ATTOSECOND TRANSIENT ABSORPTION SPECTROSCOPY:
CONTROLLING EXTREME ULTRAVIOLET LIGHT-MATTER
INTERACTION

A thesis submitted to attain the degree of
DOCTOR OF SCIENCES of ETH ZURICH
(Dr. sc. ETH Zurich)

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List of Symbols and Acronyms

Symbols

\( A(E) \) absorbance
\( N \) atomic number density
\( E_{\text{gap}} \) band-gap energy
\( f_{\text{CEO}} \) carrier-envelope-offset frequency
\( \Phi_{\text{CEP}} \) carrier-envelope phase
\( F_{\text{critical}} \) critical field strength
\( \rho(t) \) density matrix
\( \Pi(\tau) \) energy-integrated absorption
\( \Lambda(\tau) \) energy-integrated normalized absorption
\( I_p \) ionization potential
\( \gamma \) Keldysh parameter
\( n_2 \) nonlinear index coefficient
\( U_p \) ponderomotive potential
\( I_{\text{rel}} \) relative transmitted intensity
\( f_{\text{rep}} \) repetition rate
\( c \) speed of light
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<td>aluminum</td>
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<tr>
<td>AOM</td>
<td>acousto-optic modulator</td>
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<td>AOPDF</td>
<td>acousto-optic programmable dispersive filter</td>
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<td>AP</td>
<td>attosecond pulse</td>
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<td>APT</td>
<td>attosecond pulse train</td>
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<td>Ar</td>
<td>argon</td>
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<td>ATI</td>
<td>above-threshold ionization</td>
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<td>BBO</td>
<td>beta barium borate</td>
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<td>CCD</td>
<td>charge-coupled device</td>
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<td>CEO</td>
<td>carrier-envelope-offset</td>
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<td>CEP</td>
<td>carrier-envelope phase</td>
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<td>CPA</td>
<td>chirped-pulse amplification</td>
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<td>CVD</td>
<td>chemical-vapor-deposition</td>
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<td>cw</td>
<td>continuous wave</td>
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<td>DFG</td>
<td>difference frequency generation</td>
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<td>DPSSL</td>
<td>diode-pumped solid-state laser</td>
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<td>EWP</td>
<td>electron wavepacket</td>
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<td>FROG</td>
<td>frequency-resolved optical gating</td>
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<td>FROG-CRAB</td>
<td>frequency-resolved optical gating for complete reconstruction of attosecond bursts</td>
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<td>FWHM</td>
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<td>GDD</td>
<td>group-delay dispersion</td>
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<td>HCF</td>
<td>hollow-core fiber</td>
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<td>HDD</td>
<td>hard-disk drive</td>
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<td>He</td>
<td>helium</td>
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<td>HH</td>
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<td>HWP</td>
<td>half-wave plate</td>
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<td>IR</td>
<td>infrared</td>
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<td>MCP</td>
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<td>MWE</td>
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<td>NASP</td>
<td>non-adiabatic saddle-point approxima-</td>
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<td>Acronym</td>
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<td>OPCPA</td>
<td>optical parametric chirped-pulse amplification</td>
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<td>PBS</td>
<td>polarizing beamsplitter</td>
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<td>polarization gating</td>
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<td>PPLN</td>
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<td>QWP</td>
<td>quarter-wave plate</td>
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<td>RF</td>
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<td>SAE</td>
<td>single-active electron</td>
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<td>SAP</td>
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<td>SEWA</td>
<td>slowly-evolving-wave approximation</td>
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<td>SFA</td>
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<td>Si</td>
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<td>SNR</td>
<td>signal-to-noise ratio</td>
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<td>TDSE</td>
<td>time-dependent Schrödinger equation</td>
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<td>TIDR</td>
<td>time-integrated dipole response</td>
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<td>TLS</td>
<td>two-level system</td>
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<td>TOF</td>
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<td>TTL</td>
<td>transistor-transistor-logic</td>
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<td>Xe</td>
<td>xenon</td>
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<td>XUV</td>
<td>extreme ultraviolet</td>
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Publications

Parts of this thesis are published in the following journal papers and conference proceedings.

**Journal Papers**


Conference Papers


Abstract

In the framework of this thesis, we discuss the application of attosecond transient absorption spectroscopy to examine the light-matter interaction in the extreme ultraviolet (XUV) spectral range. We focus our work on the investigation and control of the optical properties of helium (He) and polycrystalline diamond on an ultrafast time scale.

Attosecond transient absorption spectroscopy is still a relatively young discipline of attosecond science. Even though femtosecond transient absorption spectroscopy is a well-known and established experimental technique, it required the creation of coherent XUV bursts of attosecond duration with higher-order harmonic generation (HHG) to extend the technique into the attosecond regime. As an all optical technique, it is based on the cross-correlation of pulsed XUV radiation with femtosecond infrared (IR) pulses in the sample under investigation and the subsequent detection of the transmitted radiation. Its high temporal resolution allows to explore electron dynamics on their natural time scale.

In this thesis, we examine the optical properties of He in the XUV spectral range in different experiments. In a first part, we present a combined theoretical and experimental discussion of the off-resonant excitation of a quantum-mechanical two-level system. The temporal evolution of the dipole response provides new insights which we exploit for the creation and control of optical absorption and gain. In a second experimental part, we discuss the role of interfering electron wavepackets (EWPs) for sub-
cycle oscillations in the transmitted XUV intensity observed in various recent publications. Our results show that the impact of EWP interference on the intensity modulations is less important than previously assumed. In a third attosecond transient absorption experiment in He, we present a new technique for the delay-zero calibration, where the maximum of the XUV and IR envelope overlap, for experiments employing an attosecond pulse train (APT) in combination with a femtosecond IR pulse. Finally, we introduce simulations for attosecond transient absorption spectroscopy in He based on the solution of the von-Neumann equation.

In addition to the experiments in He, we present attosecond solid-state transient absorption spectroscopy in a polycrystalline diamond membrane. Our experimental data reveal the fully reversible modification and control of the optical transmission of polycrystalline diamond in the XUV spectral range with the help of the femtosecond IR pulse.

einer Dauer von weniger als einer Femtosekunde, erlauben schliesslich transienten Absorptionsexperimente im Attosekundenzeitbereich.


Chapter 1

Motivation

The ability to resolve the evolution of time-dependent processes was limited by the visual and acoustic perception of human beings for a long time. A milestone for time-resolved measurements was the technical progress in the 19\textsuperscript{th} century leading to the development of photography, which allowed to reduce the observation time significantly and consequently resolve faster events. An early example for a time-resolved ‘measurement’ is the famous galloping horse by Eadweard James Muybridge recorded with the chronophotography technique [1].

Even earlier in the 19\textsuperscript{th} century Wollaston and Fraunhofer paved the way for absorption spectroscopy with their discovery of dark lines in the spectrally resolved solar radiation [2]. Some years later, Bunsen and Kirchhoff delivered the interpretation of the dark lines as caused by absorption of elements present in the atmosphere [3]. Exactly 100 years after Kirchhoff published his work on the absorption lines, Maiman demonstrated the operation of the first laser in 1960 [4]. The importance of this invention for the scientific progress in the 20\textsuperscript{th} century up to today cannot be overrated. Finally, the development of modelocked lasers allowed pump-probe experiments with unprecedented temporal resolution and marked the start for the success of ultrafast spectroscopy [5, 6].

In a pump-probe experiment a pump pulse triggers a system and a usually weak second pulse probes the response of the system under investigation as a function of delay between the two pulses. There are many pos-
sible observables in pump-probe experiments, e.g. photoelectrons, ions or the transmitted radiation, as in transient absorption spectroscopy, to mention some of them. Ultrafast pump-probe spectroscopy enabled studying many reactions and processes relevant to biology, chemistry and physics on their natural time scale, e.g. the vibrational ($\approx10^{-12}$ s to $\approx10^{-14}$ s) and rotational ($\approx10^{-9}$ s to $\approx10^{-12}$ s) motion of molecules, as well as the forming and breaking of hydrogen bonds in water ($\approx10^{-12}$ s) [7, 8, 9]. An important contribution on this new field of ultrafast science was made by Ahmed Zewail. Consequently, he was honoured with the Nobel prize in chemistry in 1999 for his work in femtochemistry [10].

The next step in ultrafast spectroscopy is to move into the sub-femtosecond domain. However, there is an obstacle on this way with conventional laser sources operating in the infrared (IR) spectral range. At a wavelength of 800 nm the duration of a single laser cycle is around 2.7 fs. Consequently, it is impossible to generate pulses with a duration below 1 fs at this wavelength. Nevertheless, there are substantial arguments to move beyond femtosecond science towards attosecond science. If we look into the relevant microscopic processes in biology, chemistry and physics we will discover that many of these processes are determined by electron dynamics. A prominent and fundamental example is the absorption and emission of light which is the result of a transition between electronic states in a quantum-mechanical system.

A wavepacket containing two bound eigenstates of a quantum-mechanical system has an oscillation period $T$ determined by the following equation [11]:

$$T = 2\pi \frac{\hbar}{\Delta E},$$

where $\Delta E$ corresponds to the energetic spacing of the two eigenstates. The energetic spacing of valence-electron states for atoms and molecules is on the electronvolt scale. For a spacing of $\Delta E = 4.1$ eV we observe an oscillation period of $\approx1$ fs. Accordingly, there is a need for sub-femtosecond resolution in ultrafast science.

The answer for the demand for sub-femtosecond pulses is higher-order harmonic generation (HHG). It proved to be a convenient way to up-convert IR radiation into the extreme ultraviolet (XUV) spectral range
where a single cycle has a duration of less than 1 fs. Even more important was the discovery that the newly generated radiation consisted intrinsically of bursts of attosecond duration [12, 13].

The focus of this thesis is on a specific ultrafast spectroscopy technique named attosecond transient absorption spectroscopy. This technique corresponds to the detection of the transmitted XUV photons through a sample in a cross-correlation experiment with a XUV and IR pulsed electromagnetic field. The XUV radiation can be either a single sub-femtosecond burst or a train of several attosecond pulses. Many of the early experiments in attosecond science were based on the detection of charged particles, e.g. in reconstruction of attosecond beating by interference of two-photon transitions (RABBITT) and attosecond streaking [12, 14]. However, the detection of charged particles holds some drawbacks. An XUV pulse with a high pulse energy can create a dense cloud of photoelectrons. The Coulomb repulsion of the charge carriers leads to effects not directly related to the system under investigation. Accordingly, space-charge effects limit the count rate for experiments detecting electrons. This limitation leads to long acquisition times of up to several hours to record a full cross-correlation trace of IR and XUV. This requires a high interferometric stability of the experiment and high stability of the XUV and IR source, respectively. A specific problem in attosecond streaking experiments is the required strong IR field. For systems with a low ionization potential this leads to a strong background signal caused by above-threshold ionization (ATI) or might even damage the system under investigation.

Attosecond transient absorption spectroscopy as an all-optical measurement technique circumvents these problems. It intrinsically does not require a strong IR pulse. The detection of the transmitted XUV photons makes the technique insensitive to space-charge effects and allows higher XUV intensities. In combination with highly sensitive charge-coupled device (CCD)-based XUV spectrometers this reduces the time for the acquisition of a single spectrum with an excellent signal-to-noise ratio (SNR) to a few milliseconds. The detection efficiency of a back-illuminated CCD sensor reaches up to 40 % in the XUV spectral range. Another advantage is the high spectral resolution of commercially available XUV spectrometers of millielectronvolts at several tens of electronvolts photon energy.
1. Motivation

Furthermore, transient absorption spectroscopy offers the possibility to directly investigate bound-bound transitions. In contrast to the detection of charged particles, transient absorption spectroscopy does not rely on the photoionization of the sample.

Even though femtosecond transient absorption spectroscopy is a well-established technique, its attosecond version is still young. An important step towards attosecond transient absorption spectroscopy was performed by Loh et al. who combined higher-order harmonics (HHs) with transient absorption spectroscopy [15, 16]. Finally, the first experiments with attosecond transient absorption spectroscopy were published almost simultaneously by three independent groups [17, 18, 19]. Holler et al. even directly presented an investigation of sub-cycle dynamics in the transmitted XUV intensity. A large number of recent publications followed these pioneering work and will be mentioned in this thesis at the appropriate place.

In this thesis, we present results of different attosecond transient absorption experiments with helium (He) and polycrystalline diamond. The workhorse for HHG and many attosecond experiments are Ti:Sapphire-based laser amplifier systems and we review in chapter 2 our amplifier system for the generation of femtosecond laser pulses. Furthermore, we present different pulse characterization and compression techniques. Chapter 3 gives the reader a brief overview over the microscopic and macroscopic aspects of the generation of attosecond pulses. Subsequently in chapter 4, we introduce our attosecond beamline, the so-called attoline, and discuss its unique characteristics. Chapter 5 presents a first transient absorption experiment in He demonstrating the control of optical gain and absorption for the specific case of an off-resonantly excited quantum-mechanical system.

Chapters 6 and 7 exploit fast oscillations in the transmitted XUV intensity observed in various recent attosecond transient absorption experiments. In chapter 6 we discuss the role of interfering electron wavepackets (EWPs) for the emergence of the fast oscillations. We demonstrate in chapter 7 how to extract information on the relative timing between the XUV and IR radiation with the help of these fast oscillations. Chapter 8 shows
simulated attosecond transient absorption delay scans in He. Chapter 9 presents the first attosecond transient absorption experiments with a polycrystalline diamond target.

Chapter 10 summarizes the work presented in this thesis and gives an outlook for future attosecond transient absorption experiments at the attoline.
Chapter 2

Generation and characterization of femtosecond laser pulses

The progress in the development of laser sources providing ultrashort pulses during the last decades opened the door for strong-field experiments and finally attosecond science. Laser pulses of femtosecond duration allowed to achieve the peak intensities which are required for these experiments [20]. Today, commercially available laser amplifier systems provide routinely femtosecond pulses with several millijoules of pulse energy with repetition rates of several kilohertz. For the future, oscillators based e.g. on a thin-disk geometry promise to directly provide intensities needed for strong-field experiments [21]. Nevertheless, we discuss here the amplifier system used in the experiments presented in the following chapters. Moreover, we review schemes for pulse compression down to \(\approx5\) fs, corresponding to roughly two optical cycles, and carrier-envelope phase (CEP) stabilization. These two characteristics play a major role in the generation of single attosecond pulses (SAPs). In the last part of this chapter we describe different pulse characterization techniques.

2.1 Laser system

The laser source employed in the experiments in this thesis is based on a multi-pass, two-stage titanium doped sapphire (Ti:sapphire) amplifier system operating at a repetition rate of 1 kHz (FEMTOPOWER PRO V CEP,
2. Generation and characterization of femtosecond laser pulses

FEMTOLASERS Produktions GmbH. Figure 2.1 displays a schematic of the amplifier system. We work with a Ti:sapphire-based Kerr-lens mod-

eロックded laser oscillator (Rainbow, FEMTOLASERS Produktions GmbH) to seed the amplifier [22]. The oscillator is pumped by a continuous wave (cw) diode-pumped solid-state laser (DPSSL) operating at a wavelength of 532 nm (Verdi V5, Coherent Inc.) with 3 W of output power. It provides pulses with a duration of ≈7 fs (full width at half maximum (FWHM)) and a pulse energy of ≈2.5 nJ at a repetition rate of ≈77 MHz. The first stage of the amplifier, the so-called pre-amplifier, is set up in a 10-pass configuration and pumped by a Q-switched neodymium-doped yttrium lithium fluoride (Nd:YLF) laser (Evolution 30, Coherent Inc.) operating at 1 kHz. The output of the pre-amplifier can be used either directly in an experiment or as a seed for the second two-pass amplification stage, the so-called power amplifier. A half-wave plate (HWP) in combination with a polarizing beamsplitter (PBS) enables us to separate and control the power we use as seed for the power amplifier. The power amplifier is pumped by two Q-switched Nd:YLF lasers (Evolution HE, Coherent Inc.). We obtained all results presented in this thesis exclusively with the output of the pre-amplifier.

Both amplifier stages of our system base on the chirped-pulse amplification (CPA) principle, first introduced by D. Strickland and G. Mourou in 1985 [23]. In this scheme the ultrashort laser pulses delivered from a seed oscillator are stretched in time before the amplification process and recompressed afterwards. The underlying idea is to reduce the peak intensity of the ultrashort pulses in the gain medium. The direct amplification of femtosecond pulses leads to extremely high peak intensities that will cause damage in the gain material due to self-focusing and other undesirable nonlinear effects, e.g. self-phase modulation (SPM), resulting in pulse distortions. In our setup, the seed pulses with an initial duration of ≈7 fs propagate through a series of glass blocks before they enter the pre-amplifier. This stretches the pulses to a duration of ≈20 ps due to dispersive temporal pulse broadening. The spectral bandwidth of the pulses remains unchanged.

The first four passes of the pre-amplifier operate with the repetition rate of the seed oscillator at ≈77 MHz. The experiments discussed in
this work require femtosecond pulses with pulse energies in the millijoule range. These high pulse energies in combination with a megahertz repetition rate poses serious problems to the heat management in the Ti:sapphire crystal. One way to overcome this limitation is to reduce the repetition rate. This decreases the heat load deposited in the gain crystal. We reduce the repetition rate in the pre-amplifier after the fourth pass by a combination of a Pockels cell with a polarizer down to the final repetition rate of 1 kHz. Subsequent to the reduction of the repetition rate an acousto-optic programmable dispersive filter (AOPDF) (Dazzler, Fastlite) is installed to control the dispersion [24, 25]. This device couples a radio frequency (RF) wave into an acousto-optical crystal. In this way the temporal profile of the RF signal is mapped to a spatially varying refractive index profile. Under the correct phase-matching conditions of the acoustic mode and the optical modes it is possible to diffract energy from one optical mode to another. Due to the phase-matching conditions the diffraction appears for each frequency component after a different propagation distance in the crystal. The different propagation velocities for the optical modes allows to introduce different group delays for different frequency components. Therefore, the AOPDF corrects up to fourth-order dispersion of the incoming pulse. The amount of diffracted signal and accordingly the power transmitted through the AOPDF is proportional to the ampli-
2. Generation and characterization of femtosecond laser pulses

The pulses pass the gain material for another six times after the AOPDF.

The power amplifier is seeded by the pre-amplifier and is set up in a two-pass configuration. For both outputs of the amplifier system we installed a transmission-grating compressor directly after the housing of the amplifier. For the pre-amplifier the pulses have a duration of $\approx 25 \text{ fs}$ with a pulse energy of 1.26 mJ after compression. The power amplifiers allows pulse energies up to 10 mJ with a comparable pulse duration.

Subsequent to the pulse compression, the output beam is sent through an evacuated tube to the attosecond beamline described in chapter 4.

2.2 Carrier-envelope-phase stabilization

The electric field $E(t)$ of a laser pulse can be written as:

$$E(t) = E_0(t)e^{i(\omega_0 t + \Phi_{\text{CEP}})} + c.c.$$, (2.1)

where $E_0(t)$ represents the complex pulse envelope, $\omega_0$ the carrier frequency of the electric field and $\Phi_{\text{CEP}}$ the CEP. $\Phi_{\text{CEP}}$ is defined as the phase difference between the maximum of the envelope $E_0(t)$ and the maximum of the electric field. This phase difference changes while the pulse propagates in a medium if the propagation velocity of the envelope, the so-called group velocity, is different from the propagation velocity of the electric field, the so-called phase velocity.

The value of the CEP usually does not have a major impact on experimental results for pulses comprising many optical cycles. The situation differs in the case of few-cycle pulses, like they are used in the polarization gating (PG) technique to generate single attosecond pulses (see section 3.2.1). Here, a shift of $\pi/2$ of the $\Phi_{\text{CEP}}$ significantly changes the electric field under the envelope and leads to observable effects measured in various strong-field experiments [26, 27, 28, 29]. Figure 2.2 shows two pulses with a duration of 7 fs (FWHM) at a center wavelength of 800 nm. The blue curve represents a pulse with $\Phi_{\text{CEP}} = 0$, where the maximum of the electric field coincides with the maximum of the envelope (dashed line). A phase shift of $\pi/2$ of the $\Phi_{\text{CEP}}$ transforms this cosine-like pulse...
into a sine-like pulse, where the electric field is zero at the maximum of the envelope. Moreover, the CEP shift reduces the peak electric field strength significantly. Hence, there is a need to measure, stabilize, and control the CEP, especially for few-cycle pulses [30]. Our laser system allows to simultaneously stabilize the CEP of one of the two outputs.

The laser oscillator delivers a train of pulses with the repetition rate of \( f_{\text{rep}} \approx 77 \, \text{MHz} \). If this pulse train is Fourier transformed from the time domain into the frequency domain we obtain a frequency comb with a spacing of \( f_{\text{rep}} \) between the comb lines. The position of the \( m^{\text{th}} \) comb line is described with the following equation

\[
f_m = mf_{\text{rep}} + f_{\text{CEO}},
\]

where \( f_{\text{CEO}} = f_{\text{rep}}\Delta\Phi_{\text{CEP}}/2\pi \) is the carrier-envelope-offset (CEO) frequency. \( \Delta\Phi_{\text{CEP}} \) corresponds to the phase slip of the \( \Phi_{\text{CEP}} \) per round trip in the oscillator. Due to fluctuations of the pulse parameters \( \Delta\Phi_{\text{CEP}} \) is not constant for each roundtrip in the oscillator. Accordingly, \( f_{\text{CEO}} \) is not constant. For the stabilization of \( f_{\text{CEO}} \), we first have to measure it. For this purpose the output of the oscillator is focused into a periodically poled magnesium-oxide-doped lithium niobate (PPLN) crystal, where the spectrum is broadened by SPM (see 2.3.1) and difference frequency generation (DFG) spectrum takes place. The interference of the DFG signal with the

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**Figure 2.2**: Electric field of a 7 fs pulse (FWHM) with a center wavelength of 800 nm corresponding to 2.6 optical cycles. The dashed line represents the pulse envelope. The blue curve corresponds to a pulse with \( \Phi_{\text{CEP}} = 0 \) and the red curve represents the electric field for the same pulse but \( \Phi_{\text{CEP}} = \pi/2 \).
fundamental signal leads to a beating, which is detected with a photodiode and gives access to $f_{\text{CEO}}$. The signal of the photodiode is transferred to the locking electronics. The locking electronics sends a feedback in a closed-loop configuration to an acousto-optic modulator (AOM) placed after the pump laser of the oscillator (see figure 2.1). The AOM modifies the pump-laser intensity. This leads to a small change in the nonlinear refractive index of the oscillator cavity and hence to a change of the intracavity nonlinear phase shift. This enables us to control the CEP slip per round trip and consequently stabilize the CEP. A pair of motorized intracavity fused silica wedges increases the control range for the CEP stabilization. This stabilization prevents fast fluctuations of the CEP.

A second stabilization system is installed after the grating compressor of the amplifier and is designed to correct long-term drifts and fluctuations originating from the amplifier of the CEP. For the CEP detection, we use a commercial $f$-to-$2f$ interferometer (APS 800, Menlo Systems GmbH) [30]. We separate a small fraction of the beam and spectrally broaden it by transmitting it through a thin sapphire plate. This delivers a coherent spectrum broader than one octave, which is a prerequisite for the use of an $f$-to-$2f$ interferometer. Then, we focus the beam with the broadened spectrum into a beta barium borate (BBO) crystal, which doubles the frequency of the fundamental signal via second harmonic generation (SHG). The overlapping fundamental and frequency-doubled spectrum detected in a spectrometer allow the extraction of $f_{\text{CEO}}$ [30]. The retrieved signal serves as input for our locking electronics, which controls the position of one of the prisms of the pulse stretcher before the amplifier with a piezoelectric actuator.

2.3 Pulse compression and characterization

The ultrashort pulses with a duration of $\approx 25$ fs directly provided by the pre-amplifier are still not sufficiently short for some applications, e.g. the generation of a SAP with the PG technique. In order to compress the pulses in time, we have to broaden the spectrum of the initial pulses originating from the amplifier system. A common approach for spectral broadening is to exploit the nonlinear interaction of the laser pulses with a
gaseous medium. Here, we describe the spectral broadening in a gas cell by filamentation (see subsection 2.3.1) and with a hollow-core fiber (HCF) (see subsection 2.3.2). For the temporal compression subsequent to the spectral broadening we use chirped mirrors [31, 32]. Both techniques deliver, depending on the selection of the parameters, pulses with a duration of $\approx 5$ fs and pulse energies of several hundred microjoules. Furthermore, it is crucial to exactly determine the pulse duration. We characterize our pulses with spectral phase interferometry for direct electric-field reconstruction (SPIDER) (see subsection 2.3.3) [33].

2.3.1 Optical filamentation

Optical filamentation in noble gases exploits two antagonistic effects, namely the self-focusing due to the Kerr effect and the plasma defocusing of the beam in the gas [34]. Under certain circumstances, these two effects result in self-guiding and spectral broadening of the beam. The origin of the self-focusing of a high-intensity laser beam lies in the intensity dependence of the refractive index $n(I)$, which is described by the following equation:

$$n(I) = n + n_2 I,$$  \hspace{1cm} (2.3)

where $I$ is the laser intensity, $n$ the refractive index and $n_2$ the nonlinear index coefficient. For a positive $n_2$, the resulting refractive-index change across the beam profile leads to a focusing of the beam. This focusing can increase the intensity up to a point where the laser pulse ionizes the gas and creates a plasma. The free charge carriers of the plasma induce a local decline of the refractive index, which in combination with diffraction defocuses the beam again. At a certain point the Kerr effect and the plasma defocusing balance and lead to a constant beam diameter, which is preserved over several centimeters in the gas cell.

In the time domain the intensity dependence of the refractive index corresponds to a nonlinear phase shift, since the intensity of an ultrashort laser pulse changes along its temporal envelope. The effect of the nonlinear phase shift is termed SPM, already mentioned in section 2.1. As a consequence, new spectral components on the trailing and leading edge of the pulse are created. For a positive $n_2$ lower frequency components
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are added on the leading edge and higher frequency components on the trailing edge resulting in strongly chirped pulses. We compensate for the chirp with chirped mirrors directly after the filaments cells.

Among the advantages of optical filamentation compared to other pulse-compression techniques, e.g. HCF-based compression (see 2.3.2), are the straightforward alignment and the relatively high throughput due to low coupling losses [35]. Optical filamentation is limited by the break-up of the filament into multiple filaments for too high intensities and/or gas pressures [36].

