
Attosecond Transient Absorption Spectroscopy

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Dedicated to my wife Stefanie.

Abstract

Motion in the microcosm unfolds via the formation of wavepackets, resulting from a coherent superposition of quantum states. Pioneered by A. H. Zewail, nuclear motion in (bio-)molecules as well as the formation and rupture of chemical bonds have been accessed extensively by femtosecond ($1\text{ fs} = 10^{-15}\text{ seconds}$) pump-probe spectroscopy. For these outstanding experiments, A. H. Zewail was awarded the Nobel prize in 1999, establishing the research area of femtochemistry. However, the resolution offered by femtosecond spectroscopy is insufficient to track the dynamics of electronic motion in atoms or molecules since they evolve on an attosecond ($1\text{ as} = 10^{-18}\text{ s}$) to few-fs time scale and thus remain elusive so far.

This thesis establishes attosecond transient absorption spectroscopy as a new approach for the exploration of electronic motion. By combining quasimonocycle (1.5 optical cycles) near infrared (NIR) laser pulses as an initiation event and non-invasive isolated extreme ultraviolet attosecond pulses in a unique exertion as probe pulses, several proof-of-concept experiments are presented. Strong-field ionization of noble gas atoms via the ultrashort NIR laser pulse produces several charged states whose formation during the ionization process has been tracked by the attosecond probe pulse and yielded the first real-time, state-resolved observation of atomic ionization, indicating a delayed formation of higher charged states with respect to lower ones.

Strong-field ionization of krypton atoms—performed with quasimonocycle laser pulses, limiting the ionization window to less than 3.2 fs—creates singly charged ions in a coherent superposition of quantum states. The subsequent evolution of the valence electron motion has been traced for the first time. Attosecond transient absorption spectroscopy, in combination with appropriate modeling, has enabled the complete reconstruction of valence electron motion, including its degree of coherence, which is not accessible by conventional time-integrated spectroscopy.

Besides the investigation of prototypical open systems, this new tool has also been successfully applied to study more complex systems. For instance various quantum beats in xenon ions have been measured in different charge states, indicating complex multi-electron dynamics.

It is shown that attosecond transient absorption spectroscopy further expands the horizon of attosecond science and holds promises to precisely access state-resolved sub-cycle ionization dynamics during strong-field ionization of matter and to explore sophisticated multi-electron dynamics including hole-hole and multi-hole correlations.

Zusammenfassung

Bewegungen im Mikrokosmos entstehen anhand der Formierung von Wellenpaketen als Resultat einer kohärenten Superposition von Quantenzuständen. Auf der Grundlage der Pionierarbeit von A. H. Zewail, konnte die Kernbewegung in (Bio-)Molekülen, sowie auch die Entstehung und Aufhebung von chemischen Bindungen durch die Anwendung von Femtosekunden ($1 \text{ fs} = 10^{-15} \text{ Sekunden}$) Anrege-Abfrage-Spektroskopie weitreichend untersucht werden. Diese hervorragenden Experimente wurden im Jahre 1999 mit dem Nobelpreis für Chemie ausgezeichnet und begründeten den Forschungsbereich der Femtochemie. Jedoch ist die Auflösung, welche Femtosekundenspektroskopie bietet, nicht ausreichend um Dynamiken der Elektronenbewegung in Atomen oder Molekülen aufzuzeichnen, da diese im Bereich von Attosekunden ($1 \text{ as} = 10^{-18} \text{ s}$) oder wenigen Femtosekunden ablaufen und somit bis zuletzt schwer zugänglich waren.

Diese Dissertation erschließt transiente Attosekundenabsorptionsspektroskopie als einen neuen Ansatz für die Erforschung der Elektronenbewegung. Ermöglicht durch die Kombination von nahinfraroten (NIR) gewissermaßen Einzykluslaserpulsen (1,5 optische Schwingungen) als Auslöseereignis und nicht invasiven isolierten extrem ultravioletten Attosekundenpulsen, welche erstmals als Auslesepulse eingesetzt wurden, werden einige grundlegende Experimente dargelegt. Die Starkfeldionisation von Edelgasatomen, erzeugt mit ultrakurzen NIR Laserpulsen, ergibt mehrere Ladungsstufen, deren Formierung während des Ionisationsprozesses durch die Attosekundenpulse ausgelesen wird und somit die erstmalige echtzeit- und ladungsstufenaufgelöste Beobachtung der atomaren Ionisation begründet, welche eine verzögerte Entstehung der höheren Ladungsstufen im Vergleich zu den niedrigeren aufweist.

Starkfeldionisation von Krypton Atomen – durchgeführt anhand von annähernd Einzykluslaserpulsen, welche das Ionisationsintervall auf weniger als 3.2 fs beschränken – hinterlässt einfach geladene Ionen in einer kohärenten Überlagerung von Quantenzuständen. Die darauffolgende Bewegung der Valenzelektronen wurde erstmals ausgelesen. Transiente Attosekundenabsorptionsspektroskopie in Kombination mit geeigneter theoretischer Beschreibung, ermöglichte die vollständige Rekonstruktion der Valenzelektronenbewegung inklusive des Grades der Kohärenz, welcher nicht anhand von konventioneller, zeitintegrierter Spektroskopie ermittelt werden kann.

