above-threshold HHG) contribute to the overall harmonic yield, even far below the threshold. Note that below-threshold harmonics were initially thought to be a perturbative response to the incident laser field [134]. However, various experiments (e.g. [133, 135]) point to the failure of perturbation theory to explain the generation of below-threshold harmonics [134]. Spott et al. [136] found in numerical calculations that the transition from the perturbative to the non-perturbative regime in low-order nonlinear processes occurs at intensities around $10^{13}$ W/cm$^2$. They note further that any deviation from the predictions of low-order perturbation theory can be taken as a reliable indicator that the perturbative series expansion is no longer applicable. The light-matter interaction then needs to be treated non-perturbatively.

Dudovich et al. [137] combine a weak second harmonic field with the fundamental field for in situ phase measurements of the emitted harmonics. This approach could also be used to gain new insights into the generation of near-threshold harmonics. In their study, Dudovich et al. further show that at higher intensities of the secondary field, they are able to control the HHG process and that by controlling the relative phase delay between the two fields they can switch the production of harmonics almost completely between the even and odd harmonics.

The following sections in this chapter present results obtained by using an 800 nm fundamental field and its second harmonic at 400 nm to generate harmonics both above and below the ionisation potential of the target. We observed interesting behaviour in the additional peaks of the harmonic spectrum depending on the relative delay between the fundamental and its second harmonic.

Whilst the study of the near-threshold harmonics generated by a combination of the
fundamental and second harmonic is interesting in itself, this experiment allowed for the optimisation of the setup for the experiment using the third harmonic (described in chapter 6) instead of the second harmonic. Due to the fact that the UVC field (third harmonic) is significantly more difficult to handle than the UVA field (second harmonic), it was beneficial to benchmark the setup with the UVA field first.
5.2 Experimental Setup and Methods

The setup used for the experiments introduced in the previous section is described in this section. The IR input laser used for this experiment is the KMLabs Red Dragon laser described in more detail in section 3.1. The output of the Red Dragon laser is centred around 785 nm and around 1 W of input power was used for this experiment.

Two different setups were used to generate the second harmonic of the IR input beam and to control the delay between the fundamental IR and the generated UVA pulses. The first setup is shown in figure 5.2. The IR input beam enters a first BBO crystal from the left. Through a type 1 phase-matching scheme, the second harmonic is generated (cf. section 2.3.1) at a polarization perpendicular to that of the fundamental beam. The delay between the fundamental IR pulses and the second harmonic pulses is controlled via a birefringent calcite plate, where the fundamental and the second harmonic propagate along different crystal axes. The calcite plate is mounted on a motorised rotation stage and as the angle of incidence changes, the effective thickness changes. Because calcite is birefringent, the refractive index also changes with a changing angle of incidence. Therefore, the delay between the two fields can be controlled by controlling the rotation of the calcite plate.

In order to find the range of angle of incidence where the two field overlap in time, an assembly consisting of a second BBO and a UVFS prism can be inserted into the beam after the calcite plate. The second BBO is a type 2 crystal where the third harmonic of the fundamental beam is generated through sum frequency generation of the fundamental and the second harmonic (cf. section 2.3.1). The prism then separates the three fields. The fundamental and the second harmonic are dumped into a beam block. The third harmonic is incident on a power meter and the third harmonic power is recorded versus the angle of incidence and therefore the delay. This is a crosscorrelation of the fundamental and the second harmonic (cf. section 2.2.1).

When the second BBO and the UVFS prism are removed, the beam enters the experimental chamber after the calcite plate. The setup inside the experimental chamber is described in more detail below.

Whilst this first setup is very stable and robust due to the fact that the two beams travel collinearly throughout the entire setup, it is limited in the range of time delay that can be introduced between the two fields before clipping the beams on the aperture of the calcite plate. The second setup for the generation of the second harmonic and the control of the delay between the fundamental and the second harmonic is shown in
Figure 5.2: Schematic of the first version of the setup for the generation of the second harmonic and for the time delay control between the second harmonic and the fundamental. The fundamental IR beam enters from the left. BBO1 (type 1, 100 \mu m, \Theta = 29.2^\circ, CLaser) generates the second harmonic. The Calcite plate (0.6 mm, \Theta = 45^\circ, Newlight Photonics) is used to compensate for the time delay between the IR and the second harmonic after BBO1. The Calcite plate is on a motorised rotation stage to scan the delay. The IR and the second harmonic then enter the experimental chamber. A second BBO crystal (BBO2, 40 \mu m, \Theta = 55.5^\circ, CLaser) and a UVFS prism can be inserted into the beam to check the temporal overlap between the IR and the second harmonic (see text for details).

Figure 5.3. The beam enters the first BBO from the right. The first BBO is the same as in the first setup described above. The second harmonic and the remaining fundamental then pass under the pick-off mirror to the first UVFS prism. After the first prism the two fields travel separately to their respective second prisms. The second harmonic is sent back by a return mirror and travels back through the two prisms. The IR beam is reflected back by a return mirror mounted on a motorised translation stage (Thorlabs Z825BV) and then travels back through the two prisms. Both return mirrors send the beams back at a slight upwards angle. Both beams recombine in the common prism and are then picked off by the pick-off mirror. A periscope then brings them up to the beam height of the experimental chamber. A dual waveplate (half-wave plate at 400 nm, full-wave plate at 800 nm) can be used to change the relative polarisation of the two fields. The same crosscorrelation assembly as described above in the first setup can be inserted into the beam path before the experimental chamber to determine the range of translation stage positions where the two fields overlap temporally. Note that the translation stage position of \( t_0 \) (zero time delay) is shifted in the interaction region compared to the measured position due to the fact that the fundamental and the second harmonic travel at different speeds through the remaining air path and the entrance window to the experimental chamber. Since the fundamental IR input pulse can be measured with a FROG (cf. section 2.2.2) the crosscorrelation measurement not only gives us the range of translation stage positions where the two fields overlap temporally, but also the pulse duration of the second harmonic. This second setup allows us to scan through the entire range of delays where the two fields overlap temporally without clipping the beams, but comes at the cost of reduced stability and temporal resolution.
Figure 5.3: Schematic of the second version of the setup for the generation of the second harmonic and for the time delay control between the second harmonic and the fundamental. The fundamental IR beam enters from the right. BBO1 (type 1, 100 µm, Θ = 29.2°, CLaser) generates the second harmonic. The residual IR and the second harmonic then pass through under the pick-off mirror. The following prism (UVFS, Newport, apex angle = 69°) separates the IR and the blue into two separate beam lines. Both beams are incident on a second prism. The blue is reflected back by a fixed return mirror. The IR return mirror is on a translation stage in order to control the delay between the IR and the blue. Both beams are sent back at a small upwards angle and after recombination in the first prism the beams are picked off by the pick-off mirror. A periscope brings the beam height up to the level of the experimental chamber. A dual waveplate (half-wave plate at 400 nm, full-wave plate at 800 nm, EKSMA) can be used to change the relative polarisation. The beams then enter the experimental chamber. A second BBO crystal (BBO2, 40 µm, Θ = 55.5°, CLaser) and a UVFS prism can be inserted into the beam to check the temporal overlap between the IR and the second harmonic (see text for details).
The optical setup inside the experimental chamber is shown in figure 5.4. The beams enter the chamber from the left through a 1 mm CaF$_2$ entrance window. The beam is then reflected by a folding mirror (Thorlabs standard silver mirror). The focussing mirror (Edmund Optics, UV enhanced Al, $f = 203.2$ mm$(\pm 2\%))$ then focusses the beams into the gas jet (cf. section 3.3). Both the folding mirror and the focussing mirror are mounted on a motorised translatable breadboard, which is used to adjust the focal spot position with respect to the gas jet. The beam then enters the spectrometer part of the setup through a slit. The slit size is chosen large enough to not clip any of the harmonic beam but small enough to enable differential pumping between the experimental chamber and the spectrometer chamber. A flat field grating images the harmonics onto the plane of the detector assembly. The detector assembly consists of an MCP with a phosphor screen. A camera (pco.pixelfly, quantum efficiency up to 62\%, 14 bit dynamic range) images the phosphor screen and feeds the recorded data to the acquisition software that also controls the motorised stages in the setup.

Since the setup shown in figure 5.3 is essentially a prism compressor or stretcher (depending on the prism insertion and apex distances), the distances were carefully set up to deliver the shortest possible pulses to the target. The necessary prism insertion and the apex separation were first estimated with a simulation written by C. Brahms with input data from measured input pulses. The exact insertion and separation was then fine tuned.
tuned by minimising the pulse duration after the prism setup.
5.3 Experimental Results and Discussion

In this section I present the results of the two-colour experiments with the setups described in the previous section. The results are presented in two separate sub-sections. One for the first variation of the setup where the delay between the IR and the UVA pulses is varied by rotating a calcite plate. The other for the variation of the setup where the IR and the UVA pulses are separated in a prism setup and the delay between them is varied by translating the return mirror of the IR arm.

5.3.1 Time delay variation by rotating calcite plate

In this section I discuss the results obtained with the setup described in figure 5.2. Here, the delay between the IR pulses and the UVA pulses is varied by rotating a calcite plate immediately after the BBO crystal where the UVA is generated from the IR. The IR is polarised along the ordinary axis of the calcite plate, perpendicularly to the optical table (s-pol.). The ordinary axis is also the axis around which the calcite plate is rotated in order to scan the delay between the two wavelengths. The UVA is polarised perpendicularly to the IR and therefore propagates along the extraordinary axis of the calcite crystal. Hence, when rotating the calcite plate, and therefore changing the angle of incidence (AOI), both the effective thickness and the effective cut angle of the calcite plate change. As a result, the function of time delay introduced versus the change of AOI in degree is not linear.

All scans presented in this section where taken in krypton at a backing pressure of 1 bar. The input power into the BBO in the IR was 1 W. The remaining IR power after the iris (diameter of 4.35 mm) was 280 mW and the remaining power in the UVA was 39 mW, 14% of the IR.

Note that the time delay shown in the figures in this section (5.3.1) is not an absolute delay between the IR and the UVA, but only a change in delay introduced by the calcite plate, where positive numbers mean that the IR is delayed with respect to the UVA. The calcite plate was capable of compensating for the delay between the IR and the UVA introduced in the generating BBO. However, the beam path through air after the generation and the propagation through the entrance window of the experimental chamber introduced an additional delay too big for the calcite plate to compensate completely within a range of rotation that does not clip the beam. This is why it was not possible to determine the absolute delay between the two pulses in the interaction region. The pulse duration of the UVA was estimated with a crosscorrelation to be around 140 fs.
outside the experimental chamber. The IR pulse duration was measured with a FROG to be 55 fs. The estimated intensities, based on the measured input powers, pulse durations and very similar spot sizes for the IR and the UVA of around 64 μm (1/e² radius), were $8.0 \times 10^{13}$ W/cm² and $4.4 \times 10^{12}$ W/cm² for the IR and the UVA, respectively.