2.3.2 Hollow-core fiber

Like in optical filamentation, also the pulse compression with a HCF is based on spectral broadening of the initial pulse by SPM with subsequent temporal compression. The power of commercial laser amplifier systems providing femtosecond pulses usually exceeds the damage threshold of a conventional fiber by far. Therefore, to circumvent this limitation Nisoli et al. came up with the idea to use instead a fiber with a hollow core filled with a noble gas [37]. Unlike in a conventional fiber, where the refractive index of the fiber material is larger than the refractive index of the surrounding media, there is no total reflection in the case of a HCF. Nevertheless, the guidance of the beam provided by the HCF gives an excellent beam profile at the exit of the fiber and enables a long interaction of the confined beam with the nonlinear medium. While the formation of a plasma is a prerequisite for optical filamentation, in a HCF a dense plasma is undesirable since it deforms the beam shape and temporal profile of the pulse. The variable pressure in a HCF allows to tune the nonlinear interaction of the beam in the HCF comparable to the variable pressure in a filament cell. The main drawback of the HCF setup is the coupling of the beam into the fiber. The diameter usually is around several hundred micrometer. The focus of the beam corresponds to \( \approx \frac{2}{3} \) of the diameter. As a consequence the coupling into the fiber and consequently the output of the HCF is very sensitive to any beam pointing fluctuation. In contrast to the HCF compression, optical filamentation introduces due to the strong spatial chirp a variation of the pulse duration along the beam profile as well. The HCF provides a more spatially homogenous beam profile with
2.3. Pulse compression and characterization

a nearly constant pulse duration [35]. After the HCF setup the pulses are compressed in time with chirped mirrors as for the filament compression.

2.3.3 Spectral phase interferometry for direct electric-field reconstruction - SPIDER

The complete characterization of a laser pulse requires the measurement of the amplitude and the phase of its electric field. The two most prominent techniques for this complete characterization are frequency-resolved optical gating (FROG) and SPIDER [38, 33]. The FROG setup is very similar to an autocorrelation setup, where the laser pulse and a replica of itself with a variable delay interact in a nonlinear medium. The delay between the two pulses is scanned and the signal resulting out of the nonlinear interaction is detected as a function of delay. The important difference of a FROG setup is that the autocorrelation signal is frequency resolved before the detection. Therefore, the obtained signal is a two-dimensional function of delay between the two separated parts of the pulse and wavelength or energy, respectively. This two-dimensional data set contains the necessary information to retrieve the phase and amplitude of the pulse.

In the work presented here, the pulse measurements were performed with a commercial SPIDER setup (FC SPIDER, APE GmbH). The SPIDER technique is based on self-referenced spectral interferometry. To retrieve the phase of the pulse, two time-delayed replicas of the initial pulse are overlapped with a fraction of the initial pulse that is spectrally sheared with respect to its carrier frequency, in a nonlinear medium and the resulting radiation is detected with a spectrometer. The recorded SPIDER interferogram contains all the required information and allows to retrieve the electric field and spectral phase.

For a possible experimental implementation the initial pulse is split into two parts. One part is sent into a Michelson interferometer, creating the two time-delayed replicas of the pulse. The second part of the initial pulse is strongly chirped, e.g. by propagating through a block of glass. In a next step, the two replicas non-linearly interact in a crystal with the strongly chirped pulse. This creates two spectrally sheared pulses, since the two delayed replicas interact with different frequency compo-
Figure 2.3: SPIDER measurement of a 7.3 fs pulse generated by the pre-amplifier with subsequent compression in a hollow-core fiber. (a) shows the SPIDER interferogram. (b) displays the spectrum (solid line) and the retrieved spectral phase (dashed line). Panel (c) shows the calculated temporal intensity profile of the pulse with a duration of 7.3 fs (FWHM). The transform limited pulse duration is 6.4 fs which corresponds to 2.9 optical cycles at the given center wavelength of 756 nm.
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components of the chirped pulse. These two spectrally sheared pulses interfere and lead to the SPIDER interferogram, which is measured with a spectrometer and presented in figure 2.3(a). The reader should note that the spectral-interference fringes are not fully resolved in the figure. For this example we used the output of the pre-amplifier with pulse compression in our HCF. The fiber was filled with argon. Figure 2.3(b) displays the spectrum of the pulse (solid line) and the retrieved spectral phase (dashed line). The reconstructed temporal intensity is shown in figure 2.3(c). The FWHM corresponds to 7.3 fs. The spectrum shown in figure 2.3(b) supports pulses with a duration down to 6.4 fs. As can be seen, the spectral phase of the pulse is not perfectly flat and accordingly, the pulse not fully compressed. Hence, the pulse duration is slightly longer than the transform limit.

The combination of the SPIDER interferogram and the initial pulse spectrum directly contains all the information for the complete pulse characterization. There is no need to perform a delay scan, like it is required in FROG. Furthermore, the non-iterative retrieval algorithm of the amplitude and phase is simpler than the pulse reconstruction with FROG [39].
Introduction to attosecond science

The indispensable ingredient for attosecond transient absorption spectroscopy are pulses with sub-femtosecond duration. An important step towards pulses with a duration on the attosecond time scale was the observation of HHs generated by focusing an intense laser pulse into a noble gas [40]. Out of the discovery that this frequency up-conversion was a convenient way to generate coherent sub-femtosecond bursts in the XUV spectral region, the new field of attosecond science emerged.

In this chapter, we review the process of HHG in general and discuss microscopic and macroscopic effects culminating in the emission of XUV bursts of attosecond duration. Moreover, we explain the generation of SAPs with the PG technique.

3.1 Higher-order harmonic generation

The generation of HHs is based on focusing an intense, femtosecond laser pulse into a target containing atoms or molecules in the gas phase. We will not discuss the HHG in solids here. The interested reader can refer to e.g. [41]. Under the proper condition, which we discuss in this chapter, the spectrum after the interaction with the gas target contains besides the fundamental spectral component additionally HHs of the fundamental. Figure 3.1 displays a simplified spectrum created by HHG. The spectrum consists of three distinguishable parts: the perturbative regime, the plateau and the cut-off region. While in the perturbative regime and the
cut-off region the intensity of the HHs decreases with the HH order, it stays nearly constant in the plateau region. This is a clear indication that HHG is a non-perturbative effect and consequently cannot be explained within the framework of perturbation theory. The reader should note that the depicted spectrum is a simplification since the single HHs are represented as sharp lines. Due to finite pulse duration in an experiment, the individual HHs will always have a finite nonzero spectral bandwidth.

In the next two subsection we briefly review the microscopic and macroscopic effects relevant for HHG.

### 3.1.1 Single-atom response

If we focus a femtosecond pulse with sufficient pulse energy, it is possible to achieve intensities of $10^{14}$ W/cm$^2$ and higher. These intensities correspond to electrical field strengths on the order of several volts per angstrom, which are comparable to the inner-atomic Coulomb field. Consequently, the strong external field leads to the ionization of the atom. In order to distinguish different ionization regimes, Keldysh introduced the...
3.1. Higher-order harmonic generation

$\gamma$ parameter defined as [42]:

$$\gamma = \frac{\omega \sqrt{2m_e I_p}}{eE} = \sqrt{\frac{I_p}{2 U_p}}, \quad (3.1)$$

where $\omega$ represents the angular frequency of the laser field, $m_e$ the electron mass, $I_p$ the first ionization potential of the gas, $E$ the electric field of the laser and $e$ the charge of the electron. The cycle-averaged quiver energy of an electron in a monochromatic electric field, also named ponderomotive potential $U_p$, is described by the following equation:

$$U_p = \frac{e^2 E^2}{4 \omega^2 m_e}. \quad (3.2)$$

With the high electric field strengths in the focus of a femtosecond pulse and a laser wavelength of $\approx 800\text{ nm}$ we obtain $\gamma \approx 1$ or smaller. In this regime, especially for $\gamma \ll 1$, the external laser field bends the Coulomb potential, creates a potential barrier and the atom can be ionized by tunnelling of the electron into the continuum. The case of $\gamma \gg 1$, which corresponds to multiphoton ionization, does not play a role in HHG.

In 1993, Corkum, Kulander et al. and Schafer et al. described the HHG with the semi-classical three-step model [43, 44, 45]. This model is based on the single-active electron (SAE) approximation which is assumes that only one electron actively participates in the process [46]. All other electrons remain in their initial state. The first step of the model is the tunnel ionization of the atom through the created potential barrier as it was briefly described in the previous paragraph.

After the electron exited the tunnel barrier it can be treated as a nearly free, classical particle. We disregard the Coulomb field of the remaining ion. This is one of the key assumptions of the strong-field approximation (SFA) [47, 48]. In the second step, the laser field accelerates the electron and drives it away from its parent atom. The resulting trajectory of the electron strongly depends on the phase of the laser field at the moment of ionization. An investigation of the electron trajectories as function of the ionization moment reveals that electrons leaving the atom between the peak and the next zero-crossing of the field return to the parent atom within one cycle of the laser field. Figure 3.2 presents classical electron
trajectories for different moments of ionization in cw laser field. The green trajectories correspond to electrons ionized in the quarter-laser-cycle after the peak of the electric field which return to the parent atom within one cycle of the laser. The red trajectory illustrates an electron ionized at a later moment that does not return.

The electrons returning within one cycle play the dominant role in the third and final step of the three-step model. In this step, the electron recombines with a certain probability to the atomic ground state under the emission of a high-energy photon. The photon energy corresponds to the ionization potential of the atom plus the kinetic energy gained by the electron in the laser field. Like the description of the tunnelling process, also the recombination is only understandable in a quantum-mechanical framework. The wave function of the returning electron interferes with the part of its own wave function that remained at the ion when the electron tunnelled through the barrier. This interference leads to an ultrafast oscillations of the atomic dipole moment. The radiation emitted by the oscillating dipole corresponds to the burst of XUV radiation. Electron that follow a trajectory that return to the atom after more than one cycle play a negligible role in the HHG due to quantum diffusion of the electron wave function.
3.1. Higher-order harmonic generation

In contrast to the first and third step the electron can be treated as a classical particle in an electromagnetic field in the intermediate step. An analysis of all possible trajectories leading to a return within one laser cycle shows that there are two trajectories leading to the same final energy. They are named short and long trajectory according to their excursion distance after they left the atom [49]. However, in the cutoff region there is only one trajectory for every final energy of the electrons. Moreover, if we study the long or short trajectories separately, we will observe that electrons of different energy show different excursion times and moments of ionization. This means that electrons of different energy recombine non-simultaneous. For the short trajectory this results in a positive chirp of the HHs, i.e. the low-energetic electrons recombine in advance of the high-energetic electrons. The HHs originating from the long trajectories are negatively chirped. This effect on the long and short trajectory HHs is named atto-chirp [50]. Furthermore, HHs from long and short trajectories exhibit a different divergence and different phase-matching conditions. This effect is exploited for the selection of HHs from either short or long trajectories as it will be discussed in the next subsection 3.1.2.

Although the semiclassical three-step model is very simple it was extremely successful since it explains many experimental observations. The model provides an explanation for the cut-off energy in the HH spectrum. Corkum, Kulander et al. and Schafer et al. found that the maximum photon energy achievable with HHG $E_{\text{cut-off}}$ is defined as:

$$E_{\text{cut-off}} = I_p + 3.17U_p.$$  (3.3)

Following equation 3.3 there are different pathways to reach higher photon energies in HHG. Since the ponderomotive potential $U_p$ linearly depends on the laser intensity, one possible approach is to simply increase the intensity of the driving pulses. This works only up to a certain point where depletion of the ground state of the target atoms due to ionization prevents the generation of HHs [51]. A second approach is to extend the cut-off energy by using longer-wavelength driving sources [52]. This allows to enter the soft-x-ray regime but suffers from the efficiency which decreases with the wavelength $\lambda$ proportional to $\lambda^{-5.5 \pm 0.5}$ [53]. Another effect explained by the three-step model is the strong ellipticity dependence
of the HHG process [54]. Only for linearly polarized light the electron is driven away from its parent atom and may return to recombine. For elliptically polarized light the electron does not return and recombine due to its lateral displacement with respect to its origin.

The process described in the three-step model is periodic and starts twice per laser cycle. In combination with the inversion symmetry of the gaseous interaction medium, this leads to a comb of HHs in the frequency domain appearing at odd multiples of the fundamental IR photon energy as it is shown in figure 3.1. In the time domain this corresponds to a train of attosecond pulses separated by half the cycle duration of the driving laser. We discuss the generation of a single XUV burst instead of the full attosecond pulse train (APT) in the following section 3.2 and show how to restrict the HHG to single half-cycle of the driving IR field.

In 1994, Lewenstein et al. presented additional to the semi-classical three-step model a fully quantum-mechanical description based on the solution of the time-dependent Schrödinger equation (TDSE) [55]. The review of the quantum-mechanical description of the HHG is beyond the scope of this thesis.

3.1.2 Macroscopic effects in HHG

The experimentally recorded HHG spectra often show significant deviations from the spectrum expected on the basis of the single-atom response. The deviations originate from the generation and propagation in a macroscopic medium. We are only able to detect HHs if the radiation emitted by the individual emitters coherently sums up in a constructive way in the propagation direction. The prerequisite for this is phase matching between the generating IR and the generated XUV radiation.

The general condition for phase matching between the generating field with wave vector \( k_f \) and the HH of order \( q \) with wave vector \( k_q = q \cdot k_f \) is that the phase mismatch \( \Delta k \) is zero:

\[
\Delta k = |k_f - k_q| = 0. \tag{3.4}
\]

However, we have to take into account additional effects for HHG in a macroscopic medium regarding the phase matching. For the generating
3.1. Higher-order harmonic generation

Field we observe a geometrical phase variation from $-\pi/2$ to $+\pi/2$ along the focus, the so-called Gouy phase [56, 57]. Another important contribution is the intrinsic intensity-dependent dipole phase [58]. The electron wave-packet accumulates a phase during the time spent in the continuum. This phase corresponds to the phase of the dipole moment and depends on the intensity of the laser field. For this contribution we obtain a space and time dependence due to the space- and time-dependent intensity profile of the laser pulse. The phase effects of the intensity-dependent dipole phase is symmetric with respect to the focus position while the Gouy phase provides an antisymmetric effect. A third contribution is the change of the refractive index induced by the free charge carriers [59]. The change of the refractive index is proportional to the density of charge carriers. This results in a blue shift of the spectrum due to SPM and a defocusing of the generating beam [60, 61]. Additionally, the generated plasma has a strong influence on the trajectories [62].

For a focus position before the center of our interaction target we obtain phase-matching for the short trajectory and for a focus position after the target for the long trajectory. This manifests amongst other things in the far-field image of the spectrum since the short trajectories have a lower divergence than HHs originating from the long trajectories. The low divergence in combination with the positive atto-chirp make the HHs based on the short trajectories preferable for experiments. The positive atto-chirp can be compensated by the transmission through a thin metallic filter (see section 4.1), e.g. aluminum (Al) provides negative group-delay dispersion (GDD) in this spectral region [63]. Therefore, the transmission through the thin metallic filter compresses the pulse in time and additionally separated the generating IR from the generated XUV radiation.

Under experimental conditions we obtain several possibilities to control the phase matching conditions. The influence of the geometrical phase variation and the intensity dependent dipole phase can be varied by moving the position of the gas jet with respect to the focus position. The gas pressure in the generation target allows us to control the plasma induced blue shift of the generating beam.
3.2 Single-attosecond-pulse generation

As already discussed, the HHG is periodic in time and repeats every half cycle. This delivers one XUV burst per half cycle. Nevertheless, some experiments require a SAP, which was first demonstrated by Hentschel et al. [14]. In the following years many different techniques for the generation of SAPs emerged, which can be divided into three main categories: spectral selection of half-cycle cutoffs, spatiotemporal gating and temporal gating [64, 65]. The spectral selection technique selects only the spectral components created by the most intense laser half cycle. This corresponds to the cut-off region. Examples for this technique are ionization and amplitude gating [66, 67, 68]. An example for the spatiotemporal gating is the attosecond lighthouse technique which exploits the spatiotemporal selection based on the tilted wavefront of the generating pulse [69]. Together with the attosecond lighthouse the techniques based on temporal gating of the generation, e.g. double optical gating or PG, are especially beneficial for the generation of broadband continua in the XUV spectral region [70, 71, 72]. In the next subsection, we briefly review the PG technique used for the SAP generation in the experiments presented in this thesis.

3.2.1 Polarization gating

The basic idea for the generation of a SAP with a temporal gating technique is to allow the creation of an XUV burst only in one half cycle of the few-cycle pulse. The PG exploits the strong ellipticity dependence of the HHG process. An ellipticity of 0.2 reduces the efficiency of the HHG by one order of magnitude [64, 73].

The PG setup, used for the experiments presented in this thesis, consists of two birefringent plates. The incoming linearly polarized few-cycle pulse passes the first plate under an angle of 45° of its polarization axis with respect to the ordinary axis of the birefringent plate. After this plate, we obtain two cross-polarized pulses with a delay with respect to each other. The delay depends on the thickness of the plate. The pulse is linearly polarized on its trailing and leading edge and elliptically polarized in the center where the two delayed pulses overlap. Now, the pulses propagate through a zero-order quarter-wave plate (QWP). The angle of the
3.2. Single-attosecond-pulse generation

QWP $\beta$ with respect to the polarization of the initial pulse can be varied. The propagation through the QWP changes the ellipticity of the pulse. For the appropriate $\beta$ angle the pulse is elliptically polarized on the leading and trailing edge. This prevents the HHG. With this angle $\beta$ and for a proper delay between the pulses, we obtain a temporal gate of linear polarization for the central half cycle of the pulse. The width of the temporal gate $\tau_g$ is defined by the following equation [70]:

$$
\tau_g = \frac{\varepsilon_{\text{thr}}^2}{\ln(2)\delta |\cos(2\beta)|}, \tag{3.5}
$$

where $\varepsilon_{\text{thr}} = 0.13$ is threshold ellipticity for efficient HHG, $\tau$ the pulse duration of the generating pulse, $\delta$ the delay between the two pulses after the first birefringent plate. We learn from equation 3.5 that the pulse duration of the driving field has to be around 5 fs in order to obtain a gate width of half a laser cycle at a center wavelength of 750 nm. The problem for larger pulse durations is that we have to increase the delay $\delta$ in order to obtain a sufficiently narrow gate. This strongly reduces the efficiency for the generation of a SAP since the intensity in the gate decreases for an increasing delay. Furthermore, we have the possibility to change the gate width by turning the angle $\beta$ of the QWP. We obtain the minimal gate

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**Figure 3.3:** Ellipticity $\varepsilon(t)$ as a function of time (red) after the transmission of a 5 fs pulse with a center wavelength of 750 nm through a PG setup consisting of two birefringent plates. The blue line indicates the intensity profile of the two cross-polarized pulses after the first birefringent plate which introduces a delay of 5.6 fs. The $\beta$ angle is set to zero. The horizontal green, dashed line indicates the threshold ellipticity of $\varepsilon_{\text{thr}} = 0.13$. The two vertical dashed lines mark the temporal gate with a width of $\tau_g$. 

---
Figure 3.4: CEP dependence of the PG technique. (a) XUV spectrum generated in Xe with the PG technique as a function of photon energy and CEP. (b) XUV spectra for two CEP values. For CEP $\Phi_0$ we obtain a continuous spectrum corresponding to a SAP. By changing the CEP to $\Phi_0 + \pi/2$ we obtain a modulated spectrum representing two XUV bursts.

width for $\beta = 0^\circ$. Figure 3.3 illustrates the PG technique. Additionally, the CEP (see section 2.2) influences the generation process. Figure 3.4(a) shows the XUV spectra generated in xenon (Xe) with the PG ‘switched’ on as a function of the change of the CEP. It reveals clearly a $\pi$-periodic change between a continuous and a modulated spectrum. Figure 3.4(b) presents two XUV spectra for a CEP of $\Phi_0$ where the spectrum is continuous and of $\Phi_0 + \pi/2$ where the spectrum exhibits discrete peaks. The origin of effect is that a change of the CEP influences if there are one or two peaks of the electric field generating the HHs within the gate width $\tau_g$. Accordingly, we switch between a SAP and multiple attosecond pulses (APs).

The spectra shown in figure 3.4(b) was used in the measurements presented in section 6.2.
Attoline

In this chapter, we introduce the beamline for attosecond experiments in the Ultrafast Laser Physics group at ETH in Zurich, the so-called attoline. All the work presented here and some additional, recently published results were obtained at the attoline [19, 74, 76, 77, 78, 79]. Several distinct properties distinguish the attoline from other beamlines for attosecond experiments [80, 81, 82]. The essential characteristics of our beamline are its versatility and flexibility. The design and construction enables the simultaneous detection of photons and charged particles. Moreover, it offers the possibility to operate different types of gas and solid-state targets and to choose between them without venting the experimental chamber. Another unique feature is the relay-image of the first interaction focus with a second toroidal mirror. This second focus can be used by any end station and enables us to measure in two spatially separated interaction volumes in coincidence.

The first part of the chapter discusses the vacuum system housing the HHG and the XUV/IR-interferometer. Furthermore, we describe the focusing and relay-imaging, different detectors and finally the temporal characterization methods for the XUV radiation.

4.1 Coupling chamber and XUV/IR-interferometer

The laser system providing femtosecond IR pulses, described in section 2.1, is not located in the same laboratory as the attoline. Therefore, the
beam propagates several meters before arriving at our beamline. To avoid dispersive pulse broadening of the femtosecond pulses in air, we send the beam through an evacuated tube starting after the grating compressor in our laser laboratory and leading to the attoline laboratory. The two output beams of the amplifier system arrive in the coupling chamber as it is depicted in figure 4.1 and 4.2. We have a separate tube for the two output beams of the pre- and power-amplifier system labeled T1 and T2, respectively. Here, we mainly discuss the output of the pre-amplifier which we exclusively used for the results presented in this thesis. Directly after entering the coupling chamber, we take the reflection of the beam from a thin fused silica plate and direct it onto a position-sensitive photodetector. The photodetector in combination with a piezoelectric-driven mirror before the evacuated tube are parts of a commercial beam-stabilization system (XY4QD Real-time Laser Beam Monitor, MRC Systems GmbH). The stabilization system prevents changes of the beam pointing. This is essential due to the long propagation distances of the beams.

For the temporal compression of the 25-fs pulses directly delivered by the laser amplifier system, we send the beam out of the coupling chamber with mirror M5 and direct them towards our filament or HCF compression setup as it is depicted in figure 4.2. As discussed in section 2.3, the filament or HCF setup compresses the pulses to sub-6 fs with a pulse energy of ≈350 µJ or ≈600 µJ, respectively. The input pulse energy for both
4.1. Coupling chamber and XUV/IR-interferometer

Figure 4.2: Coupling chamber and XUV/IR interferometer. The output of the laser amplifier system travels to the coupling chamber via the two evacuated tubes T1 and T2. The coupling chamber allows to send both output beams of the laser system out of the vacuum chambers to an external pulse compression setup. The first three chambers (Ch 1 to 3) house the HHG and XUV/IR-interferometer.

The output of both compression setups is 1.2 mJ. The output of both compression setups is coupled back into the attoline with the mirror M6.

The HHG and the XUV/IR-interferometer for pump-probe measurements are located in three cylindrical vacuum chambers with an inner diameter of 0.5 m adjacent to the coupling chamber (Ch 1 to 3). The chambers are mounted on a common aluminum base plate with a thickness of 60 mm. The dimensions of the plate are 1.0 m × 2.2 m. The plate is directly attached to the optical table. For additional stability of the interferometer and to minimize stress induced by thermal drifts, we keep the temperature of the base plate fixed with an accuracy of 0.1 K with the help of a chiller. The turbomolecular vacuum pumps (all Pfeiffer Vacuum GmbH) are not directly attached to the vacuum chambers but decoupled with the help of dampers. The dampers reduce the transmission of vibrations from the turbomolecular pumps to our vacuum chambers. In this way, we achieve a passive stability sufficient to perform experiments with sub-femtosecond interferometric stability lasting over several hours. The top cover of the first three chambers are made from acrylic glass with a thickness of 50 mm, which is convenient for visible inspection during operation while the chambers are evacuated. The chambers are sealed with rubber O-rings with the aluminum base plate and the acrylic glass covers. Rectan-
regular flanges interconnect the chambers. These flanges enable us to have differential pumping stages between the second and third chamber (Ch 2 and 3). Typical pressures in the second chamber (Ch 2) during operation of the HHG target are $2 \cdot 10^{-3}$ mbar while in the third chamber (Ch 3) a pressure of $10^{-6}$ mbar is preserved.

A beam splitter (BS, 80%/20%) at the beginning of the beam path in the first chamber (Ch 1) divides the beam into the two arms of our XUV/IR-interferometer. The main part is transmitted and passes through the PG setup (WP1 and WP2, see subsection 3.2.1). After propagating into the second chamber (Ch 2), we focus this part with a spherical mirror (FM1, ROC $= -750$ mm) into the HHG gas target (GT). A metal tube that is closed at the end serves as our HHG gas target. In the direction of the beam it has two holes. The holes are initially closed by teflon tape wrapped around the tube. We drill a hole into the tape with the focused laser beam for the HHG. This procedure creates a hole with the minimal required diameter and therefore keeps the gas load for the turbomolecular pumps low. The hole diameter in the tape increases over time, mainly through the daily alignment of the system and beam pointing fluctuations. Accordingly, the tape has to be replaced from time to time in order to keep the gas load low. The gas target is mounted on a motorized $xyz$-stage. The possibility to move the target in the beam direction with respect to the focus in combination with a motorized iris (I1) allows to vary the phase-matching conditions for the HHG process. Furthermore, we can adjust the phase-matching conditions via the backing pressure of the HHG target. After the HHG process the combined XUV and IR beam mainly consists of IR radiation due to the low conversion efficiency of the HHG process. Hence, the IR radiation is filtered out by means of thin metallic filters mounted in a motorized filter wheel (FW1). With the help of the second filter wheel (FW2) we have the possibility to combine different metallic filters for the spectral selection of parts of the XUV radiation.

The minor part reflected on the beam splitter BS travels along the second arm of the XUV/IR-interferometer. We use the reflection of the beam from a thin fused silica plate in the first chamber (Ch 1) and couple it out of the chamber. We send it through two reference irises outside of the first chamber (Ch 1) spaced by $\approx 1.5$ m. This allows a daily alignment of the at-
4.2. Refocusing and XUV diagnostics

toline by two mirrors after the pulse compression and before sending the beam back into the coupling chamber, without opening the vacuum chambers. In order to perform XUV/IR-pump-probe experiments we can vary the length of the second interferometer arm. We use a combination of two independently working translation stages (TS1) in the second chamber Ch 2. The coarse translation stage (UTS50PPV6, Newport Corporation) supports a minimal step size of 0.3 µm corresponding to a change in delay of 2 fs. The stage covers a range of 330 ps. The fine delay stage (PX100CAP, Piezosysteme Jena) changes the interferometer arm length with a piezoelectric actuator operated with a closed feedback loop. The piezoelectric actuator enables us to scan a delay range of ≈200 fs. A voltage difference of 10 mV changes the delay by 21 as. A motorized iris in this beam path enables us to change the IR intensity in our experiment independently of the intensity for the HHG. The mirror FM2 defocuses the IR beam after passing into chamber 3 to obtain a similar divergence like the XUV radiation. The XUV and IR beam are collinearly recombined by a mirror with a center hole (DM) with a diameter of 2 mm. The XUV radiation travels from the back of the mirror through the center hole, while IR radiation is reflected on the mirror.