Neben der Betrachtung von prototypischen offenen Systemen, wurde die neue Methode auch erfolgreich zur Messung an komplexeren Systemen herangezogen. Zum Beispiel wurden zahlreiche Quantenschwebungen in Xenon Ionen unterschiedlicher Ladungsstufe gemessen, die komplexe Multielektronendynamiken indizieren.

Es wurde gezeigt, dass transiente Attosekundenabsorptionsspektroskopie die Attosekundenforschung bereichert, sowie Hoffnungen birgt die zustands- und subzyklusaufgelösten Starkfeldionisationsdynamiken präzise zu erschließen und die Erforschung von anspruchsvollen Mehrelektronendynamiken unter Einschließung von Loch-Loch und Multi-Loch Korrelationen ermöglicht.

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Introduction

Dynamic processes in the microcosm, although generally imperceptible to our senses, affect our every day life. It is, for instance, protein folding, light absorption processes, energy transfer from light-harvesting complexes into the photosynthetic reaction center and a vast variety of chemical reactions involving electronic as well as nuclear correlated dynamics that determine the macroscopic behavior of matter.

Dynamics in the microcosm occur via the formation and subsequent evolution of wavepackets resulting from the coherent superposition of non-degenerate quantum states [1]. The speed of the motion, namely the oscillation period, is defined by $h/\Delta E$ where ΔE is the energy separation between the superimposed quantum states and h the Planck's constant. In atoms and molecules, this separation amounts to tens, hundreds or even thousands of millielectronvolts and hence leads to ultrafast motion from the picosecond ($1 \text{ ps} = 10^{-12} \text{ s}$) (molecular rotation), the femtosecond ($1 \text{ fs} = 10^{-15} \text{ s}$) (atomic motion in a molecule) or even electronic motion unfolding on an attosecond (as) ($1 \text{ as} = 10^{-18} \text{ s}$) to few-fs time scales. Determining the composition of the microcosm, rigorously understanding and precisely controlling the essential dynamics which determine the basic processes observed in every day life, will remain as some of mankind's greatest ambitions.

Absorption/emission spectroscopy

Among other scientific approaches, spectroscopy has played probably the most influential role in the exploration of the microcosm. One of the breakthroughs for determining certain elements was inspired by experiments dating back to 1802 when W. H. Wollaston and independently in 1814 J. v. Fraunhofer discovered the appearance of a number of dark features in the spectrum of the sun. The first spectrochemical analysis ever made was performed by Kirchhoff in 1859 where he proved that the Fraunhofer lines in the sun's spectrum are atomic absorption lines created by certain elements in the atmosphere of the sun [2, 3]. In these classic experiments, Kirchhoff and Bunsen showed that the elements in flames give characteristic emission and absorption spectra.

It is not obvious why, for the next 100 years, the spectrochemical analysis was mainly focused on emission methods. A. Walsh, one of the leading scientists in the development of atomic absorption spectroscopy in the second half of the 19th century, believes that Kirchhoff and Bunsen were limited to the visible spectral range and hence would see little advantage in using atomic absorption rather than atomic emission spectroscopy [4]. The interest in atomic absorption spectroscopy was revived in the 1950s [4, 5] when it was

realized that the types of flames which were used for emission flame photometry would be very well-suited for atomic absorption spectroscopy, especially for elements which are inappropriate photon emitters [2]. The standard atomic absorption method, or generally speaking atomic absorption spectroscopy, is still being used very extensively for instance in modern atomic absorption spectrometers for the qualitative and quantitative determination of chemical elements.

Time-resolving molecular dynamics

By the middle of the 19th century, the ability to record dynamic processes was not anymore limited to time scales of ~ 1 s, which corresponds to the blink of an eye or the responses of the ear (~ 0.1 ms), i.e. the natural observation techniques that dominated scientific inquiry until the 18th century. Some of the most famous demonstrations of these advances were for instance the time-resolving of animal and human locomotion in the years 1887 and 1901 [6] and later the well-known pictures of bullets passing through objects by Harold Edgerton in the mid 1950s. Utilizing snapshot photography, chronophotography and stroboscopy temporal resolutions down to microseconds became available.

For tracing dynamic processes in chemistry, transient absorption spectroscopy was used to track the absorbance of light at a certain photon energy or in a spectral range as a function of time. If the dynamics are slow compared to conventional shutter speeds of spectrophotometers, the temporal resolution can be obtained with a continuous probe beam. Six years after the discovery of stimulated optical radiation in ruby at ~ 694 nm [7], pulsed lasers with durations in the picosecond regime [8] became available. Based on these developments, pump-probe experiments with picosecond temporal resolution became possible, which for instance allowed the investigation of dynamics in complex molecules like the kinetics of rhodopsin in 1978. In these experiments, laser pulses centered at 1060 nm are amplified and frequency doubled to 530 nm before being spatiotemporally divided, resulting in two pulses with an adjustable delay. One acts as the excitation pulse, while the second pulse, upon its spectral broadening in a benzene cell, is employed as the probe pulse. The experiment was designed to observe transient absorption effects in rhodopsin [9]. In the following, many research groups in physics, chemistry, biology, medicine and material science have been using sub-picosecond laser pulse systems. The exploration of ever shorter dynamics in (bio-)molecular reactions had been strongly coupled to the further reduction of laser pulse durations, finally approaching sub-100 fs pulses. Experiments which measured the delay-resolved dynamic absorbance of a probe pulse, led by A. H. Zewail and G. R. Fleming [10, 11, 12], have permitted the real time observation of atomic motion inside molecules as well as the formation and rupture of the chemical bond [13]. As a result of these pioneering efforts, A. H. Zewail was awarded the 1999 Nobel prize for chemistry.