Figure 5.5 shows the evolution of the harmonic yield (integrated over divergence) versus the time delay introduced by the rotation of the calcite plate. The AOI of the beam on the calcite plate was changed between 0° and 35° in steps of 0.2°, which corresponds to an average step size in time of 1.5 fs. This time step was calculated by taking into account the change in thickness of the calcite plate as it is rotated and the change in refractive index of the extraordinary axis as the effective cut angle changes with the changing angle of incidence (the calcite plate was rotated around the ordinary axis). The refractive index data and the Sellmaier equations to calculate the group velocities for both the IR and the UVA were taken from [139].

Interestingly, the onset of the even harmonics comes at different relative time delays depending on the harmonic order. This is easier to see in figure 5.6, where the harmonic spectra at selected delays are plotted alongside the spectra generated by only the IR and only the UVA. The panel on the very right shows the harmonic spectrum when only the UVA enters the experimental chamber. These are the odd harmonics of the UVA (3.16 eV), which are even harmonics compared to the IR (1.58 eV). The second panel from the right shows the harmonic spectrum when only the IR enters the chamber. Now, for a delay of for example 68 fs (leftmost panel), only the odd harmonics of the IR (7th to 17th harmonic) and the odd harmonics of the UVA (the 3rd harmonic around 9.48 eV and the 5th harmonic around 15.8 eV) are generated. Here the delay between the pulses at the different wavelengths must be separated by more than their pulse duration, and these harmonics are generated independently. As the relative delay changes (e.g. to 224 fs, 2nd panel from left), the two pulses get closer and other even harmonics (of the IR) start appearing, because the UVA now breaks the symmetry of the IR field. The even harmonics become stronger as the delay keeps changing (e.g. at 306 fs, middle panel). Unfortunately, the calcite plate then starts clipping the beams, which is why the delay could not be scanned further.

Interestingly, the 8th harmonic (around 12.64 eV) appears at very different delays compared to harmonics 12 and 14 (18.96 eV and 22.12 eV, respectively). It is possible that

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1Note that the error in this type measurement can be very large. However, the crystal used for the measurement here is very thin. Therefore, any problems arising from GVM are likely to be very small. Other error sources have been taken into account in this error estimation based on the analysis in [138].

2Note that the step size in time delay changes slightly over the course of the scan because rotating the calcite plate to change the delay changes both the effective thickness of the calcite plate and the effective cut angle of the crystal.
IR and UVA in perpendicular polarisation

Figure 5.5: This figure shows the harmonics generated in Kr versus the changing time delay between IR and UVA pulses. Note that the shown time delay only denotes a change in time delay, not an absolute delay. The step size was around 1.5 fs. Some of the even harmonics due to the secondary UVA field are present throughout the scan, whereas other even harmonics appear at varying time delays. See figure 5.6 for the full harmonic spectra for selected time delays and a comparison of IR only and UVA only harmonics, which helps to identify the even and odd harmonics. The black dashed line shows the ionisation potential of krypton.
IR and UVA in perpendicular polarisation

Figure 5.6: Shown are the full HHG spectra for three selected time delays (left three panels). Note how different even harmonic orders appear at different time delays (cf. figure 5.5 for the full evolution of the harmonic spectra versus time delay). The right two panels show the IR only and the UVA only harmonics, respectively. The black dashed line shows the ionisation potential of krypton.

this has to do with the fact that harmonic 8 is below the ionisation potential of the target, whereas the other two even harmonic orders sit above the ionisation potential. The generation of below-threshold harmonics is significantly more efficient than the generation of above-threshold harmonics. A smaller perturbation of the generating field (here at a bigger delay between the IR and the perturbing UVA) could therefore be sufficient to lead to the generation of the below-threshold even harmonics.

Figure 5.7 shows the evolution of the yield of each harmonic, integrated over a box around each harmonic (in divergence and energy) versus the time delay. It becomes obvious that on top of the even harmonics appearing with a changing time delay, there are also underlying modulations of the harmonic yield. The modulations have a periodicity of approximately 5.5 fs. However, the step size is not small enough to provide enough data points per oscillation to get a reliable estimate of these potential sub-cycle modulations.
Figure 5.7: Shown is the evolution of the yield (integration boxes around each individual harmonic) versus the time delay. The numbering refers to the harmonic order with respect to the IR.
Figure 5.8: This figure shows the generated harmonics versus the changing time delay between IR and UVA pulses. Note that the shown time delay only denotes a change in time delay, not an absolute delay. The step size was around 0.75 fs. Some of the even harmonics due to the secondary UVA field are present throughout the scan, whereas other even harmonics appear at varying time delays. The black dashed line shows the ionisation potential of krypton.

Figure 5.8 shows the results from a similar scan as shown in figure 5.5, but over a smaller range and with a smaller step size of 0.1°, which corresponds to a time step of on average 0.75 fs. The modulations of both the even and the odd harmonics for the delay range where the two pulses overlap are now better-resolved.

Figure 5.9 shows the line outs of the harmonics shown in figure 5.8 versus the time delay. The line outs have been integrated over the same integration box as the line outs presented in figure 5.7 for the scan with the bigger step size. Qualitatively, the two scans agree very well. The resolution in time is twice as good for the scan presented in figure 5.8, and the average periodicity of the modulations is now 2.0 fs compared to 5.5 fs in the previous scan. Clearly, the time resolution in the previous scan was not fine enough. Here, with a step size of approximately 0.75 fs and a periodicity of 2.0 fs we still have less than three data points per modulation. Even compared to the cycle time of the IR of around 2.6 fs the step size is too big to truly resolve sub-cycle modulations reliably. When changing the delay between the IR and the UVA, the total field (IR and UVA combined) repeats itself every 1.33 fs (cycle time of the UVA). Therefore, we would
IR and UVA in perpendicular polarisation

Figure 5.9: Shown is the evolution of the yield (integration boxes around each individual harmonic) versus the time delay. The numbering refers to the harmonic order with respect to the IR.

We expect the periodicity of the modulations observed here to be the same as the periodicity of the UVA field. This periodicity was also observed by Dudovich et al. in [137]. We therefore need to improve the time resolution (and achieve sufficient delay stability) in order to fully resolve these modulations.

Similar scans were also performed in different targets. The results in Xe and CO$_2$ are shown in figure 5.10 and show similar quantitative features to the Kr scans presented above, particularly in the case of CO$_2$, where the delayed onset of some of the even order harmonics is visible in the left panel. Note, however, that due to time constraints the harmonic generation was not optimised to the same degree as in the case of Kr. Further, the step size in time was significantly larger at around 7.5 fs. Both the Xe data and the CO$_2$ data was taken at a backing pressure of 1 bar. The Xe data shows some modulation towards the end of the scan (closer to $t_0$). These modulations are more significant in the case of CO$_2$, where the $I_p$ is very similar to that of Kr. Since these measurements have not been optimised in the same way as the Kr results (optimised generation to increase harmonic yield by optimising gas jet position with respect to focus, gas pressure, input
IR and UVA in perpendicular polarisation

![Graph showing evolution of harmonics and yield versus time delay for Xe and CO$_2$.](image)

Figure 5.10: Shown is the evolution of the harmonics on the left (integrated over divergence) and the evolution of the yield versus the time delay on the right (integrated over divergence and energy, integration box over each individual harmonic) for Xe and CO$_2$. The Xe results are shown in the top two panels and the CO$_2$ results are shown in the bottom two panels. The numbering refers to the harmonic order with respect to the IR.

Iris size and input power) and the step size in time is so large, further measurements are necessary to really compare the measurements in different species.

5.3.2 Time delay variation by translating return mirror

In this section I present the results using the setup shown in figure 5.3 where the delay between the two pulses is changed by translating the IR return mirror in the prism setup. Whilst the collinear setup presented in figure 5.2 guarantees good spatial overlap$^3$ between the IR and the UVA, the setup used here (cf. figure 5.3) comes with the added complication of having to achieve spatial overlap of the two pulses in the interaction region by careful alignment of the return mirrors and the second prisms. Additionally, the minimum temporal step size is larger than when rotating the calcite plate to scan the delay. The big advantage, however, is that we are practically unlimited in the range over which we can scan. As a result, we can scan well past the point of zero time delay between the two pulses in both directions without clipping the beam.

$^3$Good spatial overlap is guaranteed as long as the generating crystal is thin and spatial walk-off can be neglected.
The input powers into the experimental chamber after the waveplate and the iris (diameter 5.66 mm) for the measurements presented in this section were 210 mW in the IR and 29 mW in the UVA (13.8% of the IR). The UVA pulse duration of the UVA was measured using a crosscorrelation with the setup described in section 5.2 and figure 5.3 and was around 133 fs FWHM. This is consistent with the range of delays over which the even harmonics appear in the scan.\(^4\) The IR pulse duration was measured to be 55 fs. The corresponding intensities were \(6.0 \times 10^{13} \text{ W/cm}^2\) and \(3.4 \times 10^{12} \text{ W/cm}^2\) for the IR and UVA, respectively.

Figure 5.11 shows the evolution of the harmonic spectrum versus the time delay for the case where the IR and the UV are in parallel polarisation with respect to each other. This is achieved by using a dual waveplate that is a \(\lambda/2\) waveplate for the fundamental IR and a \(\lambda\) waveplate for the second harmonic. As a result, the relative polarisation of the IR and the UVA is rotated from perpendicular after the generating BBO to parallel after the dual waveplate.

The step size used for this scan was 2 \(\mu\)m, which corresponds to a step size in time of 13.3 fs. All even harmonics in the range of the MCP appear strongly around the zero time delay.

Figure 5.12 shows the line outs (integrated over integration boxes in divergence and energy) for all harmonics showing in figure 5.11. The harmonics are numbered according to their harmonic order. It is interesting to see that the yield of the odd harmonics goes down around \(t_0\) (point of zero time delay), where the even harmonics emerge. There is a number of possible explanations for why this might be the case. In a study involving the same wavelengths as used here, Dudovich et al. [137] demonstrated that a secondary field can in fact lead to a modulation of both the even and the odd harmonics. However, their measurements were performed with significantly higher temporal resolution. Further, they observed the yield of the odd harmonics to decrease and increase periodically, depending on the relative phase of the two fields, but did not show an overall decrease. In the measurements presented here, the yield of the odd harmonics decreases around \(t_0\), where the even harmonics appear, but does not show any strong modulation (although the time resolution here is considerably worse). It is further possible that the yield of the odd harmonics decreases around \(t_0\) because the total field generates harmonics with reduced conversion efficiency. The former possible explanation could be investigated by improving the time resolution in the experiment, whereas the latter possible explanation

\(^4\)The even harmonics are essentially a higher order crosscorrelation of the IR and the UVA.
Figure 5.11: This figure shows the generated harmonics versus the changing time delay between IR and UVA pulses using the prism line and the linear delay stage (cf. figure 5.3). The step size was around 13.3 fs. The black dashed line shows the ionisation potential of krypton.

could be investigated by computer simulations.

Note also that unlike in the scans presented in section 5.3.1, none of the even harmonics are present throughout the scan. This is due to the fact that the second setup using the prism line is more lossy, which results in the UVA in the target area being too weak to generate harmonics. Additionally, the waveplate introduces a loss, which results in a lower power in the IR and the UVA going into the experimental chamber. Unfortunately the IR input power into the setup is limited by self-focussing in the prisms, which leads to the formation of hot spots if the input power is too high.