4.2 Refocusing and XUV diagnostics

After their recombination the XUV and IR beam have the same divergence and pass into the next chamber through a metal tube used as an additional differential pumping stage. The dimensions of this chamber are identical to the chambers Ch 1 to Ch 3 of the XUV/IR-interferometer. The chamber is presented in figure 4.3 and houses a toroidal mirror (TORO1, Carl Zeiss Laser Optics GmbH) which refocuses the diverging beams. The mirror consists of a Zerodur substrate with a gold coating of a thickness of 40 nm and is mounted on a motorized five-axis tilt aligner (NewFocus, Inc.). The toroidal radii are $R_{\text{merid}} = 8529.6$ mm and $R_{\text{sagittal}} = 165.2$ mm resulting in a symmetrical imaging with an arm length of 1187 mm. The angle of incidence in our setup is $82^\circ$. This focusing geometry provides us a one-to-one imaging of the focal spot in the HHG target. An important characteristic of the gold-coated toroidal mirror is its relatively constant
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Figure 4.3: Chamber housing the first toroidal mirror (TORO1) and several diagnostic devices. After the collinear recombination of the XUV and IR beam they are focused by the toroidal mirror into the interaction chamber (see subsection 4.3). The translation stage (TS2) allows to insert an MCP-based XUV beam profiler and a calibrated photodiode into the beam path for the characterization of the XUV radiation. After the toroidal chamber we have the possibility to take the IR beam out of the beamline with a movable mirror for further diagnostic.

reflectivity over a broad spectral bandwidth. This is especially an advantage over XUV multilayer mirror with a comparably narrow bandwidth. Accordingly, we are able to operate with different XUV photon energies without changing our focusing setup.

Additional to the toroidal mirror, the chamber contains different devices to characterize the XUV radiation. We have the possibility to measure the total XUV photon flux with a calibrated photodiode (NIST windowless far UV photodiode, NIST National Institute of Standards and Technology, USA). The photo cathode consists of high-purity aluminum on a polished quartz substrate while the anode is a stainless steel cylinder. The quantum efficiency (number of electrons per photon) of the diode lies between 0.1 and 0.15. In combination with an electrometer (Model 6514/E, Keithley Instruments Inc.) we are able to determine the total photon flux by measuring the photocurrent of the diode.
The second diagnostic device in the chamber is a high-resolution beam profiling system that is sensitive to XUV radiation (Model BIS-1135 with BIS-1-PH probe head with BIS-4135 remote system, Colutron Inc.). The beam profiling system consists of a micro-channel plate (MCP) in which the incident XUV pulse will release photoelectrons. The number of electrons is increased by applying a high voltage to the MCP. The electrons finally hit a phosphor screen leading to emission of light proportional to the number of electrons. The phosphor screen is connected to a coherent fiberoptic substrate. The second end of the fiber optics is in direct contact with a CCD. Accordingly, this system enables us to investigate the XUV beam profile for any inhomogeneities originating e.g. from a non-homogeneous metallic filter. The beam profiling system and the photodiode are mounted on a translation stage (TS2) and can be moved into the beam path for investigating the properties of the XUV beam.

Before the beam travels into the first interaction chamber (see section 4.3), we have the possibility to insert a silver mirror with a push-pull translator (Linear motion push-pull translator, Caburn-MDC Europe Limited) to send the beam out of the vacuum system. We positioned an IR beam profiler (Beamage-CCD12, Gentec EO) outside of the vacuum system at the position of the focus. This enables us to investigate the imaging of the toroidal mirror and the correct spatial overlap of both interferometer arms in the focal spot. Furthermore, we can direct the IR beam towards a power meter in order to measure the power. In combination with the beam profile and temporal intensity profile, this allows us to determine the peak intensity of the IR field, which is crucial for the experiments in the following chapters. We obtain the intensity profile with the help of our SPIDER setup (see subsection 2.3.3). Additionally, we send a small fraction of both beams to a spectrometer (HR400CG-UV-NIR, Ocean Optics) to determine the temporal overlap by spectral interferometry.

4.3 First interaction chamber

The common focus of the XUV and IR beam is located in the first interaction chamber (see figure 4.1(c)). The chamber houses specially designed
targets for attosecond transient absorption spectroscopy, for the detection of charged particles and a time-of-flight (TOF) spectrometer.

4.3.1 Charged-particle detection

Any external magnetic field perturbs the detection of charged particles. Accordingly, our interaction chamber possesses a $\mu$-metal shielding against external magnetic fields. The magnetic flux at the focus position is $\approx 4 \mu$T. For measurements that require an even lower magnetic flux we can insert an additional $\mu$-metal shielding at the focus position. We detect charged particles with a TOF spectrometer (electron time-of-flight ETF11, Stefan Kaesdorf). The TOF spectrometer has two electrodes at its tip, a so-called repeller and extractor electrode. By applying a suitable voltage at the repeller and extractor electrodes we are able to detect electrons and also ions. The TOF spectrometer is equipped with a differential pumping stage and a turbomolecular pump in order to operate the MCP of the TOF spectrometer even for pressures of $10^{-4}$ mbar in the interaction chamber. However, the pressure at the MCP stays in this way below its maximum operation pressure of $8 \cdot 10^{-6}$ mbar.

The target providing the gas atoms or molecules for the charged particle detection consists of a stainless-steel needle with an inner diameter of 240 $\mu$m attached to a stainless-steel tube of an inner diameter of 4 mm providing the gas. We regulate the gas flow of the target by a needle valve in combination with the backing gas pressure. We optimize the target position relative to the focus with an external $xyz$-manipulator. The stainless-steel needle ensures the efficient collection of the charged particles with the TOF spectrometer. Typically, this target is used in measurements of electrons or photo fragments of atoms or molecules, e.g. ethylene, in XUV/IR pump-probe measurements. Furthermore, we perform the characterization of the XUV radiation, e.g. attosecond streaking and RABBITT with this target as it is discussed at the end of this chapter.

4.3.2 Transient absorption targets

Attosecond transient absorption measurements require a completely different type of target. In order to observe a reasonable amount of ab-
sorption in a noble gas we need particle densities on the order of $\approx 1 \cdot 10^{17}$ particles/cm$^3$ and higher. The resulting gas load providing this particle density in a continuous gas flow target exceeds the capacity of our turbomolecular pumps of our interaction chamber by far.

The solution to this challenge is to pulse the gas flow of the target which significantly reduces the total gas load and accordingly allows for higher particle densities in the gas pulses. Figure 4.4 presents the schematic cross section of our home-built pulsed gas target. The gas reservoir is connected by a polyamide tube (inner diameter 4 mm) with the gas supply. The backing gas pressure is variable and lies in normal operation condition between 1 bar and 2 bar. We open the target by applying a voltage at the piezoelectric disk (Piezo Disk Translator P286.23, PI GmbH & Co. KG). A metal pin, which is attached via a teflon nut to the piezoelectric disk, moves down with the disk and to that effect opens the gas reservoir towards the interaction chamber. The teflon nut allows to move the metal pin up and down and accordingly to define the voltage at which the valve opens. An O-ring on top of the metal pin ensures that the reservoir is closed properly when no voltage is applied. The opening and therefore the amount of released gas is proportional to the applied voltage. We operate the piezoelectric disk with the repetition rate of the laser amplifier system of 1 kHz. Therefore, we send the output signal of the laser-timing unit to a delay generator (Model DG535, Stanford Research Systems, Inc.). The output of the delay generator is a transistor-transistor-logic (TTL) signal with adjustable amplitude and duty cycle. A voltage amplifier (HVPZT-POWER-AMPLIFIER, PI GmbH & Co. KG) increases the amplitude of the signal by a factor of 100. The duty cycle of the signal, corresponding to the opening time, and the delay of the opening with respect to the laser pulses are optimized for maximal absorption at the lowest possible gas load. The gas reservoir is mounted on a copper heat sink, which is actively cooled with a chiller. This prevents the piezoelectric disk from heating up which inhibits the proper opening and closing of the valve.

The complete pulsed target is mounted on a $xyz$-manipulator (UHV Manipulator PMM 12, VAb Vakuum-Anlagenbau GmbH). The tip of the target has a dimension of $1.5\text{ mm} \times 1.5\text{ mm} \times 10\text{ mm}$ in order to ensure that
Figure 4.4: Cut through the pulsed target for absorption measurement in the gas phase. A voltage applied to the piezoelectric disk opens the valve by moving down the metal pin. The O-ring on top of the metal pin ensures the proper closing of the valve. The T-shaped exit helps to confine the released gas and provide a high particle density. The whole target is mounted on a water-cooled copper heat that prevents the heating of the valve.

the target can be moved exactly into the focus position through a hole in the repeller electrode of the TOF spectrometer. The T-shaped exit of the target has a hole diameter of 300 µm. This confines the gas to a relatively small volume and helps to reach high particle densities in the focus. Figure 4.5 illustrates the interaction chamber with pulsed and the needle target in combination with TOF spectrometer.

As will be discussed in chapter 9 in detail we also performed attosecond transient absorption experiments in solids. In a first experiment we examined the IR-induced changes of the optical properties of polycrystalline diamond on an ultrafast time scale. We designed a sample holder for the thin diamond membranes. The sample holder is attached to the stainless-steel tube of the needle target and fits between the repeller and extractor electrode of the TOF-spectrometer. This enables to insert solid-state targets into the position of the focal spot without removing the TOF spectrometer or its electrodes. Figure 4.6 depicts the sample holder. We attach the holder with the screw on the stainless-steel tube of the needle target. A metal plate fixed with two screws presses the samples against
4.4 XUV spectrometer

After the transmission of the XUV and IR radiation through the first interaction chamber it impinges on a spherical mirror (SM, ROC = 8 m) under an angle of 80°. The mirror creates a line focus onto the entrance slit of the XUV spectrometer. The width of the entrance slit is 100 µm. Before the beam enters the spectrometer through the slit, the residual IR radiation is filtered out with an additional metallic filter. The toroidal grating of the flat field spectrometer (McPherson Model 251) has 450 grooves/mm and enables us to detect photon energies up to ≈100 eV. For the detection of higher-energetic photons the grating can be exchanged for another grating with 1200 grooves/mm. We detect the spectrally dispersed XUV
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Figure 4.7: The spherical mirror SM directs the XUV and IR radiation on path 1 to the XUV spectrometer. The residual IR radiation is filtered by metallic filters before the spectrometer. By removing the spherical mirror with a translation stage TS3 we send the beam on the second toroidal mirror TORO2 which focuses the IR and XUV beam into the second interaction region. A movable mirror allows us to extract the beam for characterization purposes.

Radiation with a XUV-sensitive CCD camera (PIXIS-XO, 400B, Princeton Instruments). The CCD has a size of 1340×400 pixels. It is possible to directly read out the full chip in an imaging mode or to spatially integrate and only read out the spectrum. The imaging mode provides information about the far-field spatial profile of the XUV radiation. The spectral resolution in the range around 25 eV is ≈30 meV. The high efficiency of the XUV-sensitive CCD camera enables us to record a full XUV spectrum with an exposure time of 1 ms under standard experimental conditions. The fast acquisition of data is a major advantage over the detection of charged particles where the acquisition of a spectrum requires at least several seconds.

It is important to note that our setup allows the simultaneous detection of the transmitted XUV radiation during a measurement detecting charged particles, e.g. during a RABBITT measurement.

4.5 Second interaction target

A prominent feature of our attoline is a second interaction focus. For the creation of this second focus we remove the spherical mirror SM out of the beam path with a motorized translation stage (TS3, ECS3070, attocube).
The diverging beam travels along the path 2 (see figure 4.7) and impacts on the second toroidal mirror (TORO2) under an angle of 80°. The toroidal mirror has an identical sagittal and meridional radius of curvature as the first toroidal mirror leading to an arm length of 1000 mm. The second focus is accessible for any end station. Figure 4.1 shows as an example a hemispherical electron analyzer for the investigation of photoemission from solid-state systems at the focus position [76]. As a first proof-of-principle experiment for a working relay-imaging and to demonstrate that we are able to perform two experiments in the two focal spots simultaneously, we performed two RABBITT measurements in the gas phase (see subsection 4.6.3 for more details).

4.6 Attosecond streaking, RABBITT and double RABBITT

The upcoming of sub-femtosecond pulses in the XUV spectral range created the demand for new pulse characterization methods. Traditional techniques for the investigation of femtosecond pulses, e.g. autocorrelation, FROG or SPIDER are not easily transferable into this new regime. The reasons for this difficulty lies in the low photon flux and the lack of a suitable nonlinear material in the XUV spectral range. Nevertheless, first intensity and interferometric autocorrelation experiments have been performed but still suffer from a poor SNR [83, 84].

As a solution for the pulse characterization the attosecond streaking and the RABBITT technique were developed [14, 85, 12, 13]. Both methods rely on the cross correlation of the XUV radiation with a synchronized IR field in a gas target and the subsequent detection of the created photoelectrons as a function of the XUV/IR delay.

4.6.1 Attosecond streaking

The attosecond streaking technique is applied for the characterization of SAPs. The impinging XUV pulse creates an electron wavepacket by single-photon ionization of an atom in the gas target. The temporal structure of the XUV radiation is transferred to the temporal structure of the elec
Figure 4.8: (a) Experimental attosecond streaking spectrogram recorded with SAP generated in Xe with the PG technique after the transmission through a 100 nm-Al filter. (b) Reconstructed spectrogram with the FROG-CRAB algorithm after $8 \cdot 10^5$ iterations.

Electron wavepacket. The photoelectron interacts with the electric field of the overlapped IR pulse directly after its release. It is important to note, that the XUV and IR pulse are inherently synchronized due to the generation of the SAP by the same initial IR pulse. An electron that is emitted with an initial velocity $v_0$ along the polarization axis of the IR field experiences a change of velocity (where we use atomic units in this subsection) $\Delta v(\tau_i) = -A_{IR}(\tau_i)$ in this direction, where $A_{IR}(\tau_i)$ represent the vector potential of the IR field at the moment of ionization $\tau_i$ [11]. For simplicity, we discuss here only the velocity component parallel to the polarization of the IR laser field. Accordingly, the final velocity $v_f(\tau_i)$ of the electron is:

$$v_f(\tau_i) = v_0 - A_{IR}(\tau_i).$$ (4.1)

By changing the delay between the SAP and the IR field, the vector potential experienced by the electron changes and following the final velocity of the photoelectron. After the interaction of the electron with the IR field is over we detect the photoelectrons with the TOF spectrometer. In this way, we record an electron spectrum for each delay step between the fields and obtain a streaking spectrogram, shown in figure 4.8(a). We clearly observe the shift of the photoelectron energy following the vec-
4.6. Attosecond streaking, RABBITT and double RABBITT

Figure 4.9: Temporal intensity profile (solid line) of a SAP generated with the PG technique in Xe after transmission through a 100 nm-Al filter. The temporal profile and the phase of the pulse (dashed-dotted line) were reconstructed out of the experimental spectrogram shown in figure 4.8 with the FROG-CRAB algorithm.

tor potential of the IR field. Additionally to the semi-classical treatment Itatani et al. and Kitzler et al. introduced a quantum-mechanical description of attosecond streaking [85, 86]. This treatment nicely reveals that the IR field modulates the phase of the photoelectron or in other words acts as a phase gate. The phase gate can be understood in analogy to FROG. Hence, it is possible to apply the pulse reconstruction methods already well-established in the FROG technique to the attosecond streaking. The reconstruction method was named frequency-resolved optical gating for complete reconstruction of attosecond bursts (FROG-CRAB) and provides the phase and spectrum of the initial XUV pulse. As an example, we show the reconstruction of the streaking spectrogram of figure 4.8(a) in panel (b) of the same figure and the reconstructed XUV pulse with its spectral phase in figure 4.9. Furthermore, the FROG-CRAB technique allows even the reconstruction of the electric field of the IR pulse.

4.6.2 RABBITT

The temporal characterization of an APT with the RABBITT technique exploits the interference of different quantum pathways leading to the same
final quantum state instead of the acceleration of the photoelectrons in the IR field like in attosecond streaking. Therefore, the RABBITT technique requires a lower peak intensity of the IR field for the cross-correlation measurement. At the heart of the RABBITT technique is a two-color two-photon transition of a ground-state electron of the noble gas target atoms to a continuum state. As figure 4.10 shows there are two pathways for the electron to the same final state in the continuum in the presence of the IR field: absorption of one XUV photon of HH \( q \) and absorption of one IR photon or absorption of one XUV photon of HH \( q + 2 \) and the emission of one IR photon. The scheme illustrates that the low intensity is important since higher intensities may lead to transitions including more than one IR photon [87]. In the photoelectron spectrum these two-photon transitions manifest in sidebands appearing energetically between the HHs at even multiples of the fundamental IR photon energy. In the absence of the IR pulse no electrons with the sideband energy appear in the electron spectrum.

The low IR intensity allows to describe the formation of the sidebands in second-order perturbation theory [12]. The transition probability to the final state and accordingly the amplitude \( S_{q+1} \) of the electron signal at the sideband neighboring HH \( q \) and \( q + 2 \) can be expressed as:

\[
S_{q+1} \propto \cos \left( 2 \varphi_{\text{IR}} + \varphi_q - \varphi_{q+2} + \Delta \varphi_{\text{atomic}}^{q+1} \right). \tag{4.2}
\]

\( \varphi_{\text{IR}} = \omega_{\text{IR}} \tau \) represents the phase of the IR field with the angular frequency \( \omega_{\text{IR}} \) and the XUV/IR delay \( \tau \). Therefore, the intensity modulates with twice the frequency of the IR field as a function of XUV/IR delay due to the interference of the two distinct quantum pathways leading to the same final state. Furthermore, the amplitude of the sideband depends on the atomic phase \( \Delta \varphi_{\text{atomic}}^{q+1} \). The contribution of the atomic phase is in comparison to the other contributions small and can be extracted from calculations with high accuracy [85]. \( \varphi_q - \varphi_{q+2} \) corresponds to the phase difference between the HH \( q \) and \( q + 2 \), respectively. Pairwise fitting of the sidebands with a cos-function provides the phases of the HHs. The phase difference between the HHs is named atto-chirp. In combination with the relative intensity of the HHs \( I_q \) the atto-chirp yields information about the average duration of a single XUV burst of the APT. It is important to note
that the RABBITT technique does not provide information on the number of pulses in the train or the envelope of the APT. The envelope of the IR pulse and its chirp define the number of pulses in the train and the spectral bandwidth of a single HH.

Except from the lower IR peak intensity the experimental technique for the characterization of an APT is comparable to the attosecond streaking since photoelectron spectra are recorded with a TOF spectrometer as a function of XUV/IR delay. Figure 4.11 shows a part of a RABBITT trace recorded with HHs generated in Xe and Ar as a target gas. The measurements exhibits the sidebands appearing between the HHs and their modulation as a function of the XUV/IR delay. Furthermore, figure 4.11 also shows that the amplitude of the signal created by the HHs modulates as well with the delay. For the pulse characterization the description of the sidebands following equation 4.2 is sufficiently accurate. However,
4. Attoline

Figure 4.11: RABBITT measurement recorded in Ar. The corresponding HHs were generated in Xe. We clearly observe the appearing of sidebands between the HHs and their oscillations with XUV/IR delay. Simultaneously, the signal is depleted and oscillates as a function of delay, too.

the RABBITT technique can be applied to extract information on photoemission dynamics [76, 88, 89, 90]. This case demands a more elaborate analysis including the phases of the continuum-continuum transition of the electron.

4.6.3 Double RABBITT

The double RABBITT is a unique measurement technique enabled by the special geometry of the attoline setup. Due to the second focus obtained by relay-imaging of the first focus with the second toroidal mirror we have the possibility to perform two XUV/IR cross-correlation measurements in coincidence in the two foci. As mentioned before, our beamline is designed for different end stations in the second focus. The double RABBITT results presented here were obtained with a hemispherical electron analyzer (Phoibos 150 WAL, SPECS GmbH) placed in the second focus. This analyzer is designed to detect photoelectrons from surfaces. In order to perform the double RABBITT we replaced the solid-state target by a needle gas target as described before in subsection 4.3.1.

As a first proof-of-principle experiment we performed a simultaneous RABBITT measurement in both foci with Ar as a target gas. Figures 4.12(a) and (b) show the two obtained RABBITT traces. The upper panel (a)
Figure 4.12: Double RABBIT recorded in Ar. The upper panel (a) shows the RABBIT of the first focus and (b) the RABBIT recorded in the second focus with the hemispherical electron analyzer. In panel (b) we subtracted the background signal for better visibility of the sidebands. The sidebands appear at the following energies: 5.6 eV, 9.0 eV, 12.3 eV and 15.5 eV corresponding to the HH order 14 to 20.

presents the RABBIT recorded in the first interaction chamber and the lower panel (b) the measurement in the relay-imaged second focus. The observation of sidebands in the photoelectron spectrum of the second focus and their modulation with twice the frequency of the fundamental IR radiation are the confirmation that the relay-imaging of the first focus works perfectly. Moreover, we conclude that the temporal profile of the APT and the IR were not significantly distorted by transmission through the first gas target since we observe the oscillations of the sidebands in the second target. The difference in the relative intensities of the HHs and sidebands for the two RABBITT measurements results from the different transmission efficiencies of the two detectors. The double RABBITT measurements shows the excellent interferometric stability of the attoline...
since the measurement took several hours for the complete delay range and lacked any instabilities of the interferometer.

4.7 Conclusion

In conclusion, we presented in this chapter the attoline at ETH Zurich, a beamline for attosecond pump-probe experiments. We described the vacuum system housing the HHG and the XUV/IR interferometer enabling us to perform time-resolved measurements with attosecond resolution. The careful design of the attoline leads to an excellent passive stability that allows interferometric measurements over several hours with attosecond stability. We discuss the ability to detect positively charged particles or electrons with a TOF spectrometer, both originating from XUV/IR cross-correlation measurements in the gas phase. Moreover, we have the ability to detect the transmitted radiation with a XUV-sensitive CCD-based spectrometer. This is a prerequisite for the attosecond transient absorption experiments presented in the following chapters. We demonstrated two specific targets for attosecond transient absorption experiments: a specially designed target for measurements in the gas phase providing a high particle density during the interaction with the XUV/IR field by keeping the total gas load low and a holder for condensed matter samples for solid-state spectroscopy. As a unique characteristic of our attoline we presented the relay-imaging of the first XUV/IR focus with a second toroidal mirror enabling us to perform simultaneous measurements in two foci. As a proof-of-principle experiment we demonstrate a double RABBITT, where we recorded two RABBITT measurements in argon (Ar) in coincidence in both foci.
Chapter 5

Time-gated optical gain and loss

The interaction of electromagnetic radiation with matter is omnipresent in nature. Absorption and transmission have been used since a long time to study the properties of matter. In particular, the invention of the laser more than 50 years ago opened the door to a variety of new spectroscopic techniques that boosted the scientific progress significantly [4]. In more recent years, the emergence of laser sources producing ultrashort lasers pulses allowed to investigate dynamical processes down to the femtosecond time scale [20]. The tremendous success of femtosecond absorption spectroscopy culminated in the Nobel Prize in chemistry in 1999 [10]. Since more than 10 years it is now possible to create light pulses even with sub-femtosecond duration with the help of HHG [11]. The combination of attosecond pulses with time-resolved absorption spectroscopy led to attosecond transient absorption spectroscopy [19, 17, 18].

Whereas the majority of experiments in attosecond science and also in attosecond transient absorption spectroscopy investigates the resonant excitation or direct ionization of matter this chapter reveals that also the off-resonant excitation holds promising results. We reveal that in combination with a second electromagnetic field a medium is not necessarily transparent to an off-resonant exciting pulse.

Here, we discuss the control of the optical properties of a medium in the XUV spectral range. We present a method to manipulate absorption and optical gain via the delay between two pulsed electromagnetic fields.
In the first part we present our theoretical model to predict the response of a two-level system (TLS) towards electromagnetic excitation. In the second part we verify our prediction with an attosecond transient absorption experiment in He.

5.1 Theoretical model

For the explanation of the experimental results shown in the second part of this chapter, we first discuss prior to this the optical response of a TLS under optical excitation. The TLS represents the simplest model for the light-matter interaction and its dipole response defines the optical properties. Therefore, we derive an expression for the dipole response of the TLS and scrutinize its temporal behavior.

5.1.1 Two-level system

We investigate an atomic system under the influence of pulsed electromagnetic fields. Atomic TLSs exposed to electromagnetic fields were already discussed in numerous publications in the past, e.g. by B. R. Mollow or C. Delagnes et al. [91, 92]. Nevertheless, the experiments investigated the TLSs in the monochromatic limit with a continuous-wave laser or with a fixed delay between the fields.

Here, the system under consideration consists of a ground state $|g\rangle$ and a manifold of excited states, labeled $|s\rangle$, $|p\rangle$ and $|d\rangle$. Furthermore, we assume energetic degeneracy of these three excited states. In a first step we study the off-resonant excitation of the system with a pulsed electromagnetic field. In order to understand the interaction of light with this atomic system, we show that the system discussed here can be treated as a simple TLS under certain assumptions. The off-resonant excitation and the chosen field strength of the exciting pulse allow us to treat the coupling of the ground state to the excited state $|p\rangle$ as a perturbation of the system. The transition from the ground state to the excited states $|s\rangle$ and $|d\rangle$ is forbidden by dipole selection rules. The resulting Hamiltonian reads:

$$H = \sum_{j=s,p,d} \Delta |j\rangle \langle j| + \left[ \tilde{V}(t) |g\rangle \langle p| + \tilde{V}(t) |s\rangle \langle p| + \tilde{V}(t) |p\rangle \langle d| + h.c. \right].$$

(5.1)
We used here and in the following theoretical description atomic units (Reduced Planck constant $\hbar = 1$, elementary charge $e = 1$, electron mass $m_e = 1$) unless stated differently. $\Delta$ corresponds to the energetic separation of the ground state and the excited states. We set the ground state energy to zero. The exciting electromagnetic field $\tilde{V}(t)$ is defined as:

$$\tilde{V}(t) = d_{gp} \tilde{E}_t \cos \tilde{\omega} t,$$

where $\tilde{E}_t = E_0 e^{-2 \ln^2 (t/T)^2}$ represents the Gaussian envelope of the electric field of the exciting pulse and $d_{gp}$ the dipole matrix element of the transition of the ground state to the excited state $|p\rangle$. $\tilde{\omega}$ is the angular frequency of the field, which is equivalent to the photon energy in atomic units. In the Hamiltonian shown in equation 5.1 we already included a second electromagnetic field $\bar{V}(t)$. Whereas the photon energy of the exciting field $\tilde{\omega}$ is comparable to $\Delta$, we define the photon energy of the second field as $\bar{\omega} \ll \Delta$. Hence, the second field cannot couple the ground state to the excited states. Nevertheless, this field is crucial for the coupling of $|p\rangle$ to $|s\rangle$ and $|d\rangle$.

These conditions enable us to transform the Hamiltonian in equation 5.1 with a unitary transformation into the following expression:

$$H = \sum_{j=-1,0,+1} \left[ \Delta + j \sqrt{2} \tilde{V}(t) \right] |j\rangle \langle j| + \sum_{j=-1,+1} \left( [j\bar{V}(t)/\sqrt{2}] |g\rangle \langle j| + h.c. \right).$$

(5.3)

It is important to note that the transformation does not depend on $\bar{V}(t)$, from now on referred to as control pulse. The Hamiltonian in equation 5.3 contains the two states $|\pm 1\rangle$, which couple to the ground state. The control pulse modulates the transition energy from $|g\rangle$ to $|\pm 1\rangle$. However, it is not possible to couple the so-called ‘dark state’ $|0\rangle$ to the ground state with $\bar{V}(t)$.

In a next step we neglect $|-1\rangle$ since the interaction of the control pulse with $|+1\rangle$ and $|-1\rangle$ is only different in the sign. With this step we finally achieve to express our atomic system containing the ground state $|g\rangle$ and the three degenerated states $|s\rangle$, $|p\rangle$ and $|d\rangle$ as a TLS built up by $|g\rangle$ and the excited state $|+1\rangle \equiv |e\rangle$. Therefore, we can write the system’s Hamiltonian in the following way after we redefined the laser pulses to
remove the factor $\sqrt{2}$ in equation 5.3:

$$H = [\Delta + \tilde{V}(t)] |e\rangle \langle e| + [\tilde{V}(t) |g\rangle \langle e| + h.c]. \tag{5.4}$$

The wave function of the system is a superposition of the two states $|g\rangle$ and $|e\rangle$ and can be written as:

$$|\psi(t)\rangle = |g\rangle a_g(t) + |e\rangle a_e(t), \tag{5.5}$$

where $a_g(t)$ and $a_e(t)$ represent the complex amplitude of the states $|g\rangle$ and $|e\rangle$, respectively. Since we treat the exciting pulse $\tilde{V}(t)$ as a perturbation to the system it is justified to assume that the ground state is not depopulated, which corresponds to $a_g(t) \equiv a_g \equiv 1$. We now have to insert the wave function expressed by equation 5.5 into the TDSE using the Hamiltonian defined in equation 5.4

$$i \frac{\partial}{\partial t} |\psi(t)\rangle = H |\psi(t)\rangle. \tag{5.6}$$

This leads us to equation 5.7, which describes the dynamics of the complex amplitude of the excited state $a_e(t)$:

$$i \frac{\partial}{\partial t} a_e(t) = [\Delta + \tilde{V}(t)] a_e(t) + \tilde{V}(t). \tag{5.7}$$
5.1. Theoretical model

$\mathcal{V}(t)$ plays the role of a source term and $\Delta + \mathcal{V}(t)$ corresponds to the transition energy of the TLS modulated by the control pulse $\mathcal{V}(t)$. The reader should note that $\Delta + \mathcal{V}(t)$ can cross the energy $\bar{\omega}$, but only at certain instances in time. Therefore, the dressed states are still regarded as off-resonant in the dressed-state picture.

5.1.2 Optical response of the two level system

Since we are interested in the optical response of our TLS we need to know in which way the incoming electric field is modified while interacting with the TLS. In any experiment the incoming field will interact with an ensemble of TLSs rather than with a single system. After the interaction with the TLS, the electric field consists out of the incoming field $E_{\text{pulse}}(t)$ and the electric field emitted by the oscillating dipole of the TLS $E_{\text{dip}}(t)$.

Under the assumption that it is allowed to treat all electric fields as plane waves, the spectral intensity, which will be observed in an experiment is given by:

$$S(\omega) = \left| \int dt e^{i\omega t} [E_{\text{pulse}}(t) + E_{\text{dip}}(t)] \right|^2 = |E_{\text{pulse}}(\omega)|^2 + |E_{\text{dip}}(\omega)|^2 + 2 \text{Re}[E_{\text{pulse}}(\omega) \cdot E_{\text{dip}}^*(\omega)].$$

We neglect all propagation effects of the radiation through the medium in this model [93]. Accordingly, we have to find the electric field emitted by the dipole $E_{\text{dip}}(t)$ for a comparison between simulated and experimental results.

The dipole field $E_{\text{dip}}(t)$ depends on the polarization $P(t)$ induced by $E_{\text{pulse}}(t)$:

$$E_{\text{dip}}(t) = \frac{2\pi}{c} \frac{\partial}{\partial t} P(t),$$

where $c$ represents the speed of light. The induced polarization $P(t)$ may be expressed with the help of the dipole moment $d(t)$ of the TLS and leads to the following expression for $E_{\text{dip}}(t)$ [93]:

$$E_{\text{dip}}(t) = \frac{2\pi}{c} n l \frac{\partial}{\partial t} d(t),$$
where \( n \) corresponds to the density of the dipoles and \( l \) to the length of the interaction medium.

This means that we have to find an expression for the dipole of the TLS to determine its optical response upon \( E_{\text{pulse}}(t) \). The general expression for the dipole reads as:

\[
d(t) = a_g(t) \langle g | r | e \rangle a_e(t) + \text{c.c.},
\]

(5.11)

where \( r \) expresses the quantum mechanical position operator. Since we assume that the excitation from the ground state to the excited state takes place in the perturbative regime, i.e. \( a_g(t) \equiv 1 \), the dipole of the TLS simplifies to:

\[
d(t) \propto a_e(t) + a_e^*(t).
\]

(5.12)

In order to determine \( d(t) \) we have to find a solution of equation 5.7 to obtain the amplitude of the excited state \( a_e(t) \). The formal solution of the Schrödinger equation gives us:

\[
a_e(t) = -i \int_{-\infty}^{t} dt' e^{-i\Delta(t-t')-i \int_{t'}^{t} dt'' \tilde{V}(t'')} \tilde{V}(t'),
\]

(5.13)

This form allows in two particular cases for an explicit analytical solution.

1. In the first case, when a control field is absent, i.e. \( \tilde{V}(t) \equiv 0 \), in the case of off resonant excitation, \(|\tilde{\omega} - \Delta| \tilde{T} \gg 1\), the dipole is given by

\[
d(t) = \frac{1}{\tilde{\omega} - \Delta} \tilde{V}(t),
\]

(5.14)

which follows from equation 5.13 by partial integration and the assumption that \( \frac{\partial}{\partial t} \tilde{V} \approx 0 \), i.e. the envelope of the excitation pulse changes slowly in time.

2. In the second case, we assume an oscillatory control field described by \( \tilde{V}(t) = \tilde{V}_0 \cos \tilde{\omega}t \). In this case, we represent the dipole as an infinite sum with Bessel functions of the first kind \( J_k \) (see appendix A):

\[
d(t) = \left( \sum_{k=-\infty}^{+\infty} \frac{[J_k(\tilde{V}_0 / \tilde{\omega})]^2}{\tilde{\omega} - (\Delta + k\tilde{\omega})} \right) \tilde{V}(t),
\]

(5.15)
The role of the Bessel functions is to give a certain weight to the individual contributions of the dressed states to the dipole response of the sum. These dressed states are separated in energy by multiples of the photon energy of the control field $\bar{\omega}$. For the transition to an electromagnetic pulse one has to replace $\bar{V}_0$ in the argument of the Bessel function with the envelope of the control field $\bar{V}_t$. This leads to the time-dependent dipole with a finite control pulse.

In a final step, we want qualitatively take into account that the control field can couple the TLS to higher excited states or to continuum states. Therefore, we introduce a parameter $\gamma_c$ in the TDSE (see equation 5.7):

$$i \frac{\partial}{\partial t} a_e(t) = [\Delta + \bar{V}(t) - i\gamma_c \bar{V}_t]a_e(t) + \bar{V}(t).$$

(5.16)

We choose the parameter $\gamma_c$ in a way that the term $\gamma_c \bar{V}_t$ is proportional to the instantaneous control field because this field dominates the coupling. The consequence of the introduction of $\gamma_c$ is the broadening of the transition. The dipole response is modified and reads as:

$$d(t) \approx \left( \sum_{-\infty}^{+\infty} \frac{\bar{\omega} - (\Delta + k\bar{\omega})}{[\bar{\omega} - (\Delta + k\bar{\omega})]^2 + [\gamma_c \bar{V}_t]^2} J_k(\bar{V}_t/\bar{\omega}) \right) \bar{V}(t).$$

(5.17)

5.1.3 Time-integrated dipole response

The expression in equation 5.17 allows us to examine the time-dependent dipole response of the TLS for an off-resonant excitation in combination with a control field. However, we first discuss the evolution of the dipole response as a function of time when the control field is absent in figure 5.2. It is important to note that the abscissa in figure 5.2 represents time and not the delay between two pulses. For the excitation we apply a pulse with a center energy of 23.37 eV and a duration of 20 fs. The upper part of figure 5.2 shows the temporal envelope of the exciting pulse peaking at time $t = 0$. The absent control field is indicated by the red zero line. The energetic separation between the ground state $|g\rangle$ of the TLS and the excited state $|e\rangle$ is 23.08 eV. The dashed line in figure 5.2 indicates the energy of the excited state $|e\rangle$. The parameters of the simulations are in principle arbitrary but chosen to match the conditions of the attosecond transient absorption experiment shown in the second part of this chapter. The response shows an oscillatory behavior including positive and
negative contributions following equation 5.14. The oscillation pattern is centered around the energy of the exciting pulse and the oscillation period is inversely proportional to the energy difference $\tilde{\omega} - \Delta$.

Although this representation is very useful to understand the processes under consideration, we want to stress here that the temporal evolution of the dipole response is usually not accessible in an experiment. Traditional spectroscopy only measures the time-integrated dipole response (TIDR). The consequences of the time-integrated detection are shown in figure 5.3. The dashed-grey line in figure 5.3 represents the temporal integration of the dipole response only for negative times $t < 0$. The dotted-purple curve shows the corresponding TIDR for positive times $t > 0$. As aforementioned, in an experiment we only can measure the TIDR over all times, which corresponds to the sum of the dotted-purple and the dashed-grey curve of 5.3. The solid-blue curve shows the result. The TIDR is zero for all energies. This emerges out of the balance of positive and negative contributions in the temporal evolution of the dipole response. The zero TIDR
corresponds to no absorption of the exciting pulse and is in agreement to our expectation for an off-resonant excitation of a TLS.

Even though the total TIDR is zero in the case of an off-resonant excitation, we observe that the dipole response contains non-zero contributions during its temporal evolution. In order to access these non-zero contribution we additionally apply the control pulse to the TLS. The control pulse has a center energy of 1.57 eV and a duration of 30 fs (FWHM). As for the exciting pulse, these parameter match the experimental study presented in the second part of this chapter. The intensity of the control pulse is not sufficient to induce multiphoton transition from the ground to the excited state of the TLS. However, the intensity if high enough to modulate the transition energy of the system. Figure 5.4 shows the temporal evolution of the dipole response for the off-resonant excitation and the additional control pulse arriving at $+15$ fs. The upper part shows the temporal envelope of the field of the exciting pulse (blue) and the field of the control pulse (red). The reader should note that the relation between the amplitudes of the fields is not presented realistically. The intensity of the control pulse is significantly higher in the simulations. We observe that the con-
Figure 5.4: Time-dependent dipole response as a function of photon energy and time for off-resonant excitation and an additional control pulse (center energy: 1.57 eV and duration: 30 fs (FWHM)) arriving at +15 fs. The negative and positive contributions of the response are color-coded in blue and red, respectively. The temporal envelope of the exciting pulse (20 fs (FWHM)) and the field of the control pulse are shown in blue and red in the upper panel, respectively. The center energy of the exciting pulse is 23.37 eV. The dashed line shows the transition energy of the TLS (23.08 eV).

trol pulse suppresses the response of the TLS. This means that the delicate balance between positive and negative contributions is broken.

Therefore, the suppression of the dipole response results in a non-zero TIDR as figure 5.5 shows. Like in figure 5.3 we present the TIDR for the total time integration and separated into an integration only over positive or negative times. The total TIDR reveals positive and negative contribution for different photon energies. While a positive TIDR corresponds to absorption, the negative TIDR represents a net emission of photons. This means that for a certain photon energy we gain photons by transmission through the ensemble of TLSs. Accordingly, we interpret a negative TIDR as optical gain. Nevertheless, if we integrate over the full spectrum we obtain no net-emission of photons due to energy conservation.

The TIDR also depends on the relative delay between the exciting and control pulse. Accordingly, we simulate a pump-probe experiment by changing the delay and calculating the corresponding TIDR. Figure 5.6 il-
Figure 5.5: TIDR of the TLS to an off-resonant excitation and a control pulse arriving at $+15\text{ fs}$ as a function of photon energy. The center energy of the excitation pulse is 23.37 eV and the excited state of the TLS is located at 23.08 eV. For a better understanding we separated the integration into two parts. The dashed-grey shows the integration for negative times and the dotted-purple the integration for positive times, respectively. We obtain a non-zero TIDR since the control pulse suppresses the dipole response.

Illustrates the calculated TIDR as a function of photon energy and delay. We stress that here the abscissa represents the delay between the two pulses and not the time as in figures 5.2 and 5.4. For a negative delay the control pulse arrives at the TLS before the exciting pulse. The obtained result is symmetric around delay-zero where the peak of both pulse envelopes exactly overlap in time and furthermore, point symmetric about the center frequency of the exciting pulse. We observe a strong positive TIDR around delay-zero corresponding to a strong absorption when both pulses temporally overlap. Additionally, we observe a delay-dependent negative TIDR for different photon energies. It is possible for certain photon energies to switch between optical gain and absorption. The magnitude of the response can be controlled by changing the delay between the exciting and control pulse. It is also important to note that the optical gain, even though it is weaker, is of the same order of magnitude as the absorption.

The calculations we presented here are generic for any TLS. Accordingly, we expect that our theoretical discussion is extendable to other systems that obtain a TLS character, e.g. molecules or low-dimensional solid-state systems. Of course, this requires a proper scaling of the photon energies and intensities. The presentation of the temporally resolved dipole
5. Time-gated optical gain and loss

Figure 5.6: TIDR as function of delay between control and exciting pulse and photon energy.

response as a function of photon energy provides an intuitive explanation for the creation of optical gain in an off-resonantly excited TLS.

5.2 Experimental results

For the verification of our theoretical prediction of the creation of optical gain, we perform an attosecond transient absorption experiment. We use the setup described in chapters 2 and 4. In the experiment the IR pulse with a duration of 30 fs and a peak intensity of $\approx 4.2 \cdot 10^{12}$ W/cm$^2$ acts as the control pulse. We create an APT with a duration of $10^{-12}$ fs via HHG in Ar [19]. The APT and the IR pulse are focused with the toroidal mirror into the pulsed gas target filled with He in the first interaction chamber. We adjust the particle density to $\approx 5 \cdot 10^{17}$ particles/cm$^3$ corresponding to $\approx 50 \%$ absorption of HH 17 right above the first ionization potential of He.

The HH 15 of our APT lies energetically at 23.37 eV with a bandwidth of $\approx 130$ meV (FWHM). This is still below the first ionization potential of He at 24.59 eV and between the two excited states 1s3p and 1s4p as shown in figure 5.7(a). Using a SAP instead of a APT would be disadvantageous for our purposes. The broad continuous spectrum of a SAP overlaps with all the excited states of He reaching even into the continuum. This prevents the off-resonant excitation that is possible with the discrete HHs of
an APT. We characterize our APT with the RABBITT technique yielding an average duration of one pulse of our APT of 350 as [12, 13].

As already mentioned and shown in figure 5.7(a) HH 15 lies between the 1s3p and 1s4p excited states. Furthermore, the dipole matrix element for the transition from the ground state to the 1s3p state is by a factor of 3 larger than to the 1s4p state [94]. Hence, we neglect the 1s4p state and get our TLS consisting of the 1s^2 state representing the ground state |g⟩ and the singly excited 1s3p state representing the excited state |e⟩.

Figure 5.7(b) presents the transmitted XUV intensity as a function of photon energy and XUV/IR delay. We discover a strong decrease of the signal around delay-zero where the APT and the IR pulse overlap temporally. The HH 15 is located ≈1.22 eV below the first ionization threshold of He. Accordingly, there is no direct one photon absorption for HH 15 possible. Nevertheless, a two-color two-photon absorption of one XUV and one IR photon suffice to excite an electron from the 1s^2 ground state into the continuum leading to an absorption of the XUV radiation when the IR pulse is present.

For a more detailed analysis of the delay scan we plot the natural loga-
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A natural logarithm of the IR-induced change of the relative signal $\Delta \alpha$:

$$\Delta \alpha = -\ln(I_{\text{IR}}/I_0), \quad (5.18)$$

where $I_0$ represents the transmitted XUV spectrum without the IR pulse and $I_{\text{IR}}$ the spectrum with the IR pulse, respectively. A positive change corresponds to an increase of absorption, like a positive TIDR. The dominant absorption feature around delay-zero is clearly visible also in this representation of the experimental data. Moreover, we observe a negative change of $\Delta \alpha$ at certain photon energies and delays. The negative change represents a net emission of photons at this energy and is in qualitative agreement with the prediction for the TLS shown in figure 5.6. The magnitude of the net emission or optical gain can be controlled by the delay between the XUV and IR field.

An important point is that we observe the optical gain even significantly below 23.2 eV and above 23.5 eV. Figure 5.7(a) shows that there are no spectral components above the noise level in these spectral regions. Since our pulse is off-resonant with respect to the excited states of He, we prevent the creation of a coherence. Accordingly, we exclude the effect of perturbed free-induction decay as the origin of the observed signal [95].
5.3 Conclusion

In conclusion, we presented the creation and control of optical absorption and gain. In a first part, we investigated the temporal evolution of the dipole response of a generic TLS after the off-resonant excitation with a laser pulse. The dipole response contains positive and negative contributions that cancel out in the time-integrated detection of traditional spectroscopy. By adding a second laser pulse, the so-called control pulse, we are able to interrupt the temporal evolution and suppress the dipole response. A variable delay between the two enables us to manipulate and control the TIDR in magnitude and switch the sign of the response. The theoretical model gives an interesting insight into the dynamics of an atomic dipole and motivates for an experiment accessing the nonzero contributions.

Consequently, we demonstrated in the second part the corresponding attosecond transient absorption experiment in He using a APT for the off-resonant excitation. We investigate the spectral region around HH 15 which is off-resonant with respect to the singly excited states of He. The additional IR pulse acts as the control pulse and allows us to control the absorption by the XUV/IR delay. As predicted with our theoretical model, we also observe a net-emission or optical gain for certain energies. As for the absorption, the magnitude of the gain can be manipulated with the delay between the pulses. Our experimental results are in agreement with the theoretical predictions.
In 2007 Johnsson and co-workers presented an experimental and theoretical study investigating the ionization dynamics of He around its first ionization threshold [96]. They demonstrated in a pump-probe experiment using an APT in combination with a moderately strong IR beam with an intensity of $1.3 \cdot 10^{13}$ W/cm$^2$ that the He$^+$ ion yield modulates as a function of delay between the APT and the IR field. The modulation period corresponds to half the period of the IR radiation. They assigned this periodic change of the ionization probability to two different effects. The weaker effect is the suppression of the atomic Coulomb potential by the IR field. Even though the intensity is too low to excite electrons from the ground state of He, the authors report that it is sufficient to suppress the Coulomb potential barrier of the atom by 7 eV at the maximum of the field. This means that all electrons promoted to an excited state by the APT are ionized by the IR field. The suggested second effect, which dominates the modulation, is the interference of transiently bound EWPs.

In the experiment, the main part of the APT is spectrally located below the first ionization potential of He. Each pulse of the APT creates an EWP, which for a certain time remains transiently bound to the parent atom, close to its origin of creation, before the IR field ionizes it. Therefore, there is the possibility that a second EWP, created by a subsequent pulse of the APT, interferes with the previous EWP. The interference influences the photoionization or photoabsorption probability of the atom and depends on the delay between the APT and the IR field. The TDSE
calculations by Johnsson et al. reveal that the modulation contrast of the ion yield dramatically declines when reducing the number of pulses in the APT. As a consequence, the excitation with a SAP results in the lowest possible modulation. However, the corresponding experiment with a SAP was not performed by the group. Nevertheless, their results motivated several other groups to examine the modulation of the ionization probability, both theoretically and experimentally, and the absorption probability, exclusively theoretically, in He [97, 98].

Finally, Holler et al. performed the corresponding transient absorption experiment and investigated the absorption probability [19]. The transient absorption technique enabled them to spectrally resolve the APT and study the absorption behavior of single HHs, which was not possible in the experiment of Johnsson and co-workers. Their results were in agreement with the transiently bound EWP picture proposed in [96].

In the work presented in this chapter, we want to review the role of EWP interference for the modulation of the absorption probability with the help of attosecond transient absorption spectroscopy. We want to exploit the predicted strong dependency of the modulation contrast on the number of pulses in the APT. Starting with a rather long APT, we will subsequently reduce the number of XUV pulses in the train. In a final step, we compare the excitation with multiple APs with the SAP excitation. Additionally, we study the influence of the ellipticity of the IR on the modulations.

### 6.1 Influence of the number of pulses

Johnsson et al. predicted an increase of the modulation strength of the photoabsorption probability with an increasing number of pulses in the APT [96]. The first transient absorption experiment investigating the modulations did not discuss this predicted dependency but used an APT with a fixed duration on the order of 10 - 12 fs [19]. The concept of EWP interference bases on the assumption that a created EWP interferes with a second EWP created by a preceding pulse of the train. Reducing the number of pulses in the train therefore decreases the probability that EWPs interfere and modulate the absorption probability. There are at least two
possible techniques to change the number of pulses in an APT. The first method, suggested also in [96], bases on the strong ellipticity-dependence of HHG [99]. With a proper design of the polarization of the IR pulse driving the HHG process one can influence the number of pulses of the APT in analogy to the PG technique for the generation of a SAP [70]. A second technique, which we will use here, is to change the duration of the driving IR field while keeping the peak intensity of the IR field constant. A reduction of the duration of the IR field directly leads to a decreased number of pulses in the train.

6.1.1 Generation and simulations of the APT

For the results presented in this chapter, we utilize the identical setup as used in chapter 5, which was described in chapters 2 and 4 in detail, as well as in [75]. The output of the laser amplifier system with a pulse energy of 850 µJ and a duration of ≈20 fs is sent to the filamentation and HCF setup. We generate the HHs in xenon and block the residual IR radiation with a 100 nm-thick aluminum filter. The opening time of the pulsed-valve target is set to ≈60 µs. The resulting gas density leads to an absorption of ≈50% of HH 17, which is located directly above the first ionization potential of He. The gas density corresponds to a particle density of ≈5 · 10^{17} particles/cm^3. We change the XUV/IR delay in steps of 10^7 as.

In order to change the pulse duration of the driving IR pulses, we modify the parameters of our compression setup. As discussed before in chapter 2.3, the spectral broadening and resulting transform limit of the pulses in optical filamentation and in a HCF strongly depends on the gas pressure. Figure 6.1(f) - (j) presents the temporal profile of the IR pulses measured with our SPIDER setup. We are able to change the pulse duration between 7.9 fs and 19.6 fs. While the 7.9 fs pulse was generated with the HCF setup, all other pulses were generated by pulse compression in the filament setup. On the left of figure 6.1 in panels (a) - (e) we show the corresponding XUV spectra of the generated APT. The blue spectra represent the generated spectrum without any gas in the pulsed-valve target, while the red spectra show the APT after it was transmitted through the target filled with He. We observe an absorption of approximately 50% of
Figure 6.1: Panels (a) - (e) on the left show the spectrum of the APT with (red) and without gas (blue) for different durations of the generating IR field. The parts of the spectrum which are located above the ionization threshold (dashed line) of He are strongly absorbed in the presence of the gas. Panels (f) - (j) show the temporal intensity profile of the generating IR pulses retrieved from the SPIDER measurements.

the XUV radiation above the first ionization threshold of He indicated by the dashed line at 24.59 eV.

Since we investigate the influence of the number of the pulses in the APT on the modulation strength it is crucial to have an estimate of this number generated for a certain IR pulse duration. Hence, we calculate the temporal profile of the APT for two IR pulse durations, namely 7.9 fs and 19.6 fs. The calculations base on the single-atom response using the
6.1. Influence of the number of pulses

Figure 6.2: Comparison of calculated and measured XUV spectra. The calculated spectra are based on the single-atom response with the NASP. (a) shows the experimental (dotted line) and the calculated XUV spectrum (solid line) for a driving field with a duration of 19.6 fs. (b) presents the corresponding results for an IR pulse duration of 7.9 fs.

As expected, we observe an inversely proportional relationship between the duration of the driving pulse and the spectral bandwidth of the individual HHs. Figure 6.4 illustrates the average spectral bandwidth (FWHM) of the HHs as a function of the driving field duration. We define the error bars as \( \pm \beta \) and \( 2\beta \) corresponds to the FWHM of the Gaussian distribution of the experimental results.

We performed delay scans with 5 different APTs each described by the spectra in figure 6.1(a) - (e) and the corresponding IR pulses shown in figure 6.1(f) - (j). In order to achieve different APTs we change the

non-adiabatic saddle-point approximation (NASP) neglecting any propagation effects [62]. This model describes the dipole moment as a coherent superposition of complex quantum pathways. The result of the numerical simulation is shown in figure 6.2 and figure 6.3. Figure 6.2 compares the XUV spectrum of the calculated APT (solid line) with the experimentally acquired spectrum (dotted line). Figure 6.3 presents the temporal intensity profile of the APT for the 7.9 fs (solid black line) and 19.6 fs (solid red line) driving IR pulse. Additionally, the dashed line indicates the envelope of the corresponding IR pulses measured with our SPIDER setup. We count those pulses in the train, which exceed the threshold corresponding to 1 % of the intensity of the strongest pulse in the train. Accordingly, we get 7 and 16 pulses for the 7.9 fs and 19.6 fs driving pulse, respectively.
Figure 6.3: Temporal intensity profile of the two APTs corresponding to the two XUV spectra shown in figure 6.2(a) and (b). The dashed line represents the envelope of the driving IR pulses with a duration of 7.9 fs and 19.6 fs, respectively. The intensity of the IR field was set to $1.75 \times 10^{14}$ W/cm$^2$ to match the experimental results. The pulses are shifted in time for better visibility.

duration of the driving IR field. For the comparability of the results of the pump-probe experiments and to extract the influence of the number of pulses in the APT, we have to verify that the IR intensity is identical for every single delay scan. Hence, we adapt the energy of the IR pulses when we change the duration of the driving field and keep the intensity at a constant value of $\approx 5.4 \times 10^{12}$ W/cm$^2$. We change the IR-pulse energy with a motorized iris (I2, see figure 4.2) in the IR arm of the XUV/IR interferometer. The resulting attosecond transient absorption scans for the driving pulse durations of 19.6 fs, 13.1 fs and 7.9 fs are presented in figure 6.5. We show in figure 6.5(a) to (c) the color-coded normalized transmitted XUV intensity as a function of XUV/IR delay and photon energy.