Figures 5.13 and 5.14 show the results for the case where the waveplate is rotated such that the polarisation of the two fields is not affected, and hence perpendicular. The integration boxes were the same as for the results for parallel polarisation presented above. The even harmonics still appear, but when the two fields are perpendicularly polarised the even harmonics are considerably weaker and the odd harmonics are less affected. The weak revival of the even harmonic signal around a delay of 280 fs in figure 5.13 is due to a back reflection in the entrance window to the experimental chamber.
Figure 5.12: Shown is the evolution of the yield (integration boxes around each individual harmonic) versus the time delay. The numbering refers to the harmonic order with respect to the IR.
IR and UVA in perpendicular polarisation

Figure 5.13: This figure shows the generated harmonics versus the changing time delay between IR and UVA pulses using the prism line and the linear delay stage (cf. figure 5.3). The step size was around 13.3 fs. The black dashed line shows the ionisation potential of krypton. The weak revival of the even harmonic signal around a delay of 280 fs is due to a back reflection in the entrance window to the experimental chamber.
IR and UVA in perpendicular polarisation

Figure 5.14: Shown is the evolution of the yield (integration boxes around each individual harmonic) versus the time delay. The numbering is from top (1, lowest order harmonic visible on MCP to bottom (11, highest order visible), cf. figure 5.11.
5.4 Conclusion and Outlook

We successfully generated harmonics near the ionisation potential of the target with comparatively low input powers. The UVA even generated harmonics with input powers as low as a few tens of mW.

The presence of the secondary field breaks the symmetry of the total generating field, which leads to the generation of even harmonics. This behaviour was observed for both cases of relative polarisation between the two fields, perpendicular and parallel. The overall yield, and particularly the yield in the even harmonics, is larger in the case of parallel polarisation. It is also clear that the yield in the odd harmonics drops as $t_0$ is approached and the yield in the even harmonics rises.

We also observed that in the case where the UVA is strong enough to generate harmonics on its own, the onset of different orders of even harmonics differs significantly in time delay. Higher orders appeared later. Unfortunately in the measurements where the calcite plate was used to introduce and vary the delay between the two fields we were not able to reach or pass $t_0$ (in these measurements the IR was preceding the UVA). In the later scans, using the prism line and a translatable mirror to scan the delay, the delayed onset of the higher order even harmonics was not as pronounced. This could be due to the weaker UVA field in that setup.

In future experiments, this behaviour could be studied further by comparing the results of measurements with different combinations of IR and UVA input powers. In the setups used here the limiting factors were the clipping of the calcite plate at bigger delays and the fact that higher input powers led to self-focussing and hot spots in the prism setup. Improvements to the setup could include a larger calcite plate that allows for a larger angle of incidence before clipping or combinations of a number of calcite plates. Other birefringent materials with bigger changes in delay for comparable changes in angle of incidence could also be used. This would however affect the minimum temporal step size. Alternatively, calcite or quartz wedges (similar to those used in chapter 4) could be used to introduce a finely controllable time delay without clipping the beam. Combining the delay control of the translation stage with the delay control of the calcite plate in the same setup would allow for coarse alignment with the translation stage and fine control of the delay with the calcite plate, avoiding the issue of clipping.

The maximum input power into the prism setup could probably be increased with better beam quality. However, increasing the beam quality into the 1st BBO does not guaran-

\footnote{Compared to other HHG experiments, cf. e.g. chapter 4.}
tee a good beam profile after the generation of the second harmonic. The depletion of the IR beam is not necessarily evenly distributed across the beam profile and symmetrical.

Higher time resolution would be desirable in order to fully resolve and understand the sub-cycle modulations showing in the harmonic yield around \( t_0 \). This could be achieved with a piezo-driven translation stage in the prism setup.

Last but not least, we demonstrated that the prism setup that separates the beams after the generation of the second harmonic and allows for independent manipulation of the two fields provides sufficient pointing stability to maintain the spatial and temporal overlap to achieve repeatable delay scans. This is an important step towards the experiment presented in chapter 6, where independent control of the two involved fields is necessary for a number of reasons.
Chapter 6

Probing Controlled Dynamics
6.1 Background

This experiment is based on an idea first developed by Suren Sukiasyan, Misha Ivanov, Jon Marangos and Amelle Zaïr in the Laser Consortium at Imperial College London. In the following I introduce the idea behind the experiment and outline the work we have done so far to implement it, as well as describe the next steps. The theoretical work by S. Sukiasyan et al. is to be published in [140].

The aim of this experiment is to harness the signature of quantum path interferences (QPI, cf. section 2.5.3) to trace sub-femtosecond hole dynamics. The idea is to generate high harmonics and simultaneously, with a secondary laser field, drive a population transfer between two levels of the molecule under investigation. The change in population between the time the contributions of the short and long trajectories recombine, driven by the secondary field, leads to a change in the recombination probability. As a result, the relative contributions of the short and long trajectories to the overall harmonic yield change, and therefore the QPI contrast changes. For his calculations, Sukiasyan chose the CO$_2$ molecule for a number of reasons. CO$_2$ possesses a suitable transition that we can access with a wavelength that can be generated from the readily available IR laser source in our laboratory. It is further relatively well understood in theory and easy to handle in experiment.

Figure 6.1 illustrates the key aspects of this idea. A shows the tunable delay between the fundamental (800 nm in our case) to drive the harmonic generation and the third harmonic (267 nm, obtained by SHG and subsequent SFG, cf. section 2.3.1) to drive the population transfer. B shows an energy level diagram of the CO$_2$. The incident 3$\omega$ (UVC) pulses drive the Rabi oscillation between the HOMO and the HOMO$-2$ level of the molecule. The third harmonic closely matches the transition between these levels. C shows a schematic diagram of the harmonic order, and therefore the electron energy, versus the excursion time on the top. The bottom is a plot of the Rabi population transfer between the two involved energy levels (cf. section 2.6). By controlling the Rabi frequency, we can control the population within one optical cycle of the fundamental driving the harmonic generation, and hence the recombination probability of the electrons at recombination. Therefore, we can control the contributions of the short and long trajectories to the overall harmonic signal. Changing contributions of the different trajectories leads to a changing QPI contrast in the intensity scan. The red lines show a case where the population is in the same state for both the long and short trajectories for a specific harmonic order. In the case of the blue lines, the population is in different states at the recombination times of the short and long trajectories.
Figure 6.1: A The pulses at $\omega$ (for HHG) and $3\omega$ (to pump the population transfer) are separated by a tunable delay $\delta\tau$ and are perpendicularly polarised. B The population transfer in the CO$_2$ molecule between the HOMO and HOMO−2 levels can be pumped by the third harmonic of the 800 nm fundamental. C The top shows a schematic diagram of the harmonic order (or equivalently electron energy) versus the excursion time during one optical cycle of the fundamental field driving the HHG. The bottom shows a schematic of the population transfer between the HOMO and HOMO−2 levels. The red lines show the case where the population is in the higher state for both the short and long trajectories of a specific harmonic order. The blue lines show the case where the Rabi frequency is chosen in such a way that the population has changed to the lower level by the time the long trajectories recombine.
In the following, I briefly summarise the methods, results and conclusions of Suren Sukiasyan’s work on the theory for this experiment (to be published in [140]). In his simulations, Sukiasyan used a model two-electron diatomic system with a fixed internuclear distance. This \( \text{H}_2 \) like model has been adjusted such that the \( I_p \) of the model closely matches the \( I_p \) of the real \( \text{CO}_2 \) molecule and the ionic excitation energy of the transition between HOMO and HOMO−2 matches that of the \( \text{CO}_2 \) molecule. This has been achieved by selecting appropriate soft core potential parameters. The polarisation of the driving IR field is perpendicular to the molecular axis and the secondary UVC field is parallel to the molecular axis. Sukiasyan solved the system Hamiltonian:

\[
H = \sum_{i=1}^{2} [\hat{T}_i + r_i E + V(r_i)] + V_{ee}(r_1, r_2),
\]

by using the multi-configuration time-dependent Hartree (MCTDH) method (see [141] for details). This method is very efficient and allows for the analysis of the individual contributions of the involved subsystems to the overall harmonic yield (contributions of different ionic orbitals). This provides important insights into the feasibility of the experiment.\(^1\)

Figure 6.2 shows the results of the analysis of the contributions to the overall harmonic yield for the different channels involved in the harmonic generation. Since the treatment of high harmonic generation was limited to one spatial dimension in order to reduce the computational cost of the simulations, all harmonic emission is projected along the laser propagation direction and not integrated over angles (as is necessary in multi-dimensional treatments). The contributions to the overall harmonic yield can be divided into different channels depending on which states are involved in the ionisation and recombination of the active electron. Direct channels refer to the cases where the electron recombines to the same state it was ionised from. If the electron recombines to a different state to the one it was ionised from (at greatly reduced recombination probability), we speak of exchange channels. The direct channel contribution of the ionic ground state (HOMO) dominates the overall harmonic signal (blue line). The direct channel contribution of the ionic excited state (HOMO−2) is significantly weaker (red dashed line) and the contribution of the exchange channels for both ionic states is negligible (green dot-dashed line and yellow dot-dot-dashed line). The HOMO−1 does not contribute as, due to symmetry reasons, the dipole moment is zero with the driving laser field polarised perpendicularly to the molecular axis.

Figure 6.3 shows the simulated QPI scan for various UVC intensities. The UVC inten-

\(^1\)Note that experimentally we only have access to the overall harmonic yield, not the individual contributions.
Figure 6.2: This figure shows the contributions of the different channels to the overall harmonic yield for an IR intensity of $2 \times 10^{14}$ W/cm$^2$. Blue solid line: direct channel yield ionic ground state; red dashed line: direct channel yield ionic excited state; green dot-dashed line: exchange channel yield ionic ground state; yellow dot-dot-dashed line: exchange channel yield ionic excited state. The dotted black line shows the overall harmonic yield, dominated by the contribution of the direct channel ionic ground state. Figure courtesy of S. Sukiasyan [140].
Figure 6.3: IR intensity scan for harmonic 15 for the ionic ground state channel for various different UV intensities. Blue line (1): $I_{UV} = 0$; green line (2): $I_{UV} = 1 \times 10^{13}$ W/cm²; black line (3): $I_{UV} = 3 \times 10^{13}$ W/cm²; purple line (4): $I_{UV} = 9 \times 10^{13}$ W/cm². The red dashed line shows the QPI scan for a UV field detuned from resonance by 20% and an intensity of $I_{UV} = 1 \times 10^{13}$ W/cm² (same as green line). Figure courtesy of S. Sukiasyan [140].

UV intensities have been chosen such that a significant population transfer is guaranteed whilst the harmonic emission caused by the UVC field is kept negligible. The blue line shows the QPI scan (IR intensity scan) in the absence of a UVC field. The green line shows the QPI scan with a UVC intensity of $I_{UV} = 1 \times 10^{13}$ W/cm², which causes the modulations to disappear for a wide range of IR intensities. The modulations in the QPI scan reappear at a higher UVC intensity (black line, $I_{UV} = 3 \times 10^{13}$ W/cm²). The red dashed line shows the QPI scan at the same UVC intensity as the green line, where the modulations disappeared, but detuned from resonance by 20%. The modulations reappear, showing that the disappearance of the QPI modulations is in fact due to the population transfer driven by the UVC field.