As already shown in figure 6.4 the spectral bandwidth of the individual HHs increases with decreasing pulse duration of the field driving the HHG. This broadening of the HHs leads to more complex behavior of the optical response since the XUV spectrum of the APT overlaps with several excited states of He. All delay scans have in common that the intensity of the transmitted XUV radiation is strongly modulated as a function of XUV/IR delay. Like we expected from the previous work by Johnsson et al. and Holler et al., the modulation period is half the laser cycle of the IR field ($2\omega$-oscillations). There is no directly observable difference in the
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![Graph showing the FWHM of the HHs as a function of the driving IR pulse duration.](image)

**Figure 6.4:** Mean of the FWHM of the HHs in 6.1(a) - (e) as a function of the driving IR pulse duration. The error bars are defined as half the FWHM of the Gaussian distribution.

oscillation strength that we can directly extract from the raw data. Consequently, we develop a method to quantify the oscillation strength of delay scans with a different number of pulses comprising the APT.

As an intermediate step to the evaluation of the oscillation strength, we extract the absorption induced by the IR field out of the experimental data. We define the induced absorption \( \Delta \text{Abs}(E, \tau) \) as a function of photon energy \( E \) and XUV/IR delay \( \tau \) as:

\[
\Delta \text{Abs}(E, \tau) = T_0(E) - T(E, \tau).
\] (6.1)

\( T_0(E) \) represents the XUV spectrum when the IR pulse is absent and \( T(E, \tau) \) is the transmitted XUV spectrum, with the IR pulse present, as a function of energy \( E \) and XUV/IR delay \( \tau \). We present the IR-induced absorption \( \Delta \text{Abs}(E, \tau) \) in figure 6.5(d) to (f). Panels (d) to (f) correspond to the measurements shown in panel (a) to (c) of the same figure. This representation allows us to easily identify absorption (red) and emission (blue).

The most prominent feature for all three scans is the absorption of HH 15 around delay-zero, where the envelopes of the APT and IR pulse exactly overlap in time. Since HH 15 is energetically located below the first ionization threshold of He, it is not able to directly ionize He. In the absence of the IR field, the APT will only be absorbed by the He atoms if it spectrally overlaps with any excited state. This can be seen in figure 6.5(d)-(f) for large positive or negative delays, e.g. around 23.7 eV, which corresponds
to the excitation of the 1s4p state. In the overlap region around delay-zero the absorption is enhanced by two-color two-photon absorption of one XUV and one IR photon. Summed up the energy of these two photons is sufficient to overcome the first ionization threshold of He.

As next step towards comparing the oscillation strength of different delay scans, we define the energy-integrated normalized absorption $\Lambda(\tau)$ as a function of XUV/IR delay $\tau$ as follows:

$$\Lambda(\tau) = \frac{\Delta Abs(\tau)}{T_0} = -\frac{\int_{\Delta E} [T(E, \tau) - T_0(E)]dE}{\int_{\Delta E} T_0(E)dE}. \quad (6.2)$$

Figure 6.5: (a)-(c) show the transmitted XUV radiation as a function of photon energy and XUV/IR delay for a driving pulse duration of (a) 19.6 fs (b) 13.1 fs and (c) 7.9 fs. (d)-(f) present the absorption induced by the IR field as defined in equation 6.1. A positive change (red) represents increased absorption, while a reduction of the absorption corresponds to negative values (blue). (g)-(i) show the energy-integrated normalized absorption $\Lambda(\tau)$ as described with equation 6.2 for the two energy-integration windows $\Delta E_{Ip}$ (red) and $\Delta E_{tot}$ (black). Both results exhibit strong $2\omega$-oscillations.
We choose two different energy-integration windows $\Delta E$ and show the resulting energy-integrated normalized absorption $\Lambda(\tau)$ in figure 6.5(g) to (i). The dashed red line represents the $\Lambda(\tau)$ for the energy integration up to the ionization potential of He: $\Delta E_{I_p} = [20.0 \text{ eV}, I_p = 24.59 \text{ eV}]$, while the solid black curve shows the results for a integration window reaching into the continuum: $\Delta E_{\text{tot}} = [20.0 \text{ eV}, 27.5 \text{ eV}]$. In other words $\Delta E_{I_p}$ only takes into account the contributions of the excited states, while $\Delta E_{\text{tot}}$ also considers parts of the continuum. We observe for both energy windows the enhancement of the absorption when the APT and IR pulse temporally overlap around delay-zero due to the two-color multiphoton absorption. The energy integration also preserves the $2\omega$-oscillations. Additionally, we see that both energy-integration results are in excellent qualitative and quantitative agreement, which leads us to the conclusion that the main contributions originate from bound states below the first ionization potential and not from excitation into the continuum.

For a comparison of different delay scans we perform a delay-frequency analysis. For this purpose we transform the energy-integrated normalized absorption $\Lambda(\tau)$ with a Gabor transform from a one-dimensional function of delay into a two-dimensional energy-delay representation [100]. The Gabor transform is a window Fourier transform where the signal is multiplied by a Gaussian window function before the Fourier transform is executed. Hence, in the situation described here the resulting two-dimensional representation holds the information which frequency component appears at which delay. We apply a Gaussian window with a width of 3.45 fs (FWHM) corresponding to $\approx 1.3$ optical cycles of the IR field. Now, we define the peak of the $2\omega$-oscillations in the two-dimensional representation as the oscillation strength. Figure 6.6(a) presents the oscillation strength as a function of pulse duration of the driving IR field. According to the theory of Johnsson et al. the oscillation strength is supposed to rapidly increase with the duration of the driving field. In contrast, figure 6.6(a) reveals that the relative oscillation strength stays constant within the error bars over the pulse-duration range we scanned. We normalize the oscillation strength to the value obtained with a driving-pulse duration of 19.6 fs. The results for the two different integration windows $\Delta E_{\text{tot}}$ and $\Delta E_{I_p}$ are in agreement within the error
bars. The disagreement between our results and the theory of interfering EWPs gives us a first hint that the interference of EWPs is insufficient to explain the observed effects.

Additionally, we investigated the influence of the IR intensity on the oscillation strength. For this purpose we keep the APT constant and only change the intensity of the IR beam. The APT is generated with driving pulses of a duration of 19.6 fs. Figure 6.6(b) shows the resulting relative oscillation strength as a function of the IR intensity, which is varied between $2.1 \cdot 10^{12}$ W/cm$^2$ and $6.5 \cdot 10^{12}$ W/cm$^2$. We observe a clear linear increase of the relative oscillation strength with increasing IR intensity for both energy-integration windows. In chapter 7 we discuss the influence of the IR intensity on the oscillations in more detail. In particular, we show that the oscillations exhibit a more complex behavior for higher IR intensities.

### 6.2 Single-attosecond-pulse excitation

In a next step we directly compare the excitation with a SAP with the excitation with multiple APs. Johnsson et al. pointed out in their work, that the contrast of the $2\omega$-oscillations should be minimized when a SAP is used. Following their idea, in this case the oscillations originate only
6.2. Single-attosecond-pulse excitation

from the modulation of the atomic Coulomb field by the IR field. We exclude the interference of EWPs with the SAP excitation since only one EWP is created. For the generation of the SAPs we apply the PG technique to the driving IR field. The technique is described in detail in subsection 3.2.1 [70, 71].

Since the PG technique requires sub-6 fs pulses, we compress the pulse duration of the IR pulses with our filament-compression setup (see subsection 2.3.1). For the generation medium we choose Xe and Ar. The SAP in Xe is described by a spectral bandwidth of \( \approx 5 \text{ eV FWHM} \) at a center energy of 27.5 eV. The generation in Ar leads to a SAP centered at 35.0 eV with a bandwidth of \( \approx 9 \text{ eV FWHM} \). A characterization with the FROG-CRAB method gives a pulse duration of \( 410 \pm 5 \text{ as} \) for Xe and \( 285 \pm 5 \text{ as} \) for Ar, respectively [101]. We obtain the pulse durations after 80,000 iterations of the reconstruction algorithm [102].

The generation of a SAP with the PG technique requires a CEP stabilized driving IR pulse. Figure 3.4(a) in chapter 3 shows the XUV spectrum obtained with the PG technique as a function of CEP. By changing the CEP of the driving IR field, the XUV spectrum changes from a continuum to a spectrum with discrete HHs. The change is periodic with a \( \pi \)-periodic dependence on the CEP. This periodic dependence allows us to switch between a continuous spectrum and a spectrum containing discrete HHs by only changing the CEP and without changing any other experimental parameter. While the continuous spectrum (CEP \( \Phi_0 \)) corresponds to a SAP, the discrete spectrum (CEP \( \Phi_0 + \pi/2 \)) represents a double or multiple AP. Figure 3.4(b) displays two XUV spectra with a CEP difference of \( \pi/2 \). Accordingly, we are able to perform two consecutive transient absorption experiments with a SAP and multiple AP excitation by only changing the CEP and without changing the setup. This allows a direct and precise comparison of the two delay scans.

Figure 6.7(a) and (b) presents a transient absorption delay scan in He with a SAP and with multiple AP generated in Xe. Panels (c) and (d) show the corresponding delay scans with the XUV radiation generated in Ar. All delay scans of figure 6.7 exhibit strong \( 2\omega \)-oscillations in the transmitted XUV radiation as a function of XUV/IR delay. The oscillation
Figure 6.7: Transmitted normalized XUV radiation as a function of photon energy and XUV/IR delay. (a) and (c) show the excitation with a SAP generated in Xe and Ar, respectively. (b) and (d) show the excitation with multiple APs generated in Xe and Ar, respectively. The PG technique allows to switch between a SAP and multiple APs by changing the CEP by \( \pi /2 \). We observe fast oscillations in the transmitted signal for SAP and multiple AP excitation.

strength seems to be independent of the generating medium or if we apply a SAP or multiple AP.

Various recent publications experimentally and theoretically investigated the atomic response of He towards the excitation with a SAP in the XUV spectral range [103, 104]. Figure 6.9 shows a schematic of the EWP-interference model in panel (a) and summarizes the main effects leading to the modulation with twice the fundamental IR frequency in the transmitted radiation in (b) and (c). One effect is the sub-cycle AC Stark shift of the resonantly excited \( 1snp \) states [105]. The second effect are so-called light-induced excited states [106]. The light-induced structures arise
6.2. Single-attosecond-pulse excitation

Figure 6.8: Energy-integrated normalized absorption $\Lambda(\tau)$. (a) shows the result for the full energy-integration window $E_{\text{int}} = [20.0\ eV, 27.5\ eV]$ and (b) for the energy integration up to the ionization potential $\Delta E_p = [20.0\ eV, I_p = 24.59\ eV]$. The solid lines represent the excitation with a SAP and the dashed the excitation with multiple APs. SAP and multiple AP excitation exhibit both $2\omega$-oscillations for positive delays and are in excellent agreement.

from two-photon two-color processes which allow to populate states that are dipole-forbidden for a single-photon transition, i.e. $s$ or $d$ states. As a third effect Mauritsson et al. identified the interference between different quantum pathways as an origin for the fast modulations [107]. A state energetically close to the first ionization threshold $1snp$ with $n > 5$ can be populated directly by the absorption of one XUV photon or indirectly by the absorption of a lower-energetic XUV photon populating the $1s2p$ state plus the additional absorption of two IR photons. These three effects are independent of the temporal structure of the XUV radiation, which means they appear for a excitation with a SAP and with multiple APs.

We observed already in figure 6.7 that the fast oscillations are still present for a SAP excitation. For a more quantitative comparison between SAP excitation and the excitation with multiple APs we perform the analysis described earlier in this chapter. Accordingly, we calculate
the energy-integrated normalized absorption $\Lambda(\tau)$ according to equation 6.2. The calculations performed by Johnsson et al. predicted additionally to the strong reduction of the oscillation contrast for a SAP a phase shift in the oscillations [96]. Figure 6.8 shows the resulting energy-integrated normalized absorption for a SAP (CEP = $\Phi_0$, solid lines) and multiple APs (CEP = $\Phi_0 + \pi/2$, dashed lines). The upper panel (a) presents the result for the full energy-integration window $\Delta E_{\text{tot}} = [20.0 \text{ eV}, 27.5 \text{ eV}]$ and the lower panel (b) for the integration window only including the contribution of bound states $\Delta E_{\text{lp}} = [20.0 \text{ eV}, \text{lp} = 24.59 \text{ eV}]$. In contradiction to the calculations of Johnsson et al. we observe that the oscillations for the SAP and multiple APs are in phase. Moreover, we do not measure a significant decline of the amplitude of the oscillations within the error bars which is corroborated by the time-frequency analysis.

The response of the signal originating from below the first ionization potential dominates the measurement. This is in agreement with our previous observations. In particular, the interference of different quantum pathways with the final states located between 24.0 eV and the ionization threshold has a strong contribution to the oscillations. When the XUV radiation precedes the IR we expect energy-tilted interference fringes since constructive interference appears at different delays for different photon energies [107]. The strong tilt for negative delays smears out the oscillations in the energy integration as can be seen in figure 6.8.

As mentioned before, the AC Stark shift contributes to the fast oscillations, too. Figure 6.7 exhibits the shift of the 1s3p (23.09 eV) and 1s4p (23.74 eV) states to higher energies. Moreover, both states show fast subcycle oscillations following the IR field. The oscillations are in phase with the oscillations based on the quantum-pathway interference and hence amplify the oscillations for positive delays.

### 6.3 Elliptically polarized infrared field

In the work of Johnsson et al. the authors explain that at the heart of the EWP-interference effect is an EWP that returns to its origin where it will interfere with an EWP created at a later moment in time [96]. This means that there will be the possibility to observe EWP interference.
6.3. Elliptically polarized infrared field

Figure 6.9: Schematic of the proposed mechanisms causing oscillations in the photo absorption probability as a function of XUV/IR delay. (a) presents the EWP interference in the case of the excitation with an APT. (b) Resonant absorption lines of the $1snp$ series modulated by the AC Stark shift and light-induced structures related to two-color two-photon transitions. The wavy lines represent the dressed states. (c) Interference of different quantum-pathways.

if it takes more than a half-cycle of the IR ($\approx 1.3$ fs) to completely ionize the atom. Until the atom is ionized the EWP interacts with the IR field which is regarded as weak for a ground state electron in He but strong for a transiently bound EWP. In the case of a linearly polarized IR field the ionized electron possesses a certain possibility to return to its parent ion once it is removed from the atom. A certain amount of ellipticity in the IR field results in a lateral displacement of the electron with respect to its parent ion as it is accelerated in the external field. The lateral displacement strongly reduces the probability for a recollision of the electron with its parent ion. This effect manifests itself in the strong ellipticity dependence of processes based on the electron recollision like the HHG process [99, 54]. An ellipticity of 0.15 suppresses the generation of XUV radiation by more than a factor of two. As a rule of thumb one uses usually the threshold ellipticity of $\varepsilon_{th} = 0.13$ where higher ellipticities are not efficient for the HHG anymore [64].

6.3.1 Polarimetry

For the investigation of the influence of the ellipticity on the oscillation strength we place a QWP (Bernhard Halle Nachfolger GmbH) on a motorized rotation stage in the IR arm of our XUV/IR interferometer. By turning the QWP with respect to the polarization axis of the IR beam we are theoretically able to change the polarization state from linearly polarized to circularly polarized. Since an ultrashort femtosecond pulse is
not monochromatic but contains different frequency components within its bandwidth, a perfect QWP for such a pulse has to provide the correct phase shift for all frequency components. If this is not the case the highest achievable ellipticity will be smaller than 1.

The toroidal mirror in our setup focuses the elliptically polarized beam into the first interaction chamber. The reflectivity of the toroidal mirror is slightly different for s- and p-polarized light. This implicates that the ellipticity is changed by the reflection on the toroidal mirror. Accordingly, we performed a polarimetry measurement after the toroidal mirror to measure the ellipticity as a function of the angle between the initial polarization axis of the IR beam and the optical axis of the QWP. The setup for the polarimetry consists of polarizer and a power meter for the measurement of the transmitted radiation after the polarizer. Both are placed in the beam path after the toroidal mirror. This setup allows to measure the ellipticity of the IR beam in the interaction focus.

Figure 6.10 presents a coarse scan of the angle between the initial polarization axis of the IR field and the ordinary axis of the QWP in (a) and in (b) a finer scan around the maximum ellipticity. The important information we obtain is that we achieve a maximum ellipticity of $\varepsilon_{\text{max}} \approx 0.66$, which is significantly lower than 1. Nevertheless, we expect that any process based on the recollision to be strongly suppressed with this ellipticity.
6.3. Elliptically polarized infrared field

6.3.2 Ellipticity dependence of the oscillation strength

We perform several scans where we vary the XUV/IR delay and record the transmitted XUV spectra as already described in in the previous part of this chapter. Additionally, we systematically scan the ellipticity from \( \varepsilon = 0 \) to \( \varepsilon_{\text{max}} \approx 0.66 \). The IR pulse duration and peak intensity stay constant at \( \approx 25 \text{ fs} \) and \( \approx 1.9 \cdot 10^{12} \text{ W/cm}^2 \), respectively. Figure 6.11 displays a direct comparison of the transmitted XUV intensity for \( \varepsilon = 0 \) or in other words linearly polarized light in (a) and for \( \varepsilon_{\text{max}} \approx 0.66 \) in (b). The spectra mainly contains HHs 13 to 19. Both delay scans exhibit strong \( 2\omega \)-oscillations for HH 13 to 17 and there is no obvious change observable on the oscillation strength from linearly polarized to elliptically polarized light. HH 19 is not shown here and does not exhibit any temporal dynamics induced by the IR field. Therefore, we exclude HH 19 from our analysis. We omit the normalization of the signal with \( T_0 \) according to equation 6.2, since we only change the ellipticity of the IR field between different delay scans. For the comparison of different delay scans we compute the oscillation amplitude as a function of ellipticity \( O(\varepsilon) \) with the Fourier transform of the energy-integrated transmitted signal: \( \mathcal{F}\{\int_{\Delta E} T(E, \tau) dE\} \).

Figure 6.12 presents for HH 13, 15 and 17 the energy-integrated signal as a function of XUV/IR delay in the three panels of (a). The width of the energy integration interval \( \Delta E \) for HH 13, 15 and 17 is 34 meV, 50 meV and
Figure 6.12: (a) Comparison of the transmission as a function of delay $T(\tau)$ for energy intervals around HH 13, 15 and 17. Solid lines show the result for a linearly polarized IR field and dashed lines for an elliptically polarized field. (b) Amplitude of the oscillations as a function of ellipticity $O(\epsilon)$ normalized with the amplitude for the linearly polarized case $O(\epsilon = 0)$. The HHs 13, 15 and 17 were evaluated in the same energy intervals as in panel (b). The black-dashed lines show the energy-integrated result with the full energy-integration window $\Delta E_{\text{tot}} = [20.0 \text{ eV}, 27.5 \text{ eV}]$. For comparison we show the relative strength of HH 21 generated in Ar (IR intensity $3.0 \cdot 10^{14} \text{ W/cm}^2$) calculated like in [99].

54 meV, respectively and is determined by the resolution of our XUV spectrometer. Figure 6.12(b) shows the oscillation amplitude as a function of ellipticity normalized with the value obtained for linearly polarized light $O(\epsilon) / O(\epsilon = 0)$. The oscillation amplitude decreases going from linearly polarized to elliptically polarized light with an ellipticity of $\epsilon_{\text{max}} \approx 0.66$ by 30\% to 40\%.

Even though the oscillation amplitude decreases with increasing ellipticity, the effect is significantly weaker than expected for an effect based on the recollision of an accelerated electron with its parent ion [108]. For a direct comparison we added in figure 6.12 the calculated relative intensity of HH 21 generated in Ar with an IR intensity of $3.0 \cdot 10^{14} \text{ W/cm}^2$ [99]. The relative intensity declines as expected with increasing ellipticity of the generating IR field. At an ellipticity of $\approx 0.13$ the intensity decreased by a factor of 2.
6.4 Conclusion

In summary, we investigated in this chapter the response of He close to its first ionization threshold with attosecond transient absorption spectroscopy using an APT in combination with a femtosecond IR pulse. We focus on the fast half-laser-cycle or $2\omega$-oscillations in the transmitted intensity as a function of XUV/IR delay. In a previous work by Johnsson et al. the interference of transiently bound EWPs was suggested as the origin for the observed oscillations [96]. Accordingly, we perform different experiments in order to check this theory.

We systematically vary the number of pulses of the APT, the IR intensity and ellipticity. Additionally, we directly compared the excitation with a SAP with a multiple APs excitation. All experimental results contradict the picture of interfering EWP excited by consecutive pulses of the APT as the origin of the $2\omega$-oscillations of the absorption probability. Accordingly, we conclude that different mechanisms are responsible for the oscillations. Two recent publications discuss the interference of different quantum pathways based on two-color multiphoton absorption as the main contribution to the oscillations [103, 104].
Chapter 7

Defining a robust delay-zero in attosecond transient absorption experiments

The previous chapters 5 and 6 already demonstrated the importance of attosecond transient absorption spectroscopy for the understanding of electron dynamics in the interaction of electromagnetic radiation with matter on the attosecond time scale. It is crucial for the interpretation of the experimental data to know the relative timing of the XUV and IR field with respect to each other. In other words, we need to have the information when the maximum of the IR and XUV envelope exactly overlap while scanning their delay. In this thesis, we name the exact overlap of the envelopes delay-zero. The challenge in attosecond transient absorption experiments is the low XUV photon flux in combination with the absence of a suitable nonlinear medium. This prevents the delay-zero calibration by a simple XUV/IR cross correlation, like in femtosecond-pump-probe spectroscopy. A number of recent publications investigated the energetic region around the first ionization threshold of He with attosecond transient absorption spectroscopy or simulated the optical response [19, 77, 78, 103, 104, 105, 106, 109, 110, 111]. Unfortunately, the complexity of the obtained experimental data in attosecond transient absorption experiments does not allow a straightforward interpretation providing a delay-zero of sufficient accuracy. Consequently, the delay-zero calibration often requires additional theoretical support.

In this chapter, we show that it is possible to extract an accurate delay-
7. Defining a robust delay-zero in attosecond transient absorption experiments

Figure 7.1: Spectrum of an APT mainly comprising HHs 13 to 21. The red arrows symbolize the photons of the fundamental IR pulse. The IR field allows to exchange energy between HHs, e.g. HH 13 and HH 17. The energy exchange depends on the XUV/IR delay. Changing the delay results in a modulation of the transmitted XUV intensity through a medium with a quarter of the fundamental IR period as a function of delay.

zero exclusively out of the experimental data of an attosecond transient absorption experiment. We present our method based on multiphoton coupling of the HHs of an APT and confirm the method by solving the TDSE. Furthermore, we discuss alternative calibration methods, e.g. via the total absorption or the well-known $2\omega$-oscillations (see chapter 6 or [19, 78, 103, 104, 105, 106, 109]) and reveal possible pitfalls in their application. Moreover, we systematically study the influence of the IR intensity on the multiphoton coupling.

7.1 Observing quarter-laser-cycle oscillations

Chapter 6 discussed in detail the origin of the half-laser-cycle ($2\omega$) oscillations observed in the transmitted XUV radiation as a function of XUV/IR delay. Besides this effect Chen et al. predicted the occurrence of quarter-laser-cycle ($4\omega$) oscillations in attosecond transient absorption experiments [109]. They simulated the optical response of IR-dressed He atoms exposed to an APT in the XUV spectral region. As the remarkable result of their work they uncovered that the intensity of the transmitted XUV radiation modulates as a function of XUV/IR-delay with a periodicity that cannot be observed neither in the initial IR pulse nor in the
7.1. Observing quarter-laser-cycle oscillations

APT. The periodic time is only a quarter of the period of the fundamental IR radiation and accordingly the oscillations are named $4\omega$-oscillations. They identified the multiphoton coupling of harmonics spaced by four IR photons as the reason for the $4\omega$-oscillations. Figure 7.1 illustrates the coupling of HH 13 with HH 17 via four IR photons. The nonlinear coupling corresponds to an energy exchange between these HHs which depends on the phase between the IR pulse and the APT and consequently on the XUV/IR delay.

The experimental setup used to obtain the following results is described in the previous chapters 2 and 4. We select Xe for the HHG, giving rise to the spectrum depicted in figure 7.2. The opening time of the pulsed valve target is 60 $\mu$s. This leads to an optical density for HH 17 at 26.7 eV of 0.79. Figure 7.2 presents the initial XUV spectrum (blue, solid line) and the spectrum after the interaction with He (black, dashed line). As can be seen clearly, the He gas heavily absorbs the HHs above the first ionization potential at 24.59 eV indicated by the green, dashed line.

Figure 7.3 illustrates the normalized transmitted intensity of the XUV radiation as a function of photon energy and XUV/IR delay. The main part of the APT spectrum consists of HH 13 to HH 21. We recorded the delay scan at an IR intensity of $4.0 \cdot 10^{12}$ W/cm$^2$. In all measurements pre-
Defining a robust delay-zero in attosecond transient absorption experiments

Figure 7.3: Normalized transmitted XUV intensity as a function of XUV/IR delay and photon energy recorded at an IR intensity of $4.0 \cdot 10^{12} \text{ W/cm}^2$. The optical density at a photon energy of 26.7 eV is 0.79. For negative delays the APT precedes the IR pulses. HHs 13 to 17 show strong $2\omega$-oscillations that are visible to the naked eye.

Presented in this chapter, we work with a delay step size of 0.2 fs. We define the delay-zero in figure 7.3 with the procedure described in section 7.3 of this chapter. There are two distinct features directly observable in the delay scan. In the first place, we note a strong decline of the transmitted XUV intensity around delay-zero in HH 13 and HH 15. This is related to two-color multiphoton absorption of one XUV photon plus one or several IR photons. Since these two HHs are energetically located below the first ionization potential of He, they are only absorbed when the IR field temporally overlaps with the APT. For HH 17 and higher we do not observe this effect since they directly ionize the He atoms. In the second place, we clearly observe $2\omega$-oscillations in HH 13 to HH 15.

For a more detailed analysis of the temporal behavior of the different HHs, we define the entropy-integrated absorption $\Pi(\tau)$ as a function of delay $\tau$:

$$\Pi(\tau) = -\frac{\int_{\delta E} [T(E, \tau) - T_0(E)] dE}{\int_{\delta E'} [S(E) - T_0(E)] dE}. \quad (7.1)$$

$S(E)$ represents the initial XUV spectrum without any interaction with the gas in the target as a function of the photon energy $E$. $T_0(E)$ is the XUV spectrum after the interaction with the gas but in the absence of the IR field, while $T(E, \tau)$ corresponds to the delay scan as a function of photon energy.
7.1. Observing quarter-laser-cycle oscillations

Figure 7.4: (a) Energy-integrated absorption \( \Pi(\tau) \) for HH 13, (b) 15 and (c) 17 at an IR intensity of \( 4.0 \cdot 10^{12} \text{ W/cm}^2 \). The optical density of the gas target is 0.79 at 26.7 eV. In HH 13 and 15 we observe an enhancement of absorption around delay-zero due to a two-color multiphoton absorption. The enhancement is absent in HH 17. All three HHs exhibit strong \( 2\omega \)-oscillations. The \( 4\omega \)-oscillations are weakly visible in HH 17 around delay-zero.

In order to disentangle the different oscillatory components we perform a delay-frequency analysis. For this purpose we apply a Gaussian-Wigner transform to the one-dimensional energy-integrated absorption \( \Pi(\tau) \). The Gaussian-Wigner transform uses the Wigner transform [112],
7. Defining a robust delay-zero in attosecond transient absorption experiments

Figure 7.5: Zoom in energy-integrated absorption $\Pi(\tau)$ for HH 17 at an IR intensity of $4.0 \cdot 10^{12}$ W/cm$^2$ corresponding to figure 7.4(c). The $4\omega$-oscillations are now clearly visible around delay-zero.

defined by the following equation:

$$W(t, \nu) = \int_{-\infty}^{+\infty} U(t + x'/2)U^*(t - x'/2)e^{-2\pi i x' \nu} dx'.$$

(7.2)

In an additional step the resulting Wigner distribution $W(t, \nu)$ is convolved with a two-dimensional Gaussian in delay and frequency space:

$$GWT(t, \nu; \delta_t, \delta_\nu) = \frac{1}{\delta_\nu \cdot \delta_t} \int dt' \int d\nu' W(t', \nu')e^{-2\pi i \frac{t - t'}{\delta_t}^2}e^{-2\pi i \frac{\nu - \nu'}{\delta_\nu}^2}.$$  

(7.3)

For the Wigner transform we choose a window size of $\delta_\tau = 5.5$ fs, which corresponds to 1.9 optical cycles of the IR field at a centre wavelength of 789 nm. The window size in the frequency domain is $\delta_\nu = 0.2$ PHz determined via $\delta_\tau \cdot \delta_\nu \equiv 1$.

The Gaussian-Wigner transform provides a two-dimensional distribution of the Fourier amplitude as a function of frequency and XUV/IR delay. This allows us to extract the appearance of different oscillation components at different delays. Figure 7.6 shows the natural logarithm of the Gaussian-Wigner transform of HHs 13 to 17 of the delay scan presented in figure 7.3 at an IR intensity of $4.0 \cdot 10^{12}$ W/cm$^2$. The $2\omega$-oscillations appear around 0.76 PHz between -20 fs and +20 fs. Additionally, we observe a second oscillations contribution centered at 1.52 PHz, so twice the frequency of the $2\omega$-oscillations. This signal corresponds to the $4\omega$-oscillations predicted by Chen et al. [109]. For a driving wavelength of 789 nm this results
7.2 Theoretical treatment of the XUV absorption

Figure 7.6: Gaussian-Wigner transform of the energy-integrated absorption of the delay scan shown in figure 7.3. (a), (b) and (c) show the color-coded natural logarithm of the Fourier amplitude for HHs 13, 15 and 17 as a function of XUV/IR delay and frequency. The signal at 0.76 PHz represents the 2ω-oscillations. The 2ω-oscillations are already visible in figure 7.4. Moreover, we observe a signal at 1.52 PHz corresponding to 4ω-oscillations.

in an oscillation period of 660 as. We restrict the discussion of the 4ω-oscillations on HH 13 and 17 since the 4ω-oscillations in HH 15 is comparably weak. The reason for this is in the lack of the coupling between HH 15 and HH 11, which is not part of the APT.

7.2 Theoretical treatment of the XUV absorption

In order to obtain a deeper insight in our experimental results and to finally define a robust delay-zero, we simulate the single-atom and macroscopic response of the He atoms exhibited to the combined XUV and IR field. The following subsections 7.2.1 and 7.2.2 summarize the theoretical treatment of the absorption calculated by our collaborators Mengxi Wu, Dr. Shaohao Chen, Prof. Kenneth J. Schafer and Prof. Mette B. Gaarde from Louisiana State University. The model is described in more detail in a recent publication [113].

7.2.1 Single-atom response

The starting point for the theoretical treatment of the single-atom response is the one-electron Hamiltonian

\[ H = H_A + z\mathcal{E}(t). \quad (7.4) \]

\( \mathcal{E}(t) \) represents the combination of the XUV and IR field, \( z \) the atomic dipole moment and \( H_A \) the atomic Hamiltonian. In the following, we use
atom units in this subsection. The calculations are based on the SAE approximation and neglect any multi-electron effects [46]. In a first step we calculate the time derivative of the energy of the atomic system $E$ in the laser field $E(t)$:

$$\frac{dE}{dt} = \frac{d}{dt} \langle \psi | H | \psi \rangle = \langle \psi | \frac{\partial H}{\partial t} | \psi \rangle = \langle z \rangle \frac{\partial E}{\partial t} \quad (7.5)$$

The total energy exchanged by the atoms with the laser field $E(t)$ can be expressed as:

$$\Delta E = \int_{-\infty}^{+\infty} \frac{dE}{dt} dt = \int_{-\infty}^{+\infty} z(t) \frac{\partial E}{\partial t} dt, \quad (7.6)$$

where we replaced $\langle z \rangle(t)$ by $z(t)$ for reasons of better readability. The electric field $E(t)$ and the dipole moment $z(t)$ are real functions. Accordingly, we can write for both functions after Fourier transforming them $\tilde{E}(-\omega) = \tilde{E}^*(\omega)$ and $\tilde{z}(-\omega) = \tilde{z}^*(\omega)$. The star represents the complex conjugate of the function.

Now, we define the frequency-dependent response function $\tilde{S}(\omega)$, which corresponds to the absorption probability per frequency $\omega$. Accordingly, the integration of $\omega \tilde{S}(\omega)$ over all frequencies yields the total exchanged energy. It can be expressed by the following equation:

$$\Delta E = \int_{-\infty}^{+\infty} \omega \tilde{S}(\omega) d\omega. \quad (7.7)$$

A comparison of equation 7.7 with the two equations 7.5 and 7.6 enables us to write the response function as:

$$\tilde{S}(\omega) = -2 \text{Im} \left[ \tilde{z}(\omega) \tilde{E}^*(\omega) \right], \quad \omega > 0. \quad (7.8)$$

### 7.2.2 Macroscopic response

A number of recent publications discussed the influence of propagation effects in attosecond transient absorption spectroscopy [109, 110, 113]. In the work presented here, we follow the approach of Gaarde et al. [113]. At the heart of this approach lies coupling of the TDSE and the Maxwell wave equation (MWE). The MWE in a frame moving with the speed of light $c$ and by using the slowly-evolving-wave approximation (SEWA) [114], reads as:

$$\nabla^2 \tilde{E}(\omega) + \frac{2i\omega}{c} \frac{\partial \tilde{E}(\omega)}{\partial z} = -\frac{\omega^2}{\varepsilon_0 c^2} \left[ \tilde{P}(\omega) + \tilde{P}_{\text{ion}}(\omega) \right], \quad (7.9)$$
where \( \tilde{E}(\omega) \) represents the Fourier transform of the full electric field consisting of XUV and IR field. The source term \( \tilde{P}(\omega) \) is calculated with the help of the single-atom dipole moment in the SAE approximation
\[
\tilde{d}_{\text{SAE}}(\omega) = \tilde{a}(\omega)/\omega^2.
\]
\( \tilde{a}(\omega) \) is the Fourier transform of the time-dependent acceleration of the electron \( a(t) \):

\[
a(t) = \frac{d^2 z(t)}{dt^2} = -\langle \psi(t) | [H, [H, z]] | \psi(t) \rangle.
\]  

Finally, we get \( \tilde{P}(\omega) = 2\rho \tilde{d}_{\text{SAE}}(\omega) \) where \( \rho \) is the atomic density. \( \tilde{P}_{\text{ion}}(\omega) \) takes the contributions of the free electrons to the refractive index into account and is computed by solving the TDSE in the SAE approximation [58]. In many cases this contribution is small compared to \( \tilde{P}(\omega) \) and consequently neglected [113].

For the calculation of the macroscopic response of the gaseous medium we compute the source term by the numerical integration of the TDSE in a plane \( z \) of the medium and the MWE delivers the linear and nonlinear response of the medium to the excitation [113]. Both the linear and nonlinear response contribute to the electric field that is used in the next plane at \( z + dz \). In this way the propagation of the radiation generated by the electric field is not separated from the propagation of the initial field. After space marching step by step through the medium we finally obtain the transmitted electric field including propagation effects.

Figure 7.7: (a) Calculated response function \( \tilde{S}(\omega, \tau) \) as a function of XUV/IR delay for HH 13, (b) 15 and (c) 17 at an IR intensity of \( 6.0 \cdot 10^{12} \text{ W/cm}^2 \). The response of all three HHs show strong \( 2\omega \)-oscillations.
7. Defining a robust delay-zero in attosecond transient absorption experiments

Figure 7.8: (a) Gaussian-Wigner transform of the calculated response function \( \tilde{S}(\omega, \tau) \) for HH 13, (b) 15 and (c) 17 of figures 7.7(a) to (c), respectively. The delay-frequency representation shows the \( 2\omega \)-oscillations at 0.76 PHz and reveals the \( 4\omega \)-oscillations in HH 13 and 17. The \( 4\omega \)-oscillations of HH 15 are weaker and not visible with the color-code used here.

7.3 Delay-zero calibration

After the short introduction to the theoretical treatment of the XUV absorption in a macroscopic medium we discuss in this section the calibration of a robust delay-zero in attosecond transient absorption experiments.

7.3.1 Calibration based on \( 4\omega \)-oscillations

We start by analyzing the response function discussed in the subsection 7.2.1 in equation 7.8. In analogy to the treatment of the experimental data in section 7.1, we apply the delay-frequency analysis to the response function here. For the simulation of the transient absorption experiments we assume a APT with a duration of 11 fs (FWHM). It consists of HHs 13 to 21 with an initial intensity relation of 0.25, 0.6, 1.0, 0.6 and 0.25, respectively. The HHs are considered to be in phase initially. The peak intensity of the APT is \( 7.0 \cdot 10^{10} \) W/cm\(^2\). We assume a particle density of \( 5 \cdot 10^{17} \) particles/cm\(^3\) and a interaction target length of 1.5 mm. The IR pulse in the simulation has a duration of 25 fs with a center wavelength of 795 nm. The IR peak intensity is varied between \( 1.0 \cdot 10^{12} \) W/cm\(^2\) and \( 1.0 \cdot 10^{13} \) W/cm\(^2\).

Figure 7.7 presents the response function including macroscopic effects obtained with an IR intensity of \( 6.0 \cdot 10^{12} \) W/cm\(^2\) for HHs 13 to 17. However, it is important to note that at these parameters for the simulations there is only a minor difference between macroscopic calculations
7.3. Delay-zero calibration

and calculations based on the single-atom response. Like in the energy-integrated absorption retrieved from the experimental data, we observe also here clear $2\omega$-oscillations. As mentioned before, we apply now the Gaussian-Wigner transform with a delay-window size of $\delta_\tau = 5.5$ fs to the response functions. Figure 7.8 displays the natural logarithm of the resulting Fourier amplitude of the response function in figure 7.7. The response function exhibits a strong $2\omega$-oscillations component around 0.76 PHz and agrees well with the experimental data shown in 7.6. Additionally, we observe $4\omega$-oscillations in HHs 13 and 17. They are weaker in HH 15 and not visible in this color-code. This agrees with the experimental findings and originates from the fact that our APT lacks HH 11. Therefore, there is no coupling of HH 15 to HH 11 possible.

Now, we exploit the fact that we exactly now the delay-zero in our simulations. We already observed in figure 7.8 that the signal caused by the $4\omega$-oscillations seems to be symmetrically centered around the delay-zero. In order to verify this, we integrate the two-dimensional delay-frequency representation in the frequency domain around the signal of the $4\omega$-oscillations. We apply an integration window of 0.6 PHz centered around 1.52 PHz. This integration yields the temporal envelope of the $4\omega$-oscillations indicating the strength of the oscillations as a function of XUV/IR delay. Figures 7.9(a) and (b) illustrate the envelope extracted out of the calculated response function of HH 13 and 17 for an IR intensity of $2.8 \cdot 10^{12}$ W/cm$^2$ and $6.0 \cdot 10^{12}$ W/cm$^2$, respectively. We disregard HH 15 because the strength of the oscillations is significantly weaker as observed in the experimental data. The envelope shows a symmetric shape centered around delay zero for HHs 13 and 17 for both IR intensities. Our calculations reveal that this behavior is robust over the investigated IR-intensity range and over a wide range of gas densities in the target.

As a next step we perform the integration in the frequency domain for the experimental data in order to be able to compare them with the calculations. Figure 7.9(c) and (d) presents the envelopes for two different IR intensities of $2.7 \cdot 10^{12}$ W/cm$^2$ and $4.0 \cdot 10^{12}$ W/cm$^2$ for HH 13 and 17. As for the calculations also in the experimental results we observe a symmetric envelope of the $4\omega$-oscillations. This observation is not affected by the IR intensity in the range we cover with our experiment from
7. Defining a robust delay-zero in attosecond transient absorption experiments

![Theoretical and experimental results](image)

**Figure 7.9:** (a) Calculated envelope of the 4ω-oscillations for HH 13 (red curve) and 15 (blue curve) at an IR intensity of $2.8 \cdot 10^{12}$ W/cm$^2$ and (b) $6.0 \cdot 10^{12}$ W/cm$^2$. The peak of the envelope coincides with the delay-zero, which is exactly known for the calculations, and shows a symmetric shape with respect to the delay-zero. (c) and (d) show the envelope extracted from the experimental data at an IR intensity of $2.7 \cdot 10^{12}$ W/cm$^2$ and $4.0 \cdot 10^{12}$ W/cm$^2$.

2.7 $\cdot 10^{12}$ W/cm$^2$ to 10.8 $\cdot 10^{12}$ W/cm$^2$. The symmetric envelope allows us to fit this envelope with a Gaussian function which provides an amplitude and a peak position. We use the resulting amplitude of the fitted Gaussian for a more systematic study of the influence of the IR intensity on the oscillations strength in section 7.4. Since the experimental data reveal a symmetric shape of the envelope independent of the IR intensity we conclude that the peak position of the Gaussian fit is an excellent way to experimentally determine the delay-zero in an attosecond transient absorption experiment.
7.3. Delay-zero calibration

We also studied alternative ways to extract the delay-zero from an attosecond transient absorption experiment and compared these methods with the calibration based on the $4\omega$-oscillations. As the first and most simple method, we investigate the energy-integrated total absorption. We present the energy-integrated total absorption for an IR intensity of $2.7 \cdot 10^{12}$ W/cm$^2$ in figure 7.10(a). The energy-integration window ranges from 19.5 eV to 38.5 eV. In order to extract a delay-zero we fit the energy-integrated total absorption with the sum of a linear function and a Gaussian. With the linear function we take the asymmetry of the integrated absorption around the delay-zero, which was defined by the $4\omega$-oscillation-based method, into account. The IR pulse precedes the APT for large positive delays. Its intensity is insufficient to excite any electron out of the ground state of He or induce any other effect influencing the XUV absorption. Accordingly, we observe the field-free XUV absorption for large positive delays. The situation is fundamentally different for negative delays when the IR pulse follows the APT. In this case effects like perturbed free polarization decay appear, leading to the expected asymmetric absorption around delay-zero [106]. The maximum of the total absorption provided by our fit function shows a discrepancy of 9.4 fs with respect
7. Defining a robust delay-zero in attosecond transient absorption experiments

to the actual delay-zero. Consequently, this method is not suitable for a precise delay-zero calibration.

Another, potentially more accurate approach is the calibration of the delay-zero via the envelope of the $2\omega$-oscillations. We expect a higher accuracy due to the higher nonlinearity of the selected effect. For this purpose we integrate the result of the Gaussian-Wigner transform of the energy-integrated total absorption in the frequency domain around the signal originating from the $2\omega$-oscillations. The integration window is centered at 0.76 PHz and has a width of 0.6 PHz. We present the emerging envelope in figure 7.10(b) for an IR intensity of $4.0 \cdot 10^{12}$ W/cm$^2$. The maximal oscillations strength does not appear at the delay-zero but more then 7 fs earlier. Additionally, the envelope splits into two separate peaks. As we are going to show in the next section, the splitting and the shape of the envelope in general strongly depend on the IR intensity. Therefore, we conclude that the envelope of the $2\omega$-oscillations of the energy-integrated total absorption is inappropriate to define the delay-zero.

A modification of the previous method is to investigate the $2\omega$-oscillation envelope of individual HHs in place of the energy-integrated total absorption. Figure 7.11 shows the envelope for the HH 13, 15 and 17. The envelopes are extracted for different IR intensities covering a range from $2.7 \cdot 10^{12}$ W/cm$^2$ to $8.1 \cdot 10^{12}$ W/cm$^2$. At an IR intensity of $2.7 \cdot 10^{12}$ W/cm$^2$ all three HHs exhibit a symmetric envelope centered around the delay-zero defined with the help of the $4\omega$-oscillations. As soon as we increase the IR intensity the shape of the envelope is strongly altered. Particularly, we observe a splitting of the symmetric main peak into two distinct peaks. Furthermore, the amplitude of the envelope decreases as we will study in more detail in the next section. For HHs 13 and 15 the peak located at negative delays on average is dominant while for HH 15 the right peak at positive delay values by trend is higher. Table 7.1 gives an overview over the asymmetry extracted out of 32 individual delay scans. The asymmetric splitting is reproduced by our calculations. In summary, the behavior of the $2\omega$-oscillation envelope as a function of IR intensity prohibits its usage for a meaningful delay-zero calibration.

Although the splitting of the envelope for the $2\omega$-oscillation is in agree-
7.4 IR-intensity dependence

Figure 7.11: (a) Intensity dependence of the $2\omega$-oscillations envelope of HH 13, (b) 15 and (c) 17 over an intensity range from $2.7 \cdot 10^{12}$ W/cm$^2$ to $8.1 \cdot 10^{12}$ W/cm$^2$. We obtain the envelope by the integration of the Gaussian-Wigner transform in the frequency domain around 0.76 PHz. The width of the integration window is 0.6 PHz. With increasing the intensity the envelope gets an more and more asymmetric shape around delay zero for HH 13, 15 and 17.

ment with the results of our calculations, the solution of the TDSE does not provide a direct explanation for this effect. Nevertheless, a possible interpretation could be the depletion of the $2\omega$-oscillations with the onset of the $4\omega$-oscillations. At the moment this idea is not verified.

7.4 IR-intensity dependence

Figure 7.11 illustrates that the oscillation strength of the $2\omega$-oscillations strongly depends on the IR intensity. Moreover, Chen et al. also predicted a dependence of the $4\omega$-oscillation strength on the intensity of the IR field [109]. In this work, we investigate an intensity range stretching from $2.7 \cdot 10^{12}$ W/cm$^2$ to $10.8 \cdot 10^{12}$ W/cm$^2$. We change the IR intensity with the motorized iris I2 in the IR arm of the XUV/IR interferometer (see figure 4.2 in chapter 4). It is important to note again that the highest IR intensity in our experiment of $10.8 \cdot 10^{12}$ W/cm$^2$ is insufficient to induce any excitation out of the He ground state or even ionize He by multiphoton ionization.

We quantify the oscillation strength at a certain IR intensity via the amplitude of the fit function. As mentioned in section 7.3, we apply a Gaussian fit to the $4\omega$-oscillation envelope. The envelope of the $2\omega$-oscillations is fitted with a sum of two Gaussians. This takes into account the double peak structure for the $2\omega$-oscillation envelope at higher intensities. Figure 7.12 presents the normalized oscillation strength for the $2\omega$-
7. Defining a robust delay-zero in attosecond transient absorption experiments

<table>
<thead>
<tr>
<th></th>
<th>before delay-zero</th>
<th>no asymmetry</th>
<th>after delay-zero</th>
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<tbody>
<tr>
<td>total</td>
<td>44.8 %</td>
<td>39.6 %</td>
<td>15.6 %</td>
</tr>
<tr>
<td>HH 13</td>
<td>75.0 %</td>
<td>25.0 %</td>
<td>0.0 %</td>
</tr>
<tr>
<td>HH 15</td>
<td>28.1 %</td>
<td>28.1 %</td>
<td>43.8 %</td>
</tr>
<tr>
<td>HH 17</td>
<td>31.3 %</td>
<td>65.6 %</td>
<td>3.1 %</td>
</tr>
</tbody>
</table>

Table 7.1: Asymmetry of the $2\omega$-oscillation envelope with respect to delay-zero. In the column ‘before delay-zero’ we show the percentage of delay scans where the dominant peak in the asymmetric splitting of the envelope of the $2\omega$-oscillations lies before the delay-zero. Accordingly, we present in the right column the percentage of scans where the dominant peak appears after the delay-zero and the column ‘no asymmetry’ presents the scans without any clear asymmetry. The rows break the percentage down for the single HHs. The red numbers indicate the maximum value for each row.

and $4\omega$-oscillations. We normalize the oscillation strength to its value at the lowest IR intensity of $2.7 \cdot 10^{12} \text{ W/cm}^2$. The $2\omega$-oscillation strength for HH 13 and 17 shows a maximum at $\approx 5.0 \cdot 10^{12} \text{ W/cm}^2$. For an increasing intensity the oscillation strength declines. This behavior agrees with the observation in figure 7.11, where an increasing of the IR intensity results in a splitting of the envelope into two peaks with simultaneous decrease of the maximum of the envelope. HH 15 shows a comparable behavior but without the local maximum around $\approx 5.0 \cdot 10^{12} \text{ W/cm}^2$.

The IR dependence of the $4\omega$-oscillations reveals more complex characteristics. In the lower intensity range up to $\approx 5.5 \cdot 10^{12} \text{ W/cm}^2$ the oscillation strength of HH 13 and 17 increases monotonically and finally reaches a local maximum. For a further increase of the intensity we enter an intensity range where the oscillation strength decreases with increasing intensity.

For a better understanding of the IR-intensity dependence, especially the decrease of the oscillation strength with increasing intensity in some intensity regions, we theoretically examined the single-atom response as a function of IR intensity and IR wavelength. It is important to note for the correct interpretation of the results that a change of the IR wavelength automatically yields an according change of the center energy of the HHs. We investigate the strength of the $4\omega$-oscillations of HH 17 and the total absorption of HH 13 and 15. The results are shown in figure 7.13. The calculations reveal for a driving wavelength of 795 nm close to the wavelength used in the experiment (789 nm) a monotonous
increase of the $4\omega$-oscillation strength as a function of intensity (see figure 7.13(a)), which disagrees with our experimental result. We observe in figure 7.13(a) two dominant structures contributing to the $4\omega$-oscillations at a driving wavelength of $\approx 770\, \text{nm}$ and $\approx 790\, \text{nm}$ and intensities above $\approx 6.0 \cdot 10^{12}\, \text{W/cm}^2$. We identify these structures as the resonant enhancement of the absorption due transition from the $1s^2$ ground state to the $1s2p$ state, that is resonant with HH 13 as can be seen from figure 7.13(b) and the Stark shifted $1s3p$ state resonant with HH 15 (see figure 7.13(b)). The resonant $1s3p$ state allows a two-IR-photon intermediate resonance in the coupling of HH 13 and 17. Where the two resonances meet we discover that the $4\omega$-oscillation strength is reduced by increasing the IR intensity due to the complex excitation dynamics. Figure 7.14 displays the $4\omega$-oscillation strength as a function of intensity for several fixed IR wavelengths. For $775\, \text{nm}$ we observe a maximum in the oscillation strength around $\approx 4.0 \cdot 10^{12}\, \text{W/cm}^2$ and a decrease for higher intensities as in the experiment (see figure 7.12(b)). We want to stress here that a change of the driving IR wavelength also changes the energetic position of the HHs since they are locked to the driving wavelength.

There are different possible explanation for the discrepancy of the calculated results and the experimental findings. One explanation might be a blue shift in the generating Xe gas jet due to plasma SPM. On the other
7. Defining a robust delay-zero in attosecond transient absorption experiments

Figure 7.13: (a) $4\omega$-oscillation strength of HH 17 as a function of IR intensity and IR wavelength calculated for the single-atom response. (b) Calculated total absorption of HH 13 and (c) 15 in the single-atom response.

Figure 7.14: Intensity-dependent $4\omega$-oscillation strength for different IR wavelengths corresponding to the results shown in figure 7.13. For a driving IR wavelength of 775 nm the oscillation strength shows a behavior comparable to our experimental observations.

In an additional experiment we investigated if our method to determine the delay-zero in an attosecond pump-probe experiment is transferable from transient absorption spectroscopy towards experiments where charged particles are detected. As described in chapter 4 our attoline enables us to switch between transient absorption experiments and an ex-
7.5. Photoabsorption and photoionization probabilities

Figure 7.15: (a) XUV spectrum of the APT. The spectrum is modified in order to have less intensity in the HHs above the first ionisation potential of He (24.59 eV). (b) Normalized ionization probability (black curve) and total absorption probability (red curve) as a function of XUV/IR delay for an IR intensity of $5.4 \cdot 10^{12}$ W/cm$^2$. The XUV spectrum is normalized with respect to the spectrum in figure 7.17(a).

![Figure 7.15](image)

Figure 7.16: Envelope of the $4\omega$-oscillations of the normalized ionization probability and total absorption probability, both as a function of XUV/IR delay. The dashed lines indicate the Gaussian fit function for both envelopes. The dotted vertical line represent the position of the peak of the fit function. The delay-zero is defined by the maximum of the envelope of the total absorption probability. The deviation of the maximum of the envelope of the normalized ionization probability from the delay-zero is less than 1 fs.

![Figure 7.16](image)

The experiment detecting He$^+$ ions within minutes simply by changing from the pulsed gas target to the needle target (see section 4.3).