Figure 6.4 shows a similar analysis to figure 6.3, but resolved for the individual contributions of the ionic ground and excited states. The blue and green lines show the contributions of the ground and excited states, respectively, in the absence of any UVC field. As can be seen by following the vertical dotted black lines, the QPI modulations of the two contributions coincide. The blue dashed line shows the combined total harmonic yield. The black and red lines show the contributions of the two states with an applied...
Figure 6.4: QPI for harmonic 15 for two different UVC intensities. $I_{UV} = 0$: blue line (1) and green line (2) show the contributions of the ionic ground and excited state channels, respectively. $I_{UV} = 3 \times 10^{13}$ W/cm$^2$: black line (3) and red line (4) show the contributions of the ionic ground and excited state channels, respectively. The dashed lines show the overall QPI scan (ground and excited states combined). The vertical black dotted lines mark the maxima of the ground state contributions at $I_{UV} = 0$. Figure courtesy of S. Sukiasyan [140].

UV field intensity of $I_{UV} = 3 \times 10^{13}$ W/cm$^2$. The black dashed line shows the combined harmonic yield. In the presence of the UV field, there is a significant phase shift between the contributions from the ground and excited state channels. Luckily, because the ground state channels dominate the overall harmonic yield, the QPI contrast does not wash out in the overall signal.
6.2 Experimental Setup and Methods

The setup described in this section represents the main engineering contribution of my PhD. I first describe the setup for the generation of the UV needed for the experiment before talking about the details of the setup for the control and manipulation of the different wavelengths and finally the delivery of the beams to the experimental chamber.

The setup for the generation of the third harmonic (UV) is shown in figure 6.5. The fundamental IR beam (shown in red) enters from the left. The arrows and crosshairs in the figure indicate the relative polarisations of the different beams. The first BBO ($\beta$-barium borate, 100 $\mu$m, $\Theta = 29.2^\circ$, CLaser) generates the second harmonic (UVA) in a type 1 phase matching scheme (see 2.3.2 for background). The second harmonic is therefore perpendicularly polarised with respect to the IR. Since the fundamental IR and the generated second harmonic have a time delay after the crystal, a calcite plate (0.6 mm, $\Theta = 45^\circ$, Newlight Photonics) is used to compensate for the delay before subsequent sum frequency generation in a second BBO crystal. The employed type 2 phase matching scheme in BBO2 generates the third harmonic (shown in purple) in parallel polarisation to the fundamental IR and perpendicularly to the second harmonic. Since the IR and the UV need to be perpendicularly polarised for the experiment, the polarisation of the IR is rotated later (see below for details). Note that the third harmonic could be produced perpendicularly to the IR and in parallel to the second harmonic if the crystal axes were rotated by 90$^\circ$. However, that implementation of the type 2 phase matching scheme results in lower conversion efficiency into the third harmonic. Unfortunately producing sufficient UV was one of the biggest challenges of this experiment (see results in section 6.3). It was therefore decided that having to rotate the polarisation of IR later on is the favourable option. After the generation setup, all three beams (wavelengths) travel to the beam separation and manipulation setup, which is described in the following.

The need for the IR and the UV beams to share a common beam path, and therefore common optical elements, presented a number of challenges. All common materials used for optical elements such as lenses, windows and wedges have significantly different refractive indices at the two wavelengths. Of course, lenses therefore also result in very different focal positions for the two colours. Reflective elements are not straightforward either. The ubiquitous silver mirror, with excellent reflectivity in the IR (typically > 97%), performs very poorly in the UV. Custom dielectric coatings with high reflectivity at both wavelength ranges are possible, but very expensive. UV enhanced aluminium mirrors are a decent compromise, with typical reflectivities between 85% and 95% for the UV (depending on polarisation, 45$^\circ$ AOI) and around 77.5% for the IR (45$^\circ$ AOI). Even though the UV enhanced Al mirrors are a significant improvement on the Ag mirrors,
their overall performance is still problematically low. This meant that minimising the number of reflections between the generation of the UV and the HHG target area became one of the most important design considerations.

There were numerous other design requirements. For example, independent intensity and polarisation control of the IR and the UV are necessary for the experiment. As a result, the IR and UV beams have to be spatially separated at some point in the setup. Further, due to the fact that I use SHG and subsequent SFG to generate the UV, I also need to get rid of the second harmonic. Unfortunately, no beam splitters exist that reflect the IR and the UV with high reflectivity and at the same time transmit the second harmonic. This would also still leave the problem of independent intensity and polarisation control unsolved.

Even if suitable beam splitters existed to separate the IR and the UV into different arms (the second harmonic could then be dumped with a second beam splitter if necessary), this approach would not be desirable due to the fact that the transmitted beam would be stretched by the substrate of the beam splitter. Further, the fact that the two beams would travel along very different paths would result in significant phase instabilities.

A setup comprising a number of prisms was therefore conceived, which allows the separation of all three wavelengths involved. The first version of that setup is shown in figure 6.6. The IR laser beam enters the third harmonic generation setup from the right. The first BBO generates the second harmonic. After the calcite plate compensated for the time delay between the fundamental and the second harmonic after BBO1. BBO2 (type 2, 40 μm, Θ = 55.5°, CLaser) generates the third harmonic (shown in purple) in a sum frequency scheme. The delay between the fundamental and the third harmonic after BBO2 will be compensated later in the prism setup. The arrows and crosshairs indicate the relative polarisation of the different wavelengths.
Figure 6.6: Schematic of the first version of the prism based setup. The fundamental IR beam enters from the right. BBO1 (type 1, 100 µm, Θ = 29.2°, CLaser) generates the second harmonic. The Calcite plate (0.6 mm, Θ = 45°, Newlight Photonics) is used to compensate for the time delay between the IR and the second harmonic after BBO1. The IR and the second harmonic then enter BBO2 (40 µm, Θ = 55.5°, CLaser). The three beams (IR, UVA, UVC) then pass under the pick-off mirror into the first and second prisms. The blue is blocked by a simple beam block. The return mirror sends the IR and UVC beams back at a slight angle, so after recombination in the first prism the pick-off mirror sends the beams towards the experimental chamber.

generated by sum frequency generation in the second BBO. All three wavelengths then pass through two large quartz prisms, which separates them in space. The second harmonic can then be blocked and both the IR and the UV return through the same prisms after being reflected back by a retro-reflector. The retro-reflector has been set up to return the beams higher than the incoming beams, so that they can be sent towards the experimental chamber by the pick-off mirror. This setup worked in principle, however it had a number of drawbacks that meant it was later replaced by a different setup. Due to the limited size of the available prisms, the separation of the beams was no bigger than around 2 cm, making independent control of intensity and polarisation difficult, as most optics mounts were clipping the other beam. Further, although the prism setup here purely serves the purpose of separating the different wavelengths to allow for independent control of various parameters, it of course also acts as a prism compressor or stretcher, depending on the apex separation and prism insertion. Using the same prisms for both wavelengths makes independent control of the pulse dispersion (and therefore pulse duration) impossible.

Alternatives to prism based setups were considered, such as Mach-Zehnder type interferometers, but ultimately discarded. The problem of separation of the UVC from the other wavelengths would remain, even if the fundamental intended for the experiment was kept separate in a different arm of the interferometer. Additionally, a different setup in the same laboratory uses a Mach-Zehnder interferometer (if for a different application), and it comes with a number of stability and synchronisation issues, even inside a vibrationally
isolated vacuum chamber, that I wanted to avoid. The prism setup described in the follow-
ing avoids some of those problems, but also comes with its own limitations.

Figure 6.7 shows the final incarnation of the full setup. The IR beam enters the setup from the right. The same sequence of crystals as described for the previous figure generates the third harmonic. All three wavelengths then pass underneath the pick-off mirror into the first prism. After the first prism, the UVA is blocked and the IR and the UVC continue to separate prisms. This allows for the dispersion of the IR and UVC arms to be adjusted individually. Optimisation of the UVC pulse duration (see section 6.3 for details) required a significantly smaller apex separation than for the IR, hence why the beams are crossing. Note that there are constraints on the locations of the prisms due to the physical dimensions of mounts and stages and due to the beam separation close to the first prism. The IR and the UVC are then reflected back at a slight angle by a simple return mirror (Ag for the IR and Al for the UVC arm). The IR return mirror is mounted on a motorised translation stage (Thorlabs Z825B DC servo actuator, 25 mm range, 0.2 \( \mu \)m smallest repeatable step size, 0.02 \( \mu \)m smallest achievable step size) that allows for the delay between the IR and the UVC to be scanned in a repeatable manner. The quarter-wave plate (QWP) just before the IR return mirror allows for the IR polarisation to be rotated. After recombination of the two beams in the first prism, the pick-off mirror sends the beams towards a periscope that brings the beams up to the height of the entrance window (CaF\(_2\), 1 mm thickness, normal incidence) to the experimental chamber. A setup consisting of a third BBO, a prism and a powermeter can be inserted into the beam path just before the experimental chamber in order to find the temporal overlap of the IR and the UVC. The axes of the third BBO are oriented in a way to predominantly phasematch the downconversion between the IR and the UVC into the UVA. The prism disperses the three wavelengths. The IR and the UVC are blocked, whereas the power of the UVA is recorded versus the position of the IR delay stage. This not only gives us the position of \( t_0 \) (the position of zero time delay), but also constitutes a downconversion crosscorrelation, which gives us a good estimate of the UVC pulse duration (the IR can be measured with a FROG available in the lab), see section 6.3 for details. This measurement was also used to optimise the UVC pulse duration by adjusting the prism apex separation and the prism insertion.

The optical setup inside the experimental chamber is rather simple (shown in figure 6.8). After entering the chamber through the CaF\(_2\) entrance window, the beam is reflected by a folding mirror (Layertec, dielectric mirror, >99% reflectivity at 800 nm, >99% reflectivity at 267 nm at 0° AOI). The beam is then focussed into the gas jet by a focussing mirror (Edmund Optics, UV enhanced Al, \( f = 203.2 \) mm(±2%), nominal >89% reflectiv-
Figure 6.7: Schematic of the final version of the setup for the generation of the third harmonic and for the time delay control between the third harmonic and the fundamental. The fundamental IR beam enters from the right. BBO1 (type 1, 100 µm, Θ = 29.2°, CLaser) generates the second harmonic. The Calcite plate (0.6 mm, Θ = 45°, Newlight Photonics) is used to compensate for the time delay between the IR and the second harmonic after BBO1. The IR and the second harmonic then enter BBO2 (40 µm, Θ = 55.5°, CLaser). The three beams (IR, UVA, UVC) then pass under the pick-off mirror into the first prism. The UVA is blocked, but the IR and the UVC continue to second prisms before being reflected by return mirrors. The return mirrors send the beams back at a slight angle, so after recombination in the first prism the pick-off mirror sends the beams towards a periscope. The IR return mirror is on a translation stage to control the time delay. The quarter-wave plate (QWP) in the IR arm is used to change the relative polarisation between the IR and the UVC. The periscope brings the beams up to the level of the entrance window of the experimental chamber. A third BBO crystal (BBO3, 20 µm, Θ = 44.3°, EKSMA) and a UVFS prism can be inserted into the beam to check the temporal overlap between the IR and the UVC (see text for details).
Figure 6.8: Schematic of the setup inside the experimental chamber. The beams (IR and UVC) enter from the left through the CaF$_2$ entrance window. After the folding mirror, the beams are focussed into the gas jet by a focussing mirror ($f = 208$ mm). The translatable breadboard is used to change the focal spot position with respect to the gas jet. The harmonic beam (and the IR and UVC beams) then enter the spectrometer chamber through a slit and a differential pumping tube. A spherical grating images the harmonics into the plane of an MCP detector assembly. The IR and the UVC beams are blocked by a zero-order block. A camera (not pictured) is then used to read out the signal from the phosphor screen.