The experiment works analogous to the transient absorption experiment except that we detect the He$^+$ ions created by the combined XUV and IR field. Comparable studies were performed several years ago by Johnsson et al. and Ranitovic et al. [96, 98].
Figure 7.15(a) presents the used XUV spectrum of the APT utilized for this experiment. A comparison of the XUV spectrum with the spectrum of the APT in the transient absorption experiment (see figure 7.2) reveals that HHs 19 and higher are reduced in intensity relative to the lower HHs. With this spectral change of the APT we avoid that the ion yield is dominated by the ions originating from the direct single-photon ionization with only one XUV photon. The resulting normalized ionization probability and total absorption probability are both presented as a function of XUV/IR delay in figure 7.15(b). The normalized ionization probability can be separated into three distinct delay ranges. For large positive delays \((\tau > +15\,\text{fs})\) the IR pulse precedes the APT and they are not overlapping in time. In this delay region only direct ionization by the HHs above the first ionization threshold of He contributes to the ion yield. The intensity of the IR pulse arriving before the APT is not sufficient to induce multi-photon ionization or excite any ground-state electrons of He. For large negative delays \((\tau < -20\,\text{fs})\) the APT arrives before the IR pulse in the interaction region. Additional to the direct ionization we have in this delay region a contribution to the signal from atoms ionized by the IR field out of an excited \(1snp\) state. The excited states are populated by the HHs below the first ionization threshold. The ionization probability will decrease for larger negative delay values to the level measured for large positive delays. Unfortunately, we cannot observe this decrease since the natural lifetime of the excited states in He of up to several tens of nanoseconds exceed the delay range of our pump-probe setup \([115]\). The third delay range is between \(-20\,\text{fs}\) and \(+15\,\text{fs}\) where the APT and the IR pulse temporally overlap. In this region, we observe strong \(2\omega\)-oscillations visible already by the naked eye. The behavior in the three separate delay regions agrees with previous results \([98]\). For the total absorption probability presented in figure 7.15(b) we integrate the absorption between 19 eV and 35 eV. The total absorption probability presented in figure 7.15(b) shows also \(2\omega\)-oscillations around delay-zero visible with the naked eye.

The delay-frequency analysis, introduced in section 7.1, of the normalized ionization probability and the total absorption probability exposes that both signals contain besides the \(2\omega\)-oscillations also a \(4\omega\)-oscillation component around delay-zero. Figure 7.16 shows the envelope after the
7.5. Photoabsorption and photoionization probabilities

![Graph](image)

**Figure 7.17:** (a) XUV spectrum of the alternative APT. The APT spectrum resembles the spectrum of the APT employed in the transient absorption experiments in the beginning of this chapter. The HHs located above the first ionization threshold of He have a higher relative intensity compared to the spectrum shown in figure 7.15. (b) Normalized ionization probability (black curve) and total absorption probability (red curve) as a function of XUV/IR delay for an IR intensity of $4.3 \cdot 10^{12}$ W/cm$^2$.

![Graph](image)

**Figure 7.18:** Envelope of the $4\omega$-oscillations of the normalized ionization probability and total absorption probability, both as a function of XUV/IR delay. The dashed lines indicate the Gaussian fit function for both envelopes. The dotted vertical line represent the position of the peak of the fit function. The delay-zero is defined by the maximum of the envelope of the total absorption probability. The deviation between the maximum of the envelope of the normalized ionization probability is slightly increased to 3.4 fs compared to figure 7.16.

integration of the result of the Gaussian-Wigner transform of the $4\omega$-oscillations for the ionization and absorption probability. The modulations in the envelope of the ionization probability are a numerical artefact. The peak position of the Gaussian fit for the ionization probability deviated less than 1 fs from the delay-zero defined here by the Gaussian fit of the absorption probability.
7. Defining a robust delay-zero in attosecond transient absorption experiments

In a second experiment we apply an XUV spectrum that resembles the spectrum initially used for the transient absorption measurements (see figure 7.2). The important difference between the spectrum for the first ion measurement (see figure 7.15(a)) and the spectrum of this measurement (figure 7.17(b)) is the higher relative intensity of the HHs above the first ionization threshold of He. Figure 7.17(b) presents the normalized ionization probability and the total absorption probability. The corresponding envelope of the $4\omega$-oscillations is depicted in figure 7.18. We observe a deviation of the peak position of the envelopes for the ionization and absorption of 3.4 fs. Different experimental uncertainties might possible reasons for this deviation. The main point is a saturation of the TOF spectrometer. Moreover, additional effects as quantum beating, which has not been observed in attosecond transient absorption spectroscopy, could play a role for the deviation. Nevertheless, we conclude that the method of the delay-zero calibration with the $4\omega$-oscillations is extendable also to pump-probe measurements detecting ions, but has to be carefully tested.

7.6 Conclusion

In conclusion, we measured and discussed sub-cycle oscillation in an attosecond transient absorption experiment around the first ionization threshold of He. We use an APT in combination with a femtosecond IR pulse in our investigation. We reveal in our experimental data besides the well-known $2\omega$-oscillations additionally $4\omega$-oscillations. A periodicity which is non-existent in the initial APT or IR pulse. In a next step, we demonstrate a delay-zero calibration for attosecond transient absorption experiments using an APT based only on the experimental data. Our experimental results are in excellent agreement with the solution of the TDSE. The comparison with the TDSE reveals that the method based on the $4\omega$-oscillations is more accurate than other methods, we investigated for comparison, i.e. the total absorption or the $2\omega$-oscillations. Moreover, we presented a systematic investigation of the IR dependency of the $4\omega$-oscillations and discuss the influence of resonances on the oscillation strength. In a final experiment, we compare the $4\omega$-oscillations in the total absorption with the signal obtained by the detection of the He$^+$ ions.
The ion yield exhibits $2\omega$ and $4\omega$-oscillations, respectively. The delay-zero obtained from the $4\omega$-oscillations in the ion yield is in agreement with the result based on the total absorption.
Chapter 8

Simulation of attosecond transient absorption in helium

The interaction of XUV attosecond pulses in combination with a moderately strong IR field in He plays an important role in several pioneering experiments in attosecond transient absorption spectroscopy [19, 103, 105]. The reasons for using He as a target medium are manifold. Its singly excited states lie in an energy range between the 1s2p state at 21.22 eV and the first ionization potential \( I_p = 24.59 \text{ eV} \). This range is easily accessible with many HHG sources. Moreover, the He atom is one of the more simple quantum-mechanical systems. This is helpful for the interpretation of the experimental results. The simplicity of the system is also convenient for the calculation of the optical response of He atoms towards electromagnetic radiation. Accordingly, a great amount of theoretical and experimental work on attosecond transient absorption spectroscopy in He was published in recent years [19, 77, 78, 104, 106, 109, 111, 116].

In this chapter, we discuss the theoretical simulations of an attosecond transient absorption experiment in He around its first ionization potential \( I_p \). We mainly focus on the influence of the IR characteristics, e.g. photon energy, on the absorbance and compare our first results with previous publications. Moreover, we exploit the possibility to disable or enable the coupling between states in order to investigate light-induced structures.

The goal of our simulations is to qualitatively reproduce the data ob-
tained in attosecond transient absorption experiments in He. The focus of our theoretical model and its implementation is on short computational time and to gain a first insight into the observed effects. For a more accurate description our model has to be extended as we will discuss in the conclusion of this thesis.

8.1 Theoretical model

For the calculation of the absorption of He atoms in the combined XUV and IR field we apply a model recently suggested by A. N. Pfeiffer and S. R. Leone [116]. They discussed the transmission of a SAP through an ensemble of three-level systems under the influence of a dressing IR field. For the energies of the three-level system they chose the ground state and two core-hole states of Xe. The focus of their work lay on the splitting of the absorption lines and the influence of the XUV/IR delay on the shape of the absorption spectrum.

The starting idea is to treat the interaction of the light field with the model system in the time domain. Here, we include in total nine states in our model in order to simulate He atoms in the proximity of the first ionization threshold $I_p$. Even though, we present simulations for He, the model is applicable to any other few-level system. The Hamiltonian of the model system in the interaction with an electric field $F(t)$ takes the following form:

$$H = H_0 - d \cdot F(t).$$  \hspace{1cm} (8.1)

$H_0$ represents the field-free Hamiltonian of our model system, $d$ is the dipole transition matrix and $F(t)$ the full electric field including the XUV and IR radiation. $H_0$ reads as (we use atomic units for the description of our theoretical model in this chapter):

$$H_0 = \text{diag}(\omega_1, \cdots, \omega_9) = \begin{pmatrix} \omega_1 & 0 & \cdots & 0 \\ 0 & \omega_2 & \cdots & \vdots \\ \vdots & \ddots & \ddots & 0 \\ 0 & \cdots & 0 & \omega_9 \end{pmatrix},$$ \hspace{1cm} (8.2)

where the diagonal of the matrix contains the transition energies starting from the ground state the the excited states as described in table 8.1 [117].
### 8.1. Theoretical model

<table>
<thead>
<tr>
<th>$\omega_i$</th>
<th>Energy (eV)</th>
<th>Final state</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_1$</td>
<td>0</td>
<td>1s$^2$</td>
</tr>
<tr>
<td>$\omega_2$</td>
<td>20.616</td>
<td>1s2s</td>
</tr>
<tr>
<td>$\omega_3$</td>
<td>21.218</td>
<td>1s2p</td>
</tr>
<tr>
<td>$\omega_4$</td>
<td>23.087</td>
<td>1s3p</td>
</tr>
<tr>
<td>$\omega_5$</td>
<td>23.742</td>
<td>1s4p</td>
</tr>
<tr>
<td>$\omega_6$</td>
<td>22.920</td>
<td>1s3s</td>
</tr>
<tr>
<td>$\omega_7$</td>
<td>23.673</td>
<td>1s4s</td>
</tr>
<tr>
<td>$\omega_8$</td>
<td>23.074</td>
<td>1s3d</td>
</tr>
<tr>
<td>$\omega_9$</td>
<td>23.736</td>
<td>1s4d</td>
</tr>
</tbody>
</table>

**Table 8.1:** Transition energies of the model system referring to the 1s$^2$ ground state.

<table>
<thead>
<tr>
<th>Initial state $i$</th>
<th>Final state $j$</th>
<th>$d_{ij}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s$^2$</td>
<td>1s2p</td>
<td>0.729</td>
</tr>
<tr>
<td>1s$^2$</td>
<td>1s3p</td>
<td>0.3604</td>
</tr>
<tr>
<td>1s2p</td>
<td>1s2s</td>
<td>5.0507</td>
</tr>
<tr>
<td>1s2s</td>
<td>1s3p</td>
<td>1.5813</td>
</tr>
<tr>
<td>1s$^2$</td>
<td>1s4p</td>
<td>0.2266</td>
</tr>
<tr>
<td>1s2s</td>
<td>1s4p</td>
<td>0.8012</td>
</tr>
<tr>
<td>1s3s</td>
<td>1s4p</td>
<td>2.6737</td>
</tr>
<tr>
<td>1s3d</td>
<td>1s4p</td>
<td>1.6749</td>
</tr>
<tr>
<td>1s4s</td>
<td>1s4p</td>
<td>22.6093</td>
</tr>
<tr>
<td>1s2p</td>
<td>1s3s</td>
<td>1.8680</td>
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<tr>
<td>1s2p</td>
<td>1s4s</td>
<td>0.6559</td>
</tr>
<tr>
<td>1s2p</td>
<td>1s3d</td>
<td>6.8454</td>
</tr>
<tr>
<td>1s2p</td>
<td>1s4d</td>
<td>2.4186</td>
</tr>
<tr>
<td>1s3s</td>
<td>1s3p</td>
<td>12.3814</td>
</tr>
<tr>
<td>1s3p</td>
<td>1s4s</td>
<td>4.6268</td>
</tr>
<tr>
<td>1s3p</td>
<td>1s3d</td>
<td>14.1014</td>
</tr>
<tr>
<td>1s3p</td>
<td>1s4d</td>
<td>11.0567</td>
</tr>
</tbody>
</table>

**Table 8.2:** Elements of the dipole matrix $d_{ij}$ for the transitions between the states presented in table 8.1.

We define the energy of the ground state as 0 eV. Table 8.2 presents the dipole matrix elements of $d$ for all the transitions of our model system [117]. All elements of $d$ which are not listed in table 8.2 are set to zero.

For the simulation of the absorption of the XUV radiation in our atomic model system, we calculate the temporal evolution of the density matrix $\rho(t)$. The equation of motion for $\rho(t)$, the so-called von-Neumann equa-
tion, defines the evolution in time [118]:

\[
\frac{\partial}{\partial t} \rho(t) = -i[H, \rho(t)] - i\Gamma \rho(t).
\] (8.3)

The second term on the right side of equation 8.3 describes the decay of the population. The components of the matrix \( \Gamma \) represent the decay rates. We defined \( \Gamma_{00} = 0 \) meV, \( \Gamma_{ij} = 5 \) meV for \( i \neq j \) and \( \Gamma_{ij} = 10 \) meV for all other elements [110].

For the optical response of our model system towards the exciting field we have to know its polarization \( P(t) \). We express the polarization as the expectation value of the dipole matrix multiplied with the atomic number density \( N \). Now, we take advantage of the fact that we already calculated the time-dependent density matrix \( \rho(t) \) with equation 8.3, which allows to write the polarization as [118]:

\[
P(t) = N \text{Tr}[\rho(t)d].
\] (8.4)

After we obtained the polarization as a function of time, we move into the frequency domain by Fourier transforming \( P(t) \) and obtain the polarization as a function of angular frequency \( \tilde{P}(\omega) \). We calculate the spectrum after the interaction with the He atoms \( \tilde{E}_{\text{out}}(\omega) \) depending on the initial spectrum \( \tilde{E}_{\text{in}}(\omega) \) with the help of \( \tilde{P}(\omega) \):

\[
\tilde{E}_{\text{out}}(\omega) = \tilde{E}_{\text{in}}(\omega) \exp \left( \frac{2\pi \omega}{c} \frac{NP(\omega)}{\tilde{E}_{\text{in}}(\omega)} L \right)
\] (8.5)

where \( L \) corresponds to the length of the interaction medium and \( c \) represents the speed of light. Consequently, we calculate the absorbance \( A(E) \) as:

\[
A = -\ln \left( \frac{|\tilde{E}_{\text{out}}(\omega)|^2}{|\tilde{E}_{\text{in}}(\omega)|^2} \right).
\] (8.6)

### 8.2 Autler-Townes splitting

The Autler-Townes effect or dynamic Stark splitting occurs in quantum-mechanical systems exposed to an electromagnetic field that resonantly drives a transition of the system [119]. In this section, we investigate an atomic three-level system as depicted in figure 8.1 where the ground state
is coupled to an excited state with an electromagnetic field. In the example of figure 8.1 an SAP excites electrons from the $1s^2$ ground state of He to the $1s2p$ excited state. Moreover, we have a second electromagnetic field which couples the two excited states. These two states are in the example represented by the $1s2p$ and $1s3s$ state. If the second field is in resonance with the transition the absorption line of the $1s2p$ state will fork into two separate lines and we obtain the Autler-Townes doublet [119]. The spacing of the two doublet lines depends on the intensity of the field that couples the two excited states. Therefore, we expect the spacing of the doublet to change with the delay between the two fields since we investigate pulsed fields.

### 8.2.1 Simplified three-level system

In a first test of our simulations, we examine the three-level system described in the previous paragraph and depicted in figure 8.1. For the excitation from the ground state we apply a SAP energetically centered at 22.5 eV with a peak intensity of $1.0 \cdot 10^{10}$ W/cm$^2$ and Gaussian envelope in time with a FWHM of 200 as. The IR has an intensity of $1.0 \cdot 10^{12}$ W/cm$^2$ and a Gaussian temporal envelope with a FWHM of 10 fs, corresponding to 4.1 optical cycles.

We investigate the delay-dependent absorbance around the singly ex-
Figure 8.2: Absorbance \( A(E, \tau) \) of He three-level system as function of XUV photon energy and XUV/IR delay for different IR photon energies around the 1s2p excited state at 21.218 eV. The calculation includes only three states of the He atom: 1s\(^2\), 1s2p and 1s3s as shown in figure 8.1. (b) shows the symmetric Autler-Townes splitting of the 1s2p absorption line for a zero detuning \( \Delta = 0 \) meV of the IR photon energy with respect to the 1s2p-1s3s transition energy. For a detuning of \( \Delta = \pm 50 \) meV presented in panel (a) and (c), we observe an asymmetric splitting of the absorption line.

cited 1s2p state at 21.218 eV for different IR-photon energies. We start with an IR photon energy of 1.702 eV, which exactly matches the energy difference between the 1s2p and 1s3s state. For this condition of a zero detuning, \( \Delta = \omega_{IR} - (E_{1s3s} - E_{1s2p}) \), we expect to observe the symmetric Autler-Townes splitting of the 1s2p state [119]. Figure 8.2(b) shows the result of our simulation of the absorbance \( A(E, \tau) \) as function of photon energy \( E \) and XUV/IR delay for \( \Delta = 0 \) eV. The 1s2p absorption line starts to split into the Autler-Townes doublet for negative delays where the SAP precedes the IR pulse. The spacing of the two individual lines of the doublet varies as a function of XUV/IR delay because the intensity of the IR
overlapping with the XUV changes as their relative delay is varied. For positive delays when the pulses do not overlap anymore and the IR precedes the SAP, we only observe the field-free 1s2p absorption line and no splitting anymore. Our results are in excellent agreement with a recent theoretical discussion of attosecond transient absorption spectroscopy in He by Chini et al. [111]. Their simulations are based on the solution of the TDSE in the SAE approximation.

We convolve our numerical results with a Gaussian of \( \approx 70 \) meV to simulate the finite resolution of the XUV spectrometer used for the detection in an experiment. This helps to achieve a better agreement between simulations and the experiment but does not change qualitatively the results of the calculations.

In a next step we slightly detune the photon energy of the IR pulse by \( \Delta = \pm 50 \) meV with respect to the 1s2p-1s3s transition. The resulting absorbances as a function of photon energy and XUV/IR delay are shown in figure 8.2 panels (a) and (c), respectively. For a detuning of \( \Delta = \pm 50 \) meV the splitting becomes asymmetric. For a better illustration of the asymmetry, we present in figure 8.3 a line cut of the panels (a) to (c) of figure 8.2 at a delay of \( -6.4 \) fs. The black curve shows the resonant case with \( \Delta = 0 \) meV and the blue and red curve the cases with \( \Delta = \pm 50 \) meV, respectively. The asymmetry to higher and lower photon energies is clearly visible. For a photon energy of 1.702 eV the center wavelength of the IR pulse corresponds to 728.5 nm. A detuning of \( \pm 50 \) meV leads to a shift of the center wavelength of \( \approx 20 \) nm.

Finally, we compare the Autler-Townes splitting in the resonant case of the three-level system with a model including all the states shown in table 8.1. Figure 8.4 presents in panel (a) the absorbance \( A(E, \tau) \) as a function of photon energy and XUV/IR delay for the three-level system and for the nine-level system in panel (b). The reader should note that figure 8.4(a) corresponds to figure 8.2(b) but applies a different color scaling and a larger span of the energy axis. As an important difference, we observe in panel (b) the absorbance caused by the transition from the ground state to the 1s3p (23.087 eV) and 1s4p (23.742 eV) excited state. Moreover, we discover a light-induced structure around 20.2 eV and around 22.3 eV, which
we will discuss in more detail in the next section. Due to the coupling to other states the symmetric Autler-Townes splitting of the 1s2p state observed for the three-level system becomes strongly asymmetric on the case when more states are included shown in panel (b). Especially, the coupling with the 1s3d at 23.074 eV, corresponding to a detuning of $\Delta = 154 \text{ meV}$, leads to the symmetry. Accordingly, the Autler-Townes splitting in a transient absorption experiment will always be asymmetric for $\Delta = 0 \text{ meV}$, i.e. in the case of resonant coupling of the 1s2p and 1s3s state.

### 8.3 Light-induced states

We already mentioned in subsection 8.2.1 the selective switching-off of the coupling between states. In this subsection here, we describe how to use this to identify effects observed in our simulations or experimental data, respectively. As an example, we investigate the light-induced structure around 22.3 eV visible in the simulated delay-scan presented in figure 8.3 [106]. We performed an additional simulation with slightly different parameters for the IR field. The IR intensity is $2.0 \cdot 10^{12} \text{ W/cm}^2$, the pulse duration is 14.0 fs (5.4 optical cycles) and the photon energy 1.5804 eV. The
8.3. Light-induced states

Figure 8.4: Calculated absorbance $A(E, \tau)$ as a function of photon energy and XUV/IR delay with an IR photon field in resonance with the 1s2p-1s3s transition. (a) Calculation including three states as already presented in figure 8.2(b). Panel (b) shows the calculation with all nine states shown in table 8.1 included.

Photon energy represents a typical value in our experiments with a center wavelength of $\approx 785 \text{ nm}$.

Figure 8.5 displays the simulated IR scans with different states included or excluded, respectively. In panel (a), we show the result for all transitions of table 8.2 included. The light-induced structure centered around 22.3 eV in a delay range $-15 \text{ fs} < \tau < 5 \text{ fs}$ is clearly visible. There are different possibilities leading to this structure. The absorption of one XUV at 22.3 eV plus the absorption of one IR photon leads to a final energy of $\approx 23.8 \text{ eV}$, where the singly excited 1s4s and 1s4d states are located. For the absorption of one XUV photon and emission of one IR photon we end up at an energy of $\approx 20.7 \text{ eV}$. Here, we possibly can access the 1s2s state. Therefore, we switch-off the coupling to these three excited states in a first simulation. We present the result in figure 8.5(b). The simulation clearly shows that the light-induced structure has disappeared and consequently, originates from the coupling with one of these states.

Panel (c) shows the result of a simulation that includes coupling to the 1s2s state but still neglects the coupling to 1s4s and 1s4d states. We ob-
Figure 8.5: Investigation of the light induced structure around 22.3 eV. We show in panel (a) to (d) the calculated absorbance \( A(E, \tau) \) as function of photon energy and XUV/IR delay. (a) presents the result including all transition listed in table 8.2. In (b) we neglect the transition to the 1s2s, 1s4s and 1s4d state resulting in the disappearance of the light-induced structure. In (c) and (d) we additionally enable the coupling to the 1s2s or 1s4s, respectively. We conclude that the main contribution originates from the coupling with 1s2s state.

serve a strong light-induced structure around 22.3 eV. Along the lines of panel (c), we illustrate in panel (d) the simulation including only the coupling to the 1s4s state. Also here, we observe a light-induced structure at 22.3 eV revealing positive and negative absorbance. Nevertheless, the contribution related to the 1s2s state is dominant. The weakest contribution comes from the 1s4d state which is not shown here.

Accordingly, the selective switching-off of the coupling of the states allows to disentangle the contributions of different states to the light-induced structures also observed in attosecond transient absorption experiments [106]. In the specific case of the light-induced effects around 22.3 eV the structure is a superposition of contributions emerging from the coupling to the 1s2s, 1s4s and 1s4d singly excited states dominated by the contribution related to the 1s2s state.
8.4 Conclusion

We performed calculations of the absorbance in attosecond transient absorption experiments. Our simulations are based on a model introduced by Pfeiffer and Leone [116]. We solved the equation of motion of the density matrix, the von-Neumann equation, and calculated with the help of the density matrix the polarization of the system. Finally, we computed the spectral intensity after the transmission through the interaction medium and with this the absorbance. In connection to the previous chapters, we investigated the absorbance of He here.

After the introduction of the theoretical model, we investigated the Autler-Townes splitting for different IR photon energies. We demonstrated that a detuning of the photon energy with respect to the transition energy results in an asymmetric splitting. In the second part, we studied the origin of light-induced structures in the absorbance. The selective disabling of certain transition allowed us to identify the relevant states.
Chapter 9

Attosecond control of the optical properties of polycrystalline diamond

The first experiments in attosecond transient absorption spectroscopy investigated exclusively the absorption in noble gases [17, 18, 19]. The advantage of working with noble gases, especially He, was discussed in the previous chapters and many other publications [77, 78, 79, 103, 105, 106, 110]. The next logical step is the investigation of small molecules such as molecular nitrogen or hydrogen, which was already presented by Sansone et al. and Cheng et al. [120, 121]. Of course, the mid- and long-term goals of attosecond transient absorption spectroscopy is the investigation of more complex systems like targets in solution and condensed matter. The latter, we present in this chapter.

Solid-state systems are of special interest since the understanding of ultrafast processes in condensed matter is of great importance for many applications in optical communication and electronics. Recently, the modification of the optical properties of a solid-state system with the electric field of a femtosecond IR pulse was presented [122]. Schultze et al. showed reversible changes in the absorbance and reflectivity on a sub-femtosecond time scale in the XUV and IR spectral range, respectively.

In this chapter, we demonstrate the control of the optical properties in the XUV spectral domain by applying an APT in combination with a femtosecond IR pulse to a thin polycrystalline diamond membrane. The
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Figure 9.1: Picture of the diamond membrane taken with an optical microscope. The light-grey area in the center shows the diamond membrane with a thickness of $\approx 48 \text{ nm}$. The diameter of the free-standing diamond membrane is $1 \text{ mm}$. The outer dark-grey area shows the Si ring holding the diamond.

The mechanical, thermal and optical properties of diamond make it an extremely interesting material for various applications in industry and research. However, the most interesting properties for the experiments are the transparency of diamond in the IR spectral range due to its large band gap energy $E_{\text{gap}}$ of $5.5 \text{ eV}$ and the strong XUV absorption. This enables us to examine the XUV absorbance in combination with a strong IR field. Here, we describe the diamond membranes and determine their thickness with an absorbance measurement in the XUV spectral range. Additionally, we introduce our home-built shutter system for an improved SNR in the XUV/IR delay scans and investigate the membranes with attosecond transient absorption spectroscopy for different IR intensities.

9.1 Polycrystalline diamond samples

A main challenge for attosecond transient absorption experiments in the XUV spectral range below 100 eV is the low transmittance of many solid-state systems. In combination with the low photon flux of the APs this demands for extremely thin samples. For the measurements presented here, we use diamond membranes with a thickness of $\approx 40 \text{ nm}$ as specified by the manufacturer. The membranes are grown by chemical-vapor-deposition (CVD) on a silicon (Si) disk with a diameter of $4 \text{ mm}$ and a thickness of $500 \text{ µm}$. The Si substrate is removed in the center by etching resulting in a free-standing diamond membrane with a aperture of $1 \text{ mm}$ mounted on a Si ring. The membranes are provided by Diamond Mate-
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Figure 9.2: (a) XUV spectrum before (red) and after (black) transmission through the diamond membrane. We observe strong absorption especially below 40 eV. (b) Extracted absorbance from the two spectra shown in (a). The dashed-black line shows the absorbance of a 48 nm-thick carbon layer.

Figure 9.2: (a) XUV spectrum before (red) and after (black) transmission through the diamond membrane. We observe strong absorption especially below 40 eV. (b) Extracted absorbance from the two spectra shown in (a). The dashed-black line shows the absorbance of a 48 nm-thick carbon layer.