Figure 6.9 shows the gas jet assembly inside the experimental chamber (left) and the available adjustments on the outside of the chamber (right). The gas pipe (Swagelok, 6 mm) enters the chamber via a feedthrough that allows for both height and lateral adjustments of the gas jet position. The gas pipe is fixed inside the chamber by means of an adjustable mount. This mount consists of two metal plates that are screwed together to compress an O-ring around the gas pipe. This fixes the gas jet position in place, but at the same time allows for the pipe to be pushed through the O-ring to adjust the height and as the angle through the mount can also change within a few degrees, the lateral position of the jet can be adjusted too. The design for this mount is closely based on a design previously used in the group. The actual gas jet is simply a Swagelok blank end cap with a 200 µm hole drilled through the centre.
Figure 6.9: Left: A photo of the gas jet assembly inside the experimental chamber. The gas pipe enters the chamber through a feedthrough at the bottom of the chamber. The gas pipe then passes through an adjustable mount. The adjustable mount fixes the gas jet in place, but allows its height and lateral position to be adjusted via controls on the outside of the chamber. The mount consists of two metal plates screwed onto each other. A small O-ring fitted around the gas pipe is squeezed in between them to fix the gas pipe in a way that keeps the gas jet still but allows it to be adjusted. The gas jet itself is simply a Swagelok end cap with a 200 µm hole drilled into it. On the left in the picture you can see the breadboard mounted on a motorised translation stage before the folding mirror and focussing mirror have been installed.

Right: Outside of the chamber, the height and the lateral position of the gas jet are adjustable via micrometer screws.
Because the signal levels were significantly lower in CO\textsubscript{2} than in Kr, higher backing pressures were needed. The required backing pressures resulted in the ambient pressures in the experimental chamber and the spectrometer chamber to go up to levels beyond where safe operation of the vacuum pumps and the MCP can be guaranteed. Therefore, a differential pumping jacket was installed around the gas jet. This jacket was developed by Allan Johnson and modified to fit the assembly used here. As a result, the possible backing pressures increased dramatically, well beyond what was necessary here. A schematic of the differential pumping jacket is shown in figure 6.10. The beam enters through a hole in the side window of the jacket from the left and interacts with the gas jet before exiting the jacket on the other side through a second hole. The gas jet inside the jacket is identical to the one used for the experiments in chapter 5 and described in more detail in section 3.3. The gas jet enters the differential pumping jacket through a feedthrough that allows for adjustments of the height and the lateral position of the gas jet. A 40 mm tube at the top of the jacket leads to a vacuum pump.
6.3 Experimental Results and Discussion

In this section I discuss the results obtained with the setup described in the previous section and with the objectives in mind that were outlined in section 6.1.

Figure 6.11 shows a typical UVC spectrum produced with the third harmonic generation setup described in the previous section. The spectrum is centred around 264 nm with a FWHM of 2.77 nm. The Fourier limited pulse duration is 37 fs (FWHM) assuming a Gaussian envelope and 27 fs assuming a sech² envelope. These numbers were calculated using the time-bandwidth product introduced in section 2.1 with the constraint factors listed in table 2.1.

The measured pulse duration of the UVC was typically around 300 fs just before entering the experimental chamber. This is significantly longer than the Fourier limit calculated above. This was partly caused by physical constraints in the alignment of the prism setup, which meant that the dispersion accumulated by the UVC pulses could not be fully compensated. It is also possible that higher order dispersion, which cannot be compensated by a prism compressor, contributed to the stretching of the pulses. The pulse duration was measured with the crosscorrelation setup described in figure 6.7. This measurement also determined the point of \( t_0 \), where the time delay between the IR and the UVC is zero. Note that the pulses still travel through some air and the entrance window after the point where the crosscorrelation is measured, so the delay stage position for \( t_0 \) is different inside the chamber. The air path and the entrance window were found to have a minimal impact on the UVC pulse duration in a crosscorrelation measurement performed inside the experimental chamber (under atmosphere). The pulse duration of the IR pulses was measured with a FROG after the prism setup to be 55 fs.

Figure 6.12 shows typical focal spots of the two beams. These were taken with a UV CCD camera (ehd imaging, EHD-704UV). The FWHM spot size of the IR (average of width and height) shown in the left panel is 75 µm. The focal spot shows significant structure, which is due to depletion and hot spots in the beam entering the experimental chamber. The UVC (centre panel) is very elongated. Its spot size (geometric mean of height and width) is 60 µm. The overlap of the two is shown in the panel on the right. Note that the overlap has been aligned such that the hole in the IR beam is avoided, as this gave the best results in the experiment.

The stated estimates of peak intensity in this section are based on the assumption of a Gaussian beam profile. Intensity estimates are made for the focal spot and therefore constitute an upper bound of the intensity in the interaction volume. The Rayleigh
Figure 6.11: Typical spectrum of the third harmonic generated with the setup described in section 6.2. The spectrum is centred around 264 nm (4.7 eV with a FWHM of 2.77 nm. Assuming a Gaussian shape, the Fourier limited pulse duration this spectrum can support is 37 fs (FWHM).

Figure 6.12: Typical beam profiles at the focus. Imaged with UV CCD camera (ehd imaging, EHD-704UV). The left panel shows the IR only. The centre panel shows the UVC only and the right panel shows the overlap between the IR and the UVC. The beam diameters for the IR and the UVC are (geometric mean of height and width FWHM) 75 µm and 60 µm, respectively.
length\(^2\) \(z_R\) using the focusing setup described in section 6.2 is approximately 1.6 cm for the IR and 4.8 cm for the UVC. At a distance of \(z_R\) from the focus, the peak intensity drops to half its value at the focus. The peak intensity of a Gaussian beam is given by 
\[ I_{\text{peak}} = \frac{2P}{\pi w^2}, \]
where \(P\) is the power and \(w\) the beam radius. The intensity estimates take into account the nominal reflectivity of the mirrors inside the chamber (after the point where the power measurement is made). Note that the Rayleigh lengths are 80 times (IR) and 240 times (UVC) larger than the gas jet nozzle diameter. With the beam sizes stated above and the beam aligned as close to the nozzle as possible without clipping, the Rayleigh lengths are significantly larger than the longitudinal thickness of the gas target, even with significant spreading of the gas after exiting the nozzle.

6.3.1 Delay Scans

In the following I present delay scans where the delay between the IR and the UVC has been scanned by means of translating the return mirror in the IR arm of the prism setup (cf. figure 6.7). All spectra presented in this section have been recorded with an integration time of 2 s and were averaged over 5 acquisitions.

First I present results obtained in krypton before moving on to the main target of this experiment, CO\(_2\). The ionisation potential of krypton is very similar to that of CO\(_2\) (14.00 eV and 13.78 eV, respectively), and krypton can be seen to be the ‘atomic partner’ of CO\(_2\). As discussed in section 2.5.2, there are some complicating factors with high harmonic generation in molecules. Comparing the recorded spectra of the molecule to spectra recorded with its ‘atomic partner’ can help disentangle those effects from the signatures of other phenomena we are looking for. Krypton does not have a transition that closely matches the energy of the third harmonic, so any effects due to a population transfer driven by the UVC field will not be present in the Kr measurements.

6.3.1.1 Krypton

Figure 6.13 shows the evolution of the harmonics versus the time delay in krypton for the case of parallel polarisation between the IR and UVC fields. The backing pressure was 1 bar. The IR power into the experimental chamber after the iris (diameter 8.12 mm) was 328 mW and the power in the UVC was 9.8 mW, 3% of the IR. The corresponding estimated maximum peak intensities are \(7.4 \times 10^{13}\) W/cm\(^2\) and \(7.9 \times 10^{11}\) W/cm\(^2\) for the IR and the UVC\(^3\), respectively. The harmonic spectra for each delay step were integrated

\(^2\)The Rayleigh length of a Gaussian beam is defined as \(z_R = \frac{\pi w^2}{\lambda}\), where \(w_0\) is the 1/e\(^2\) beam radius at the waist.

\(^3\)The intensity was calculated from the measured power, pulse duration and the spot size determined by taking the geometric mean of the height and width of the UVC spot (elongated spot). Note that the intensity was also calculated by integrating the measured beam profile and using it in conjunction with the measured power to generate an intensity profile. The values determined by both methods agree quite well (within 10%). The error in determining the height of the UVC spot (and therefore the intensity) is quite high since the FWHM of the height is only around 4 pixels.
Figure 6.13: This figure shows the generated harmonics versus the changing time delay between IR and UVC pulses in parallel polarisation. The step size in time delay was 13.3 fs. The black dashed line shows the ionisation potential of krypton. The yield was integrated over divergence. The integration box was chosen to be off-centre as the modulations showed better contrast there. Shown are harmonics 7 through to 17.

over a range of divergence off-centre of the harmonics due to the fact that the contrast of the modulations was biggest there (cf. figure 6.16). When integrating over the entire harmonics, the modulations were still visible but at reduced contrast (see comparison of the two different integration boxes below). Note that the relative change in harmonic yield is bigger for lower order harmonics.

Figure 6.14 shows the line outs of the harmonics shown in figure 6.13. Each data point is integrated over divergence and energy (divergence box is the same as in figure 6.13). The enhancement due to the secondary field around the zero time delay point varies dramatically. The yield increases by a maximum of 4.7% for the 11th harmonic (yellow line) and by only 1.1% for harmonic 17 (light blue line). The step size for the time delay is clearly too large to resolve the modulations fully, but the delay dependence is clear and the range over which the modulations can be seen is consistent with the measured pulse durations.

Figure 6.15 shows a line out of the same data, but using a different integration box,
Figure 6.14: This figure shows the harmonic yield (integrated over divergence and energy) versus the time delay. Integrated over off-axis integration box. Measurement in Kr, with IR and UVC in parallel polarisation. The numbering refers to the harmonic order.
IR and UVC in parallel polarisation

Figure 6.15: This figure shows the harmonic yield (integrated over divergence and energy) versus the time delay with an integration box over the entire harmonics. Measurement in Kr, with IR and UVC in parallel polarisation. The numbering refers to the harmonic order.

which encompasses the entire harmonics. The different integration boxes are shown in figure 6.16. With this integration box, the contrast of the modulations is worse for most harmonic orders. Interestingly, integrating over an integration box off-centre on the other side of the harmonics (in the divergence direction) shows even worse contrast than the integration box over the entire harmonics. The enhancement of the harmonic yield with this integration box varies between no visible enhancement at all for harmonic 17 (light blue line) to 6.4% for harmonic 7 (dark blue line).

The two different integration boxes are shown in figure 6.16. The left panel shows the off-centre integration box used for most line outs presented in section 6.3.1. The right panel shows the integration boxes over the entire harmonics. Note that the results obtained with the two different integration boxes show the same phenomena, but the off-axis integration box results in improved contrast. This is possibly due to overlap and beam quality issues. For example, note that the IR beam shown in figure 6.12 exhibits a hole and various hot spots, and that the elongated UVC beam has been aligned to overlap with the most intense part of the IR beam, which is off-axis. It is likely that the results obtained
Figure 6.16: Shown are the two different integration boxes used in the analysis of the results presented in this section. The left panel shows the off-centre integration boxes and the right panel shows the integration boxes over the entire harmonics.

using the off-axis integration box are more sensitive to intensity fluctuations and pointing fluctuations. Therefore, it would be beneficial to repeat the measurements with improved beam quality (see section 6.4 for suggestions on how the beam quality can be improved).

Figure 6.17 shows the evolution of the harmonic spectra versus the time delay for the case where the IR and the UVC are perpendicularly polarised. Note that the IR input power is now significantly lower at 196 mW after the iris due to the fact that the quarter-wave plate reduces the amount of power significantly when oriented to rotate the polarisation of the IR. This corresponds to an intensity of $4.4 \times 10^{13}$ W/cm$^2$. The UVC input power is not affected. To compensate for the reduced harmonic yield, the backing pressure was increased to 2.5 bar, compared to 1 bar for the previous scan at parallel polarisation.
Figure 6.17: This figure shows the generated harmonics versus the changing time delay between IR and UVC pulses in perpendicular polarisation. The step size in time delay was 13.3 fs. The black dashed line shows the ionisation potential of krypton. The yield was integrated over divergence. The integration box is the same as the one used for the case of parallel polarisation. Shown are harmonics 7 through to 17.
Figure 6.18: This figure shows the harmonic yield (integrated over divergence and energy) versus the time delay (off-axis integration box). The IR and UVC were in perpendicular polarisation. The numbering refers to the harmonic order.

Figure 6.18 shows the line outs of the harmonics shown in figure 6.17. The integration box over divergence and energy is the same as the off-centre integration box used for the case of parallel polarisation. The contrast of the modulations is now significantly reduced. This is interesting because the UVC field is now stronger in comparison to the IR field. Unfortunately, the results are not directly comparable because of the necessary change in backing pressure and therefore target density. Note also the slight shift in the centre of the delay dependence because the quarter-wave plate introduces a slightly different delay between the two fields in this orientation. The enhancement factor is now between no enhancement for harmonic 17 and 11% for harmonic 11 (yellow line). The enhancement for harmonic 11 is higher than in the case of parallel polarisation, but the overall signal is noisier, making it more difficult to distinguish the range of time delays around $t_0$ from the noisy background.
Figure 6.19: This figure shows the generated harmonics versus the changing time delay between IR and UVC pulses in parallel polarisation in CO\textsubscript{2}. The step size in time delay was 13.3 fs. The black dashed line shows the ionisation potential of krypton. The yield was integrated over divergence. The integration box is the same as the one used for the Kr measurements. Shown are harmonics 7 through to 17.

6.3.1.2 CO\textsubscript{2}

Figure 6.19 shows the evolution of the harmonic spectra versus the time delay for the case of parallel polarisation of the two fields in CO\textsubscript{2}. The backing pressure is 3.6 bar. The input powers are the same as in Kr for the case of parallel polarisation, 328 mW and 9.8 mW for the IR and UVC, respectively. The corresponding intensities are therefore also $7.4 \times 10^{13}$ W/cm\textsuperscript{2} and $7.9 \times 10^{11}$ W/cm\textsuperscript{2}, respectively. The integration box is the same off-centre integration box as for the previous scans in Kr. The effect of the UVC on the yield is smaller here than it was in the case of parallel polarisation in Kr. Overall, the yield of the harmonics is smaller in CO\textsubscript{2}, making it more difficult to get meaningful data.

The line outs of the harmonics are shown in figure 6.20. The effect of the UVC field is still clearly visible around $t_0$, but the contrast is significantly lower than in Kr. The same off-axis integration box was used. As before, the impact of the secondary field on the overall yield is bigger on the lower order harmonics. The enhancement varies between 0.8\% for the 7th harmonic (dark blue line) and 2.4\% for harmonic 11 (yellow line). The yield of harmonic 17 increases throughout the scan, but does not show any obvious signs
IR and UVC in parallel polarisation

Figure 6.20: This figure shows the harmonic yield (integrated over divergence and energy) versus the time delay (off-axis integration box). Data taken in CO₂, with the IR and the UVC in parallel polarisation. The numbering refers to the harmonic order.

...of enhancement around \( t_0 \).

Unfortunately, the signal in CO₂ for the case of perpendicular polarisation between the two fields is relatively poor. The evolution of the harmonic spectra versus the time delay for this case is shown in figure 6.21. As before in the case of perpendicular polarisation, the IR input power dropped to 196 mW. The backing pressure was increased slightly compared to the case of parallel polarisation to 4 bar.

Figure 6.22 shows the line outs for this case. There does still seem to be an effect of the secondary field around \( t_0 \), but the contrast is now very poor.

The delay scans presented above were able to show the presence of an effect of the secondary field on the harmonic yield around the zero time delay point. However, the step size was too big to resolve those modulations. The minimum achievable step size

\[ \text{Note that the manufacturer distinguishes between a minimum repeatable step size (0.2 \( \mu \text{m} \)) and the minimum achievable step size used here.} \]
IR and UVC in perpendicular polarisation

Figure 6.21: This figure shows the generated harmonics versus the changing time delay between IR and UVC pulses in perpendicular polarisation in CO$_2$. The step size in time delay was 13.3 fs. The black dashed line shows the ionisation potential of krypton. The yield was integrated over divergence. The integration box is the same as the one used for the Kr measurements. Shown are harmonics 7 through to 17.
IR and UVC in perpendicular polarisation

Figure 6.22: This figure shows the harmonic yield (integrated over divergence and energy) versus the time delay (off-axis integration box). Data taken in CO$_2$. IR and UVC in perpendicular polarisation. The numbering refers to the harmonic order.
Figure 6.23: This figure shows the generated harmonics versus the changing time delay between IR and UVC pulses in perpendicular polarisation in CO$_2$. The step size in time delay was 0.34 fs. The black dashed line shows the ionisation potential of krypton. The yield was integrated over divergence. Shown are harmonics 7 through to 17.

of the translation stage used to scan the delay is 0.05 µm, which corresponds to a step size in time of 0.34 fs.

Figure 6.23 shows the result of a delay scan at the smallest achievable step size of the translation stage over a small range around the point of zero time delay between the two fields. The scan was performed with the two fields in perpendicular polarisation. The target gas was CO$_2$ at a backing pressure of 2 bar. The input powers were 226 mW in the IR and 12.6 mW in the UVC. The corresponding intensities are $5.1 \times 10^{13}$ W/cm$^2$ and $10.2 \times 10^{11}$ W/cm$^2$, respectively. There is clearly a modulation of the harmonic yield visible for most harmonic orders. However, it is difficult to tell whether this modulation is systematic or due to fluctuations.

The line out of the delay scan shown in figure 6.23 is shown in figure 6.24. The modulations in the harmonic yield are very noisy as this delay scan only includes delays around $t_0$ and therefore even very small changes in overlap (both spatially and temporally) have a relatively large impact on the yield.
IR and UVC in perpendicular polarisation

Figure 6.24: This figure shows the harmonic yield (integrated over divergence and energy) versus the time delay. The numbering refers to the harmonic order. The IR and the UVC were perpendicularly polarised. The step size in time was 0.34 fs.
A Fourier analysis of the line outs presented in figure 6.24 provides more insight. The result for the different harmonic orders is shown in figure 6.25. Clearly, the signal is very noisy, but there is a dominant peak around the wavelength\(^5\) of the third harmonic. This peak is particularly dominant for harmonics 13 and 15. The third harmonic has a cycle time of around 0.9 fs, so at a step size of 0.34 fs, we are sampling above the minimum sampling rate required by the Nyquist theorem for faithful reproduction of the signal. The timing stability of the delay line is questionable, as the stability measurements presented in section 6.3.3 show.

6.3.2 Comparison of measurements with and without the UVC field

In the previous section we looked at measurements where both the IR and the UVC fields were present, and the delay between the two was varied. The harmonic signal was clearly dependent on the delay, but it is difficult to compare the effect of the additional UVC field on different harmonic orders. In this section, harmonic spectra recorded in presence and in absence of the UVC field at fixed delays are compared. This allows a comparison of the effect of the secondary field on different harmonic orders and on the on-axis and off-axis (i.e. short and long trajectory) contributions.

All measurements shown in this section are integrated over 2 s and averaged over 10 acquisitions. The backing pressure in CO\(_2\) was 4 bar, unless otherwise stated. The relative time delays stated refer to the time delays used in the delay scans presented in

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\(^5\)Note that the frequency axis resulting from the Fourier transformation has been converted to wavelength for easier comparison with the laser wavelengths involved in the experiment (strong field physicists are more accustomed to thinking in wavelengths than frequencies).
the previous section. The two fields were perpendicularly polarised for all measurements presented in the following. The IR input power was 280 mW, corresponding to an intensity of $6.3 \times 10^{13} \text{W/cm}^2$. The UVC power was 8.0 mW, corresponding to an intensity of $6.4 \times 10^{11} \text{W/cm}^2$.

Figure 6.26 shows a comparison of the harmonic yield in absence and in presence of the UVC field. The upper panel shows a comparison of the normalised yields (both spectra normalised individually with respect to their maximum). The lower panel shows the integrated yields (integrated over divergence, same integration box for both cases). The blue curves show the spectra obtained with the IR field only and the red curves show the spectra in the presence of the UVC field. These spectra were taken at a fixed delay between the two fields of 26.7 fs.

Looking at the upper panel, we can see that in the presence of the UVC field some harmonic orders are enhanced relative to others. The long trajectory contributions that are visible for the lower order harmonics are not affected. The lower panel shows that overall, the harmonic yield has increased in the presence of the UVC field. Again, it is clear that the long trajectories have not been affected by the additional field. The long trajectory contributions of the lowest harmonic order shown are highlighted in the lower panel by black circles.

Figure 6.27 shows the comparison of the two cases at a fixed relative delay between the two fields of 60.0 fs. Looking at the upper spectrum, different harmonic orders are again enhanced by different amounts. Overall, the effect of the UVC field is very similar to the previous case of a delay of 26.7 fs. However, looking at the lower panel, the increase in the yield of the harmonics with the UVC field is smaller now than for the case of a smaller time delay.

Figure 6.28 shows the comparison of the two cases at a delay of 93.4 fs. At the bigger delay, the effect of the UVC field on the yield of the harmonics is smaller, as expected. Interestingly, harmonic 15 (23.7 eV) is essentially unaffected, whilst harmonic 13 and 17 increase in harmonic yield.