9.1.1 Characterization of the samples

Before we perform pump-probe measurements with the diamond membranes we have to characterize the optical properties in the IR and XUV spectral range. We have a special interest in the damage threshold of the membrane in the IR. We performed first damage tests under ambient conditions outside the vacuum system for membranes with 40 nm, 110 nm and 170 nm thickness. As a result of these measurements we extracted that the diamond samples endure pulse energies up to \( \approx 5 \mu \text{J} \) corresponding to an intensity of \( 6.3 \cdot 10^{12} \text{ W/cm}^2 \) with a pulse duration of \( \approx 9 \text{fs} \). Additionally, we observed that the focus position of the IR on the diamond is important because the supporting Si ring strongly absorbs the IR radiation. If the focus of the beam hits the support ring, this will lead to a heating up of the rim and finally will damage the membrane.

In a next step we transferred the diamond membranes to test their XUV transmission under experimental conditions. As described in subsection 4.3.2 the diamond membranes are attached to the needle valve in the first interaction chamber. We vary the position with respect to focus position with the external manipulator for the needle valve. Figure 9.2(a) shows the XUV spectrum before the interaction with the diamond membrane in
red and after the transmission in black. The initial XUV spectrum was generated with ≈9fs IR pulses which were compressed in the filament setup. We optimized the HHG spectrum for a high cut-off energy since the absorbance of diamond decreases with increasing photon energy in this energy range. We detect no signal below ≈35 eV above the noise level of the spectrometer due to the strong absorption in the membrane. In panel (b) of figure 9.2 we present the absorbance extracted out of the two spectra in (a) as the solid blue line. Here, the absorbance $A(E)$ as a function of photon energy $E$ is defined as:

$$A(E) = -\ln \left( \frac{I_L(E)}{I_0(E)} \right),$$

where $I_L(E)$ represents the spectrum after transmission through the diamond membrane with a thickness $L$ and $I_0(E)$ the initial spectrum. The characteristics of the absorbance confirm our observation that the absorption directly below 40 eV increases significantly. Additionally, we show the absorbance of a 48 nm-thick carbon layer. The corresponding transmission data are extracted from [123]. For the calculation of the absorbance we assume a density of the diamond membrane of 3.515 g/cm$^3$ which is provided by the manufacturer of the membranes. Accordingly, the diamond membranes are slightly thicker than specified by the manufacturer.

### 9.1.2 Diamond as substrate

Additionally, to our attosecond transient absorption experiments we performed a proof-of-principle test for using the diamond membrane as a substrate. Therefore, we investigated the possibility to spin-coat a molecule onto the diamond membrane. We chose C$_{60}$ fullerene dissolved in 1,2-dichlorobenzene. The concentration of the C$_{60}$ was 20 mg/mL. The spin-coater operated with a maximum speed of 3000 rpm. The diamond membrane showed no damage due to the spin-coating and we were able to deposit a layer of several tens of nanometers of C$_{60}$ on top of the diamond membrane. Unfortunately, we observed no specific signal originating from the C$_{60}$ in a first attosecond transient absorption experiment. The measurement was dominated by the signal originating from the diamond.

Nevertheless, the diamond membranes might be suitable substrate for
other molecules. One possibility is to select a molecule which exhibits a distinct feature in the XUV absorption spectrum. This would allow a distinction from the diamond substrate. Another possibility are molecules which show IR-induced effects for intensities significantly lower than the threshold where effects in diamond become detectable.

9.2 IR-induced changes of optical properties

The first attosecond transient absorption experiments with the polycrystalline diamond membranes showed that the effects induced by the IR field are significantly weaker compared to the effects observed with noble gases as an interaction medium. Consequently, we improved our experimental setup in order to observe effects which were below the noise level of the initial configuration. The next subsection describes a home-built vacuum-compatible shutter system that allows to record IR-induced changes in the relative intensity of less than 1%.

9.2.1 Shutter system

In order to extract the changes in the XUV-absorption spectrum originating from the IR field we have to record a spectrum with and without the IR pulse for each delay step. The initial setup allowed only to record a
reference spectrum without the IR field right before and after the delay scan. An interpolation between these two reference spectra was used for the extraction of the IR-induced changes in the complete delay scan. This procedure has the disadvantage that fluctuations of the XUV spectrum and changes induced by the IR pulse cannot be disentangled.

Therefore, we develop a mechanical shutter which is opening and closing the IR beam path of our XUV/IR interferometer. The shutter system can be operated under vacuum conditions. The design is based on a commercial hard-disk drive (HDD) [124, 125]. Figure 9.3 shows a schematic of the shutter system. We attach a stainless steel blade to the head of the HDD to block the IR beam. If we now apply a electrical current to the coil attached to the arm, which is positioned in the field of a permanent magnet, the arm will move depending on the polarity of the current into the open or close position. This is the same principle as for the reading and writing process of the HDD. In this way we open and close the beam path of the IR pulse. The arm is damped at both end position by two stainless-steel springs. We added an additional O-ring between the ball bearing of the arm and the home-built case for a fine adjustment of the damping. Additionally, we monitor the current position of the shutter with a light barrier (TCST2103, Vishay Intertechnology, Inc.).

Before we integrated the shutter into our experimental setup, we performed a careful characterization. We triggered the shutter with a TTL signal from a frequency generator and measured the opening and closing behavior with the help of a helium-neon laser and a photodiode. We observe a delay between the trigger signal and the opening of the shutter of less than 5 ms, both for opening and closing. After the integration of the shutter into our experimental setup, we perform different attosecond transient absorption experiments in He. An analysis of the noise reveals that we expect to be able to observe IR-induced changes of less than 1%. Further details about the mechanical and electrical design and the full characterization of the shutter system can be found in [126]. The shutter system can be operated at 20 Hz. In our experimental setup the shutter was operated at a lower repetition rate of about 4 Hz due to the long read-out time of the XUV spectrometer.
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9.2.2 Transient absorption measurements

We use the setup described in chapters 2 and 4 to investigate the IR-induced changes in the optical properties of the diamond membranes with attosecond transient absorption spectroscopy. We compress the output pulses with the filament setup to $\approx 9$ fs and investigate the response for three different IR intensities: $2.5 \cdot 10^{12}$ W/cm$^2$, $5.0 \cdot 10^{12}$ W/cm$^2$ and $6.3 \cdot 10^{12}$ W/cm$^2$. For the lowest intensity, we start to observe IR-induced effects in the diamond, as we will show below. The highest experimental intensity corresponds to a pulse energy of $5 \mu$J, right below the damage threshold, as we already mentioned in section 9.1. For the highest intensity we obtain an electrical field strength of $F_{\text{max}} = 1.35$ V/Å. The critical field strength $F_{\text{critical}}$ is defined as [122]:

$$F_{\text{critical}} = \frac{E_{\text{gap}}}{|e|a},$$

(9.2)

where $E_{\text{gap}}$ represents the band-gap energy, $e$ the charge of the electron and $a$ the lattice constant. For diamond with $E_{\text{gap}} = 5.5$ eV and $a = 3.57$ Å we have a critical field strength of $F_{\text{max}} = 1.54$ V/Å [127]. It is important to note that all observed effects are fully reversible. Even after several hours of permanent irradiation of the sample we detect no degradation.

Figure 9.4 displays delay scans with the three different IR intensities. Instead of the transmitted XUV intensity as in previous chapters, we present here the relative transmitted intensity $I_{\text{rel}}(E, \tau)$ as a function of photon energy $E$ and XUV/IR delay $\tau$. We obtain this quantity by dividing the transmitted spectral intensity for each delay step with a reference spectrum without the IR pulse. This procedure visualizes the changes of the absorption caused by the IR field. Accordingly, values larger than one, indicated with the blue color, represent an increase of the signal induced by the IR pulse. The red colour for values smaller than one represent a decrease of the relative intensity, respectively. We indicated the delay-zero with a vertical dashed line in each delay scan. The method for the delay-zero determination will be discussed further below. The reader should note the range of the color scale spanning over $\pm 2\%$.

Figure 9.4(a) shows the delay scan with the lowest IR intensity of $2.5 \cdot 10^{12}$ W/cm$^2$. The IR radiation produces an increase of the relative
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Figure 9.4: Relative transmitted intensity $I_{\text{rel}}$ as function of photon energy $E$ and XUV/IR delay at an IR intensity of (a) $2.5 \cdot 10^{12}$ W/cm$^2$, (b) $5.0 \cdot 10^{12}$ W/cm$^2$ and (c) $6.3 \cdot 10^{12}$ W/cm$^2$. The delay-zero is marked in every panel with a vertical dashed line and defined with the help of the fit function given by equation 9.4.
9.2. IR-induced changes of optical properties

Figure 9.5: XUV spectrum transmitted through the diamond membrane normalized to the intensity of the initial APT. The dashed red boxes represent the six energy integration windows $\Delta E$ (i) to (vi).

Intensity around the delay-zero at a photon energy of 34.6 eV. The increase is periodically modulated and the oscillation period corresponds to twice the frequency of the IR field. A second, periodically modulated signal appears around 44 eV.

In figure 9.4(b), we display the delay scan with the medium IR intensity of $5.0 \cdot 10^{12}$ W/cm$^2$. As a result of the higher intensity, the increase of the relative intensity at 34.6 eV and 44 eV is more pronounced. In addition to the structures observed in the previous scan, new oscillating changes are induced by the IR with the higher intensity, e.g., an oscillation at 40 eV. In figure 9.4(c), we present the relative intensity of the delay scan at the highest intensity. A direct comparison of panel (b) and (c) reveals no significant differences. For a deeper analysis of the obtained data, we select different energy ranges, integrate the relative intensity in energy over an energy window and normalize it as described in the following equation:

$$ f(\tau) = \frac{1}{\Delta E} \int_{\Delta E} I_{\text{rel}}(E, \tau) dE, \quad (9.3) $$

where $\Delta E$ represents the corresponding energy window. Figure 9.5 illustrates six different energy windows $\Delta E$ labeled from (i) to (vi). The different energy windows represent the regions with the strongest oscillations in the relative intensity. Apparently, the strongest oscillations appear on
the lower energetic shoulder of the HHs between 34 eV and \( \approx 45 \) eV. The oscillations in the energy window (iv) are an exception as they are placed exactly between two HHs. Furthermore, we observe in the windows (v) and (vi) the oscillations occurring at the energetic center of the HHs. The results of the energy integration \( f(\tau) \) are shown as a function of XUV/IR delay \( \tau \) in figure 9.6.

The three columns of figure 9.6 represent the three different IR intensities and the rows correspond to the different energy windows. For a further analysis we fit the results obtained by the energy integration according to equation 9.3 with the following expression:

\[
f(\tau) = a + a_0 \left[ 1 + b \cos(\omega(\tau - \tau_0) + \phi) \right] e^{-\frac{(\tau - \tau_0)^2}{2\sigma^2}}. \tag{9.4}
\]

We choose this expression to match the experimental results and it is not derived from any theoretical model. \( a, a_0, b, \phi, \omega, \tau_0 \) and \( \sigma \) are the fit parameters. The value of \( \tau_0 \) defines the center of the Gaussian in equation 9.4. We exploit the value of \( \tau_0 \) for the result obtained with the integration of window (i) to define the delay-zero. Figure 9.6 reveals that the IR intensity of \( 2.5 \cdot 10^{12} \) W/cm\(^2\) leads to the starting of IR-induced changes of the optical properties. However, the effects are diminutive and almost disappear within the noise. We are able to fit the oscillation with the fit function \( f(\tau) \) only at certain photon energies, see panel (a), (e) and (f).

As it is already directly observable in the relative transmitted signal in figure 9.4, a rise of the intensity to \( 5.0 \cdot 10^{12} \) W/cm\(^2\) results in a significant increase of the IR-induced effects. In energy window (i), which is displayed in panel (g), we observe an increase of the relative signal with a Gaussian envelope in combination with fast oscillations. The FWHM of the envelope is 9.4 fs. For the next two energy windows (ii) and (iii), we exclusively observe the fast oscillations. The increase of the relative signal following a Gaussian envelope is not present. Especially in energy window (iii) the signal experiences even a weak reduction. The third column representing \( f(\tau) \) for the highest IR intensity shows that the increase in intensity is not resulting in a significant change of the IR-induced effects. Furthermore, figure 9.6 nicely shows the improvement achieved with the shutter system mentioned in the beginning of this section. It allows us to
Figure 9.6: Energy-integrated relative transmitted intensity $I_{\text{rel}}$ for energy windows $\Delta E$ (i) to (vi) as shown in figure 9.5. Each column corresponds to a distinct IR intensity. The red lines represent the experimental data and the blue lines the fitted curve corresponding to equation 9.4.
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Figure 9.7: Photon-energy dependence of the peak of the Gaussian $\tau_0$ as defined on equation 9.4 for an IR intensity of $2.5 \cdot 10^{12}$ W/cm$^2$ (green), $5.0 \cdot 10^{12}$ W/cm$^2$ (red) and $6.3 \cdot 10^{12}$ W/cm$^2$ (blue). The error bars represent the standard deviation obtained by the fit procedure. The dashed lines are a guide to the eye. Additionally, we show the XUV spectrum transmitted through the diamond normalized to the initial spectrum.

distinguish effects induced by the IR from the noise for changes of less than 1%.

In figure 9.7 we present the peak position of the Gaussian $\tau_0$ as a function of photon energy for the different energy integration windows. The dashed lines are a guide to the eye. The error bars correspond to the standard deviation we obtain by the fitting procedure. Additionally, we show the XUV spectrum transmitted through the diamond, normalized for the initial spectrum. As described before, the delay-zero is defined with $\tau_0$ for the first energy integration window (i). For an increasing photon energy the peak of the Gaussian shifts to negative delay values. This corresponds to the situation where the XUV precedes the IR pulse. We observe a minimum around 41 eV. For higher photon energies $\tau_0$ approaches zero. The value of $\tau_0$ at 49.5 eV for an intensity of $6.3 \cdot 10^{12}$ W/cm$^2$ results from the fit of figure 9.6(r). There is no clear envelope visible anymore leading to the large error bars. Even though, we could not extract a $\tau_0$ for all energy windows at the lowest intensity of $2.5 \cdot 10^{12}$ W/cm$^2$, the three values we obtained are in good agreement with the two higher intensities. Moreover, we observe an offset between the two higher different intensities, especially around $\approx 42$ eV. A future repetition of the measurements including
intermediate intensities values has to show if the difference is caused by the IR intensity or other factors.

### 9.2.3 Interpretation of the experimental data

The interpretation of results in attosecond transient absorption experiments with condensed matter systems is especially challenging without theoretical support. However, in agreement with the work of Schultze et al., we observed a modulated increase of the signal when an IR field is present. They explained their observation with a quantum-mechanical model as a combination of a temporary change in the density of states and the influence of the electric field on the population in the conduction band and the polarizability [122]. They also investigated a large band-gap material, namely fused silica (SiO$_2$). Nevertheless, there are significant differences between the results shown here and the work of Schultze and co-workers. They operated with a considerably higher photon energy which enabled them to excite electrons from the Si 2p orbitals. Therefore, it is not sure that their suggested model can be applied in our case since the photon energy in our experiment is insufficient to excite electron of the carbon core levels. An alternative approach for the interpretation of our data might be time-dependent density functional theory (TDDFT) which already showed its applicability for the interaction of strong fields with condensed matter on an ultrafast time scale [128, 129].

We show in figure 9.7 the change of the peak position of the Gaussian $\tau_0$ with the photon energy. If we assume this dependence is not originating from an intrinsic property of the IR or XUV radiation it must be a property of the diamond. Consequently, we would have observed an energy-dependent response of the electrons upon the IR field. This would have two consequences. In the first place, the delay-zero determination would not be correct since a negative peak position of the Gaussian envelope corresponds to the situation that the system responds to the IR field before it arrives on the sample. Even more important is the point that photon-energy dependence implies that the change of the optical properties is not following the IR field instantaneously for all photon energies. This would be in contradiction to the previous work of Schultze et al. [122].
An additional interesting point are the relative phases of the oscillations at different photon energies. As we observe in figure 9.6, the oscillations are not in phase. Like the energy-dependent position of the Gaussian, the phase relationship for different energy windows demands for theoretical support for further discussion.

9.3 Conclusion

In this chapter, we presented attosecond transient absorption experiments in condensed matter. The sample under investigation is a sub-50 nm-thick polycrystalline diamond membrane. We performed measurements to determine the damage threshold with respect to the IR pulses and the static XUV absorption. In order to be able to detect relative changes induced by the IR field of less than 1%, we developed a shutter system based on HDD. With this improvement of our setup, we measured the IR-induced relative change of the transmitted XUV radiation as a function of XUV/IR delay.

We observed a periodic modulation of the diamond absorption as a function of delay at certain photon energies. The period of the oscillations is half a IR laser cycle, as observed in the previous chapters for attosecond transient absorption experiments in He. Besides the oscillations, we also detected a decrease in the absorption on a femtosecond time scale following a Gaussian envelope. The changes of the optical properties of the diamond membranes are fully reversible. A first analysis of the experimental data reveals that the peak position of the Gaussian decrease of the absorption depends on the XUV photon energy. Moreover, we observe that the oscillations of the transmitted XUV intensity are not in phase for all photon energies. For a further interpretation of these first experimental results, in order to exclude that the observed effects are caused by the intrinsic properties of the XUV or IR radiation, we need theoretical support for a better understanding.
Chapter 10

Conclusion and outlook

In this thesis, we discussed theoretically and experimentally different attosecond transient absorption experiments in He and polycrystalline diamond. Attosecond transient absorption spectroscopy is the extension of the well-established technique in the femtosecond domain into attosecond science. It is based on the detection of transmitted XUV radiation through a sample in XUV/IR cross-correlation experiments. Even though transient absorption spectroscopy is an extremely young section of attosecond science, it has been extremely successful and shown its usefulness in recent years [74]. Its various advantages over the charged-particle detection, e.g. the possibility to probe bound-bound transitions or the high detection efficiency of photons leading to short acquisition times, make it an extremely powerful tool. In this chapter, we shortly recapitulate the results of the previous chapters and provide an outlook for the future of attosecond transient absorption spectroscopy.

After a brief discussion of the fundamentals of femtosecond laser pulses and their characterization in chapter 2 and an introduction to HHG in chapter 3, we reviewed in chapter 4 the attoline at ETH Zurich in the Ultrafast Laser Physics group, a beamline for attosecond pump-probe experiments. Besides its flexibility regarding different targets and detectors, an important characteristic of the attoline is the second focus, which is obtained by relay-imaging of the first focus. This opens the door for a variety of future experiments, especially also with external collaborators, since the second focus is accessible for any experimental end station. As a
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In the first experiment a simultaneous RABBITT measurement in both foci was performed. This allowed to extract the phase difference originating from the propagation of the radiation and reflection on the second toroidal mirror. The information on the propagation phase is crucial as a calibration for every future experiment [76, 130].

Recent publications investigated the role of propagation effects in attosecond transient absorption spectroscopy [110, 109, 113]. They are supposed to play an important role in the case of a long interaction region and/or high particle densities in the interaction region as it is the case in our pulsed gas target for transient absorption measurements. The attoline with the second focus allows us to perform an attosecond streaking or RABBITT measurement in the second focus while the XUV radiation propagates through the high particle density in the first interaction focus. In combination with a pulse characterization in the first interaction focus with low gas density and the knowledge of the propagation phase, these measurements provide direct information on the propagation effects. This result will be crucial for any following attosecond transient absorption experiment in the gas phase for the future. A further extension of the attoline would be the ability to detect simultaneously to the XUV also the transmitted IR radiation. This allows to extract additional information out of measurements and could be used for transient absorption measurements but also for the detection of charged particles.

In chapter 5, we presented theoretically and experimentally the creation and control of optical absorption and gain. The theoretical discussion illustrates the temporal evolution of the dipole response of a TLS after off-resonant excitation with a pulsed electric field. The observed positive and negative contributions cancel out in the time-integrated detection but can be mapped out with a control pulse with a variable delay. The corresponding attosecond transient absorption experiment in He verifies the theoretical prediction and reveals optical absorption and gain of equal magnitude which can be controlled by the XUV/IR delay. Our theoretical discussion uses the parameters of the experimental investigation of He. However, the model is generic and not exclusively restricted to the description of He. Therefore, the next step is to apply our model to other systems. With the appropriate scaling of intensities and photon energies
the discussion might be applicable to low-dimensional condensed matter or molecular systems.

We introduced in chapter 7 a new experimental technique to extract the delay-zero out of the experimental data in an attosecond transient absorption experiment with an APT. The technique is based on quarter-laser-cycle oscillations in the transmitted XUV intensity as a function of XUV/IR delay. We demonstrate the new technique with an attosecond transient absorption experiment around the first ionization potential of He. The quarter-laser-cycle or 4ω-oscillations originate from the four-photon coupling of HHs. A comparison with the solution of the TDSE reveals that the delay-zero coincides with the maximum of the envelope of the 4ω-oscillations for different IR intensities and gas densities. A careful further investigation of the TDSE solution describes the important role of resonances for the IR-intensity dependence of the 4ω-oscillation strength. Moreover, we demonstrate that the new delay-zero calibration technique is transferable to attosecond pump-probe measurements detecting ions.

In the investigation of the intensity dependence in chapter 7, we observed for the envelope of the 2ω-oscillations an asymmetric splitting of the envelope with increasing intensity. As already mentioned in chapter 7 the origin of the splitting is not yet well understood. A first hypothesis is that the onset of the 4ω-oscillations at a certain IR-intensity results in a decline of the 2ω-oscillations around delay-zero. Therefore, the envelope of the 2ω-oscillations separates into two distinct peaks. It is also not clear at the moment why the envelope splits into peaks of different height and what decides whether the dominant peak appears at positive or negative delays. Both questions motivate for further careful investigation of the influence of the IR intensity on the 2ω- and 4ω-oscillations. Moreover, the occurrence of 4ω-oscillations in attosecond transient absorption experiments using SAPs should be examined. They were already observed by Chini et al. but not discussed [103]. Especially the question at which photon energies these oscillations appear is highly interesting since the spectrum of SAP is continuous and not consisting of discrete HHs as for the APT.

In chapter 8, we introduced simulations for attosecond transient ab-
sorption experiments. In particular, we discussed the absorbance of He excited by a SAP. The theoretical model enables us to exclude specific transitions and therefore, identify different effects observed in the experimental data. Accordingly, we investigated the asymmetry in the Autler-Townes splitting as a function of the IR photon energy and the origin of light-induced states. Currently, our simulations include only nine states. In a next step, besides including more discrete states, the coupling of the excited states to the continuum should be included in order to obtain a more accurate model of He.

Attosecond transient absorption spectroscopy in He with an IR wavelength around 800 nm was already intensively investigated in many recent publications. As already shown in chapter 8, using different photon energies is interesting for resonant coupling of excited states. A driving wavelength around 728 nm leads to the Autler-Townes splitting of the 1s2p state by coupling it to the 1s3s state. Another path resulting in an Autler-Townes splitting is an IR field with 1.6 µm center wavelength, which couples the 1s2p with the 1s2s state [113]. Our simulations allow us to study theoretically the effects emerging at these new wavelengths. Moreover, the simulations will help to understand results in attosecond transient absorption obtained in future experiments with sources operating at different wavelength, e.g. high-power thin disk lasers at 1030 nm or optical parametric chirped-pulse amplification (OPCPA) systems in the mid IR [21, 131].

We presented in chapter 9 for the first time attosecond solid-state transient absorption spectroscopy in polycrystalline diamond. We investigated the IR-induced changes of the absorbance of a polycrystalline diamond membrane. The IR field induces periodic modulations of the transmitted XUV radiation around the energetic position of the HHs. As already observed in experiments with He presented in this thesis, the modulation period corresponds to half a cycle of the IR field. Moreover, we observe at some photon energies a decrease of the absorbance following the intensity envelope of the IR pulse. At the peak of the envelope, we measure a change in the relative signal of 2 % and amplitude of the oscillations of around 1 % and below. We stress here again that all observed effects are fully reversible and accordingly, allow the damage-free con-
control of the optical properties. The modulated decrease in absorbance is in agreement with a recent attosecond transient absorption experiment in fused silica (SiO$_2$) [122]. Additionally, we investigated the peak position of the femtosecond envelope, which we extract with the help of a fit function. The peak position exhibits a photon energy-dependent shift with respect to the delay-zero. This effect might indicate an effect caused by the electronic structure of the polycrystalline diamond. However, this interpretation demands for theoretical support in order to exclude e.g. effects originating from the inherent characteristics of the XUV or IR radiation. Another interesting aspect of the experimental data are the relative phases of the oscillations at different photon energies, but also here we need to have a better understanding to obtain a correct interpretation. A promising approach to interpret the interaction of condensed matter with strong, ultrashort laser pulses is TDDFT [128, 129].

The first successful demonstrations of attosecond solid-state transient absorption spectroscopy open the door to study and control electron dynamics on a sub-femtosecond time scale in condensed matter systems. Our example of polycrystalline diamond shows ultrafast and reversible manipulation of the absorbance. A better understanding of the processes potentially may help to increase the observed effects to a level where they will become attractive for application, e.g. signal processing with petahertz bandwidth.

Since attosecond solid-state transient absorption spectroscopy is still in its infancy there are plenty of future experiments. A possible approach is to move to longer driving wavelength. This allows to investigate materials with a smaller band gap. A driving wavelength of 3.5 µm as it is delivered by our own OPCPA system, corresponds to a photon energy of 0.35 eV. This is already significantly smaller than the band gap of many semiconductors and hence allows to study these materials without absorbing the driving field. Additionally, we presented in chapter 9 that the spin-coating of the diamond-membranes is possible. Therefore, the diamond membranes can serve as a substrate for the deposition of small molecules or maybe polymers. In contrast to measurements in the gas phase, the substrate might enable the investigation of oriented molecules on the substrate without laser alignment of the molecules. Those are only some
ideas exploiting the possibilities arising by the application of attosecond transient absorption spectroscopy on condensed matter systems.
Appendix A

Bessel functions of the first kind

The Bessel function of the first kind are a solution to the Bessel’s differential equation with the complex number $k$, which is a second-order, ordinary differential equation [132]:

$$x^2 \frac{d^2 y}{dx^2} + x \frac{dy}{dx} + (x^2 - k^2)y = 0.$$  \hspace{1cm} (A.1)

The Bessel function of the first kind are defined as:

$$J_k(x) = \sum_{r=0}^{\infty} \frac{(-1)^r \left( \frac{x}{2} \right)^{2r+k}}{\Gamma(k + r + 1)r!}$$  \hspace{1cm} (A.2)

with the Gamma function $\Gamma$:

$$\Gamma(z) = \int_0^{\infty} t^{z-1}e^{-t}dt$$  \hspace{1cm} (A.3)

where $t \in \mathbb{R}_{>0}$.
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09/2009 - 09/2010  Optical and spectroscopic investigations on semiconductor disk lasers
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