Figure 6.29 shows the comparison of the two cases at the same delay as shown in figure 6.26 (26.7 fs), but at a backing pressure of 2 bar instead of 4 bar of CO$_2$. Note that this measurement was taken on a different day to the measurements above, but has been repeated at various different delay positions without a qualitative change of the effect of the secondary field. The IR input power for this measurement was 197 mW, corre-
IR and UVC in perpendicular polarisation

Figure 6.26: This figure shows a comparison of the harmonic yield (integrated over divergence) at a fixed time delay between the IR and UVC fields (26.7 fs) in absence and in presence of the UVC field. The top panel shows the normalised yield (both spectra individually normalised with respect to their maximum). The bottom panel shows the harmonic yield for the two cases, integrated over the same integration box. The blue curves show the harmonic yield generated with the IR field only. The red curves show the harmonic yield in the presence of both fields. The black circles in the lower panel highlight the long trajectory contributions to the lowest harmonic order shown.
IR and UVC in perpendicular polarisation

Figure 6.27: This figure shows a comparison of the harmonic yield (integrated over divergence) at a fixed time delay between the IR and UVC fields (60.0 fs) in absence and in presence of the UVC field. The top panel shows the normalised yield (both spectra individually normalised with respect to their maximum). The bottom panel shows the harmonic yield for the two cases, integrated over the same integration box. The blue curves show the harmonic yield generated with the IR field only. The red curves show the harmonic yield in the presence of both fields.
Figure 6.28: This figure shows a comparison of the harmonic yield (integrated over divergence) at a fixed time delay between the IR and UVC fields (93.4 fs) in absence and in presence of the UVC field. The top panel shows the normalised yield (both spectra individually normalised with respect to their maximum). The bottom panel shows the harmonic yield for the two cases, integrated over the same integration box. The blue curves show the harmonic yield generated with the IR field only. The red curves show the harmonic yield in the presence of both fields.
IR and UVC in perpendicular polarisation

Figure 6.29: This figure shows a comparison of the harmonic yield (integrated over divergence) at a fixed time delay between the IR and UVC fields (26.7 fs) in absence and in presence of the UVC field. The top panel shows the normalised yield (both spectra individually normalised with respect to their maximum). The bottom panel shows the harmonic yield for the two cases, integrated over the same integration box. The blue curves show the harmonic yield generated with the IR field only. The red curves show the harmonic yield in the presence of both fields.

The harmonic yield is influenced by the presence of the UVC field, and more importantly, different harmonic orders are affected in varying degrees. Further, the effect of the secondary field on the long trajectory contributions is different to that of the short trajectory contributions. However, in light of the significant fluctuations in both input power and harmonic yield (see next section), the effect of the secondary field is expected to be small.
UVC field on the harmonic yield is still relatively small. Although the largest enhancement factor was 1.3, this was only the case in one of the measurements (see figure 6.26). All other measurements presented in section 6.3.2 show significantly smaller enhancement factors, with the smallest enhancements close to the fluctuations of harmonic yield measured in the following section. Nevertheless, the presence of an effect of the UVC field on the generation process in some of the measurements integrated over 2 s and averaged over 10 acquisitions suggests that the effect is real. It is not surprising that the effect is smaller (or non-existent) at delays far away from $t_0$. However, further measurements with longer integration times and averaged over a larger number of acquisitions are necessary to reinforce this conclusion. The measurements could also be taken at a larger number of different delays near $t_0$ in order to establish whether a larger effect exists at other points where the overlap between the two fields is good. There was an issue with repeatability of these measurements since the delay calibration was not precise enough to achieve similar results on successive days at nominally identical delays. Again, further measurements are necessary to establish whether repeatability is achievable on the same day (e.g. with measurements separated by a few hours). The long trajectory contributions are very small and only present at lower order harmonics, making observations regarding the effect on these trajectories even more difficult.

### 6.3.3 Repeatability and stability tests

The measurements presented in the previous sections suffered from a number of sources of instabilities. This section aims to put numbers on the most important sources of fluctuations.

Figure 6.30 shows a power stability measurement for the IR (red, left $y$-axis) and the UVC (blue, right $y$-axis). The $x$-axis shows the number of the power measurement. With approximately two power measurements per second, this figure shows the power fluctuations over approximately 200 s. The mean of the IR power measurements is 291.3 mW with a standard deviation of 0.76 mW. The mean of the UVC measurements is 3.19 mW with a standard deviation of 0.15 mW. The fluctuations relative to the mean power are significantly larger for the UVC (standard deviation 4.7% of mean power for UVC, but only 0.3% for the IR). This is to be expected, since the UVC is generated from the IR through a series of two second-order nonlinear processes, where relatively small changes in input translate to relatively large changes in output. Here, the fluctuations relative to the mean powers differ by a factor of approximately 16 between the IR and the UVC, which makes sense for two consecutive second-order nonlinear processes ($16 = 2^4 = (2^2)^2$).

Figure 6.31 shows the fluctuations in harmonic yield (integrated over a box around the
Figure 6.30: Shown are the power stability measurements of the IR (red curve, left \(y\)-axis) and the UVC (blue, right \(y\)-axis). The mean of the IR power for this measurement is 291.3 mW with a standard deviation of 0.76 mW. The mean of the UVC measurements is 3.19 mW with a standard deviation of 0.15 mW.
Figure 6.31: This figure shows the fluctuations in harmonic yield over 50 acquisitions. Each acquisition had an integration time of 2 s. The solid lines show the stability measurement for IR only. The dashed lines show the stability measurement for the IR and UVC at perpendicular polarisation at a fixed delay of −20 fs. The target was CO₂ at 2 bar backing pressure.

harmonics in divergence and energy) versus the number of measurement for a fixed delay of −20 fs. Each measurement was integrated over 2 s, so this plot shows the fluctuations over 100 s. The solid lines show the case of harmonics generated by the IR field only. The dashed lines show harmonics generated with the IR field and the UVC field in perpendicular polarisation. The input powers were 197 mW (corresponding intensity 4.4 × 10¹³ W/cm²) and 14.5 mW (corresponding intensity 11.7 × 10¹¹ W/cm²) for the IR and the UVC, respectively. The target was CO₂ at a backing pressure of 2 bar. The largest ratio of standard deviation to mean harmonic yield for the IR only case was 3.1% for harmonic 17 (factor of 12 larger than power fluctuations of IR). In the case where both fields were present the largest ratio was 2.4% for harmonic 15 (factor of 9 larger than power fluctuations of IR). The UVC field results in an overall enhancement of the harmonic yield, but the large fluctuations of the UVC power seemingly do not translate into larger absolute fluctuations of harmonic yield. As a result of the increased harmonic yield, but comparable absolute fluctuations in harmonic yield, the relative fluctuations of harmonic yield are smaller in the presence of the UVC field.

Figure 6.32 shows a comparison of two delay scans recorded under identical conditions,
IR and UVC in perpendicular polarisation

Figure 6.32: Comparison of two delay scans (one in solid lines, the other in dashed lines) with the same conditions and same scan range and step size, performed immediately one after the other. The target was CO$_2$ at 2 bar backing pressure, with the IR and the UVC fields polarised perpendicularly. The IR input power was 281 mW and the UVC input power was 11.4 mW.

immediately one after the other. The first scan is shown in solid lines and the second scan is shown in dashed lines. The harmonics were generated in CO$_2$ at 2 bar backing pressure. The harmonic yield was integrated over both divergence and energy. The same integration boxes over the entire harmonics were used for both scans. The IR input power was 281 mW (corresponding intensity $6.3 \times 10^{13}$ W/cm$^2$) and the UVC input power was 11.4 mW (corresponding intensity $9.2 \times 10^{11}$ W/cm$^2$), with the two fields perpendicularly polarised with respect to each other. The step size in time was 6.7 fs.

There are some significant differences in the modulations between the two scans, especially for higher order harmonics (harmonics 13 to 17, purple, green, light blue curves). Qualitative agreement is better for the lower order harmonics (7 to 11, blue, orange and yellow curves). The agreement in terms of periodicity is best for the lower order harmonics for time delays between $-200$ fs and 0 fs.
Figure 6.33: Comparison of a delay scan with the UVC field (solid lines) and in absence of the UVC field (dotted lines). The target was CO$_2$ at 2 bar backing pressure, with the two fields perpendicularly polarised in the case of the solid lines. The IR input power was 281 mW and the UVC input power was 11.4 mW.

Figure 6.33 shows a comparison of the first scan in figure 6.32 and a scan without the UVC field (i.e. the UVC field is blocked but the delay is still scanned as this is done by scanning the IR return mirror). The difference is very clear for the lower order harmonics (7 to 11), where the modulations largely disappear in the absence of the UVC field (dotted lines). The higher order harmonics (13 to 17) show significant modulations or fluctuations even in absence of the UVC field. This also explains why the agreement of the repeat scan with the original scan is better for lower order harmonics (cf. figure 6.32).
6.4 Conclusion and Outlook

The results presented in the previous section are a promising step towards the realisation of the experiment introduced in section 6.1. A clear dependence of the harmonic yield on the time delay between the IR and the UV field has been shown. Further, the presence of the secondary field affects the yield of different harmonic orders differently. The long trajectory contributions are also affected differently than the short trajectory contributions. However, the fluctuations in input power and harmonic yield make it difficult to draw any definite conclusions. Additionally, the instabilities in pointing and therefore the overlap between the IR and UV focal spots will have a significant impact on the ability to observe the dynamics we are looking for.

The fact that the depth of the modulations depends strongly on the integration box, even for harmonic orders where no long trajectory contributions are visible, suggests that the effect of the secondary field on the ionisation dynamics plays a significant role. Further, the contrast of the modulations is worse for the case of perpendicular polarisation. In the case of parallel polarisation, the secondary field has a larger effect on the amplitude of the overall field. Since this led to an improved contrast of the modulations compared to the case of perpendicular polarisation, this suggests that the secondary field is mainly affecting ionisation, rather than the population of the cations. In the case of CO$_2$, if we were in the right regime for an efficient population transfer as predicted by the theory described in section 6.1, we would expect a stronger effect for the case of perpendicular polarisation.

Comparing the intensities used by S. Sukiasyan in the simulations (cf. section 6.1) to the UVC intensities achieved in the experiment explains why we did not see a strong signature of population transfer in CO$_2$. The estimated intensities in the experiment are two orders of magnitude smaller than the values used in the simulation. Lower intensities result in a slower population transfer. If the difference in intensity is not too big, the slower population transfer would simply result in reduced contrast. Alternatively, one could investigate other harmonic orders, where the excursion times of the short or long trajectories match slower population transfer frequencies. However, at intensities two orders of magnitude lower, the population transfer is too slow for any signature of the change in cation population to be detectable with our apparatus.

In order to take this experiment further, a number of improvements to setup and methodology can be made.

As we have seen, the major limiting factor in the realisation of this experiment is the
availability of sufficient UV intensity in the target area. Ultimately the conversion efficiency from the fundamental IR beam at around 800 nm to its third harmonic around 267 nm is the bottleneck. Together with the high losses due to the low reflectivity of even UV enhanced aluminium mirrors, the necessary intensities could not be reached in the target interaction area. Direct third harmonic generation is not very efficient due to the weak third-order susceptibility of the available non-linear media. The highest reported conversion efficiency for direct third harmonic generation with an output in the UV (51 nm, 8 mJ IR input) is 6% [142]. Schemes that use second harmonic generation and subsequent sum frequency generation (as was used in the experiment described in this chapter, see section 6.2) achieve slightly better efficiencies of up to around 10% [143–145]. This is consistent with the conversion efficiencies achieved in our setup. These conversion efficiencies are also in line with what commercial systems can produce.

However, there are a number of ways in which the maximum output power in the UV could be improved in our setup without changing the scheme used to generate the third harmonic. The key is to increase the IR intensity in the crystals without damaging the crystals. This could be achieved by improving the beam profile of the fundamental beam. With a more Gaussian beam profile, the input power could be increased to higher values before causing hot spots that damage the crystals. The spatial profile of the input pulses could be improved by using a vacuum spatial filter or by using a deformable mirror similar to the one described in section 4.2. Even though these improvements would be comparatively simple, the benefits are likely to be quite small, not least because the maximum input power into the setup is further limited by self-focussing in the prism setup used to separate and manipulate the IR and the UV separately. It is hard to estimate exactly by how much improvements in beam quality would allow us to increase the input power into the setup without causing damage. Based on experience with different test beams in the setup with varying beam quality I estimate that an additional 50% in UV intensity is possible if the beam quality can be improved significantly. The prism setup is also the reason why we do not focus into the generation crystals. The IR and the UV beams would exit the third harmonic generation setup with different divergences, which would make the subsequent handling of the beams and the delivery to the target area very difficult.

Alternatively (or in addition), the crystals and prisms could be replaced with bigger optics. The bigger clear aperture would allow us to increase the input energy whilst keeping the intensity below the damage threshold and the critical intensity for self-focussing. To some extent, the improvement factor of this method is only limited by the size of the optics available. However, this becomes very expensive very quickly. The BBO crystals
used in the generation setup are already the largest standard diameter available. Larger prisms with equal surface quality are also only available as custom optics.

There are alternative third harmonic generation schemes that provide higher conversion efficiencies but require expensive specialised optics. One such scheme is described in [146]. Kardaš et al. use a custom ‘sandwich’ crystal that combines the SHG step, the compensation of temporal and spatial walk-off and polarisation management and the SFG step into one compound optical element. They optimised the individual components of their compound optical element by solving the unidirectional pulse propagation equation [147]. Their optimised compound optical element achieved a conversion efficiency from the fundamental 1040 nm laser to the third harmonic of 31%. Their tools can be used to design similar optics for applications at different wavelengths, e.g. suitable for our needs. However, their input pulses were 190 fs in duration, so relatively thick crystals could be used without restricting the phase-matching bandwidth too much. In our case, thinner crystals would have to be used, which would reduce the conversion efficiency. Without simulations of this technique for our pulse parameters it is not possible to say whether we could expect any significant improvements in the conversion efficiency in our case.

Another alternative that is capable of providing far more than the required amount of UV are optical parametric amplifiers. For example the Artemis laser facility at the Rutherford Appleton Laboratory in Oxfordshire uses a HE-TOPAS from Light Conversion that can provide in excess of 100 µJ of UV at 250 nm, which is about ten times what we can currently deliver to the target area in our lab. As long as the IR and the UV can be delivered to the target area with relative stability, access to this or other similar facilities would be a big step forward for this kind of experiment. The intensity at Artemis would still be one order of magnitude lower than that used by Sukiasyan in the simulations, but of the suggested improvements presented here this is by far the most significant increase in available UV intensity. Since the results achieved here are already promising, a tenfold increase in UV intensity would probably lead to very interesting further results.

Besides improvements to the conversion efficiency, improvements to other parts of the setup are also possible. Currently, the mounts for the prisms are quite cumbersome because they need to provide a whole range of adjustments for the alignment of the setup. Custom mounts would allow the prism setup (where the IR and the UV travel along separate beam paths) to be more compact and would therefore minimise phase and pointing jitter between the two beams. Custom mounts would also remove some physical constraints on the independent alignment of the IR and UV beam paths. Ultimately, a fully
boxed or even vacuum system would decrease the stability problems arising from the non-collinear part of the setup even further.

Further, due to the physical dimensions of the prism mounts, there were some constraints on how the prisms could be arranged on the optical table, which lead to an increased pulse duration of the UVC. However, even without those constraints, it may not be possible to compress the UVC pulses down to the Fourier limit due to higher order dispersion. The potential for improvement is large though (the measured pulse duration was around a factor of 10 larger than the Fourier limit).

The current setup uses mostly UV enhanced aluminium mirrors. Those mirrors are superior to silver mirrors in terms of reflectivity in the UV, but far from ideal. Silver mirrors also limit the IR power delivered to the target area. More custom dielectric mirrors specifically designed for the angles of incidence and the IR and UV wavelengths used in this experiment would greatly increase the energy in both beams at the target. Replacing all UV enhanced aluminium mirrors in the current setup with custom dielectric mirrors would increase the UV intensity delivered to the target by around 80%. Currently, the setup has been designed to minimise the number of reflections needed to deliver the beams to the target. With more efficient mirrors available, different configurations might prove beneficial.

As discussed in section 2.5.2, structural interferences can play a significant role in HHG from molecules. Since the CO$_2$ molecules in this experiment were not aligned, the signal was an average over all orientations in the randomly oriented sample in the interaction volume. Since the coupling of the UV field to the transition between the HOMO and HOMO$-$2 in CO$_2$ is polarisation dependent, aligning the molecules accordingly would increase the contrast of the modulations we are looking for. Note that the average coupling efficiency in a randomly aligned ensemble of molecules is reduced by 50% compared to a perfectly aligned sample. The alignment of the molecules can be achieved by laser alignment. For example, Vozzi et al. [148] use a strong non-resonant ultrashort laser pulse for dynamic alignment of the linear CO$_2$ molecules in their investigation of structural interferences (more details on dynamic alignment of molecules in [149,150]).

As was already hinted at in the introduction to this chapter (cf. section 6.1), the principle behind this experiment is not limited to the case of CO$_2$ but applicable to any system were appropriate energy levels and laser fields can be found. In the future it would be interesting to extend this investigation to N$_2$ and maybe other suitable species. In N$_2$ the generating field would be 1600 nm and the population transfer would be driven by an
800 nm field.
Chapter 7

Conclusion and Outlook

The experiments presented in this thesis explored various aspects of the combination of different fields to manipulate and control the HHG process. The different experiments took advantage of combinations of readily available wavelengths and combinations with new wavelengths to enable control over the ionisation step, trajectory control and population control of the cation. This chapter briefly summarises the most important results and discusses the implications of the results for future experiments.

The experiment presented in chapter 4 demonstrated a very simple and cost effective way to achieve frequency tunable high-order harmonics. Of course, tunable HHG from an optical parametric amplification (OPA) based system or using a dazzler (commercial acousto-optical dispersive system) is possible, but comes with a number of drawbacks compared to the method presented in chapter 4. Our setup provides a very inexpensive way to retrofit the capability to tune the central wavelength of the generating laser field and therefore that of the harmonics. Tuning the central wavelength by simply changing the insertion of wedges made of birefringent crystal is technically very easy to achieve. Of course, the dazzler can also be retrofitted to manipulate the field of the pulses. Typically, dazzlers are fitted before the amplification stage in the CPA chain due to their comparatively low damage threshold (e.g. Fastlite states a maximum input energy of 30µJ for the HR 800 dazzler). There are a huge number of different versions of the dazzler for different wavelength ranges, repetition rates and achievable resolutions. Our approach is compatible with any wavelength range (within the transparency range of the birefringent material) and can easily be placed after the amplification stage but before the compressor to handle very high pulse energies, and works independently of the repetition rate. Our setup is in principle compatible with the generation of few-cycle pulses, for example by coupling the synthesised field into a hollow core fibre, as presented in [66].

The field synthesis setup could be used as an alternative to the more complex setup
proposed in [151] and partly implemented in [152] to introduce a frequency shear for a technique called extreme ultraviolet spectral phase interferometry for direct electric field reconstruction (XUV-SPIDER). This technique allows for single shot characterisation of attosecond pulses.

In the experiment presented in chapter 5, we successfully generated harmonics near the ionisation potential of the target, both with the IR and the UVA fields as driving fields. When combining the two fields, the symmetry is broken and even-order harmonics are generated. We found that when scanning the time delay between the IR and the UVA pulses, the onset of different even-order harmonics differed in time delay.

Usually in two-colour experiments of this kind, the fundamental IR field is used to generate the harmonics and the second harmonic field in the UVA is used to control and manipulate the trajectories. Since the UVA field in the experiments presented here is strong enough to generate harmonics on its own, we are in an interesting regime where both fields are generating harmonics and both fields are influencing the trajectories. The generation of harmonics by the UVA field is comparatively efficient due to the shorter wavelength of the driving field. By working to reduce the UVA pulse duration, the cut-off could easily be extended towards higher photon energies. The UVA is interesting for time-resolved measurements involving the short and long trajectories, because the excursion times are truly in the attosecond regime (cycle time around 1.3 fs and cut-off excursion time around 865 as for a 400 nm field). Additionally, at the shorter wavelength of the UVA, a smaller bandwidth (in wavelength) is necessary for short pulses.

Finally, the regime of interaction changes with the generation of harmonics from the UVA, where the barrier oscillations are faster. HHG from the UVA has not been studied as comprehensively as the ubiquitous harmonic generation from the IR. Therefore, in order to further our understanding of near-threshold high harmonic generation with shorter wavelengths, experiments giving insight into trajectories and phase accumulation that have long been done in the IR should be revisited in the UVA.

Here, the experiment discussed in chapter 5 presented an important stepping stone towards the UVC experiment presented in chapter 6. The UVA is easier to handle than the UVC, and was used here to benchmark the performance of the setup before moving on to the more challenging UVC experiment.

The results presented in chapter 6 represent a significant step towards the realisation of the experiment introduced in the introduction to that chapter, but more work is neces-
sary in order to fully implement the idea. We have shown that the secondary UVC field affects the yield of different harmonic orders and of the different trajectory contributions differently. The observed effects are delay dependent and we have demonstrated that the setup designed and built by myself is in principle capable of the proposed experiment. The major limiting factor in the realisation of the experiment was the UVC intensity, and a number of improvements to the setup and alternative setups have been discussed in section 6.4.

In principle, a flattop intensity profile in the UVC would be ideal to ensure a constant frequency of the population transfer across the interaction volume, although this would be very difficult to implement in practice and would result in further significant losses in UVC power. Martin Arnold, a former student in the group, worked on the generation of temporal and spatial flattops in the IR during his PhD. The techniques used in his work are in principle transferable to the UVC wavelength range.

A big challenge with this experiment and in designing the setup is the fact that the UVC is relatively hard to handle, at least without specialised (and therefore expensive) optical components. The fact that the IR and the UVC, so the fundamental and the secondary field, are so far apart in the optical spectrum but share a common path and therefore optics in most of the setup, proved difficult. However, the principle of the experiment is transferable to other targets and wavelengths that might be easier to handle. As previously mentioned, N$_2$ is a candidate where the harmonic generation could be driven by a 1600 nm field and the population transfer could be driven by an 800 nm field. When selecting possible targets and the wavelength combinations that go with those targets, care must be taken as to not violate the underlying assumptions gone into the derivation of the Rabi oscillations. Other wavelength combinations might be easier to handle and prove less challenging in terms of generating sufficiently strong fields.
Chapter 8

Bibliography