By advancing ultrafast laser systems, it was soon possible to generate as well as to utilize few-cycle visible laser pulses in pump-probe absorption experiments [14, 15, 16]. Spectral dispersion of those pulses in spectrometers yielded besides the higher temporal resolution, due to shorter pulse durations, also a higher spectral resolution and a wider probe spec-

trum which allowed for a simultaneous probing of dynamics encoded on several absorption resonances. Sub-50-fs frequency tunable pulses, generated by excimer amplifiers or via optical parametric amplification [17, 18, 19, 20, 21], allowed the specific tailoring of pump-probe pulses for the study of ultrafast molecular dynamics from the ultraviolet (UV) to near infrared (NIR) wavelengths.

In order to facilitate inner-shell excitations in atoms, the photon energy of the light pulses has to be extended towards extreme ultraviolet (XUV) or x-ray photon energies. Pulsed synchrotron x-ray pulses enabled the measurement of hole-orbital alignment of Kr^+ photoions [22]. Femtosecond XUV light pulses, generated via high-order harmonic generation have been used to interrogate the complete quantum state distribution of Xe^+ produced by optical strong-field ionization [23] and to investigate the dissoziative ionization of CH_2Br_2 induced by NIR strong-field irradiation [24].

The millielectronvolt-scale spacing of vibrational energy levels implies that changes in molecular structure occur on a multifemtosecond timescale and can thus be accessed by femtosecond pump-probe spectroscopy. However, electronic phenomena in the valence band are one hundred to one thousand times faster and so have remained elusive thus far. Femtosecond laser systems, in combination with pump-probe transient absorption experiments, have shed light onto an incredible range of dynamics in several areas of science over the last three decades, but still can not access these fundamental but very fast electron dynamics. Yet, this limitation is only due to the femtosecond temporal resolution afforded by the probe pulse.

Motivation for time-resolving electronic motion and first experiments

The ability to access electronic coherence is a key to determine the time-resolved electronic dynamics of quantum systems, such as the electronic motion in the valence shell. So far, only a few experiments have been performed recently which study the electronic motion in kinematically complete experiments. For instance, the core hole localization in nitrogen molecules (N_2) following the absorption of a x-ray photon was studied by utilizing Auger electron angular emission patterns as an ultrafast probe [25]. From these experiments the electron motion can be inferred but it is not directly observed. Except for the simplest systems, experimental techniques are unable to probe all degrees of freedom. Therefore one generally has to consider an open system, which can then only be characterized in terms of ensemble-averaged quantities (observables) predicted by the system's density matrix. Under these circumstances, the synchrony of wavepacket dynamics in the specimens of the ensemble (that is the wavepacket's *coherence*) is indispensable and only time-resolved measurements can provide direct access to the observables of the motion.

On the other hand, it has been shown that sub-laser-cycle electron pulses (continuum electron wavepackets) created by strong field ionization can probe upon their recollision with the parent ionic molecule vibrational wavepacket dynamics, for instance in ionic hydrogen molecules (H_2^+) [26] and deuterium (D_2^+) [27], which are launched during the ionization process. If the created continuum electron wavepacket is sufficiently energetic, the struc-

ture of the molecule is imprinted on the diffracted electron distribution or on recollision-induced fragments of the molecule. For the observation of dynamics, it is essential that both wavepackets (the probed vibrational and the continuum electron wavepacket) are correlated and one of them can be controlled by the strong laser pulse. The excursion time, namely the time it takes the electronic wavepacket to recollide after ionization, defines the pump-probe equivalent delay. Scanning the wavelength of the driving pulse thus changes the pump-probe delay which is only possible in rather strict and narrow limits. Recently, it was reported that a recolliding electron which originates from one or more electronic states that form the bound state wavepacket, imprints—upon its recombination—specific characteristics about the relative motion of the continuum and bound wavepackets onto the spectrum of the emerging attosecond pulse/high-harmonic spectrum [28]. Finally, the combination of the powerful concepts of correlated measurement and high-harmonic interferometry have recently uncovered signatures of electronic coherence, the relative phase between different channels in strong field ionization, and the resulting dynamics in an ensemble of ionizing CO_2 molecules within a temporal window of ≈ 1 fs following ionization [29]. However, the degree and the persistence of coherence have not been measured and the method is limited to the scrutiny of systems with large (≥ 10 eV) ionization potentials and to processes occurring under strong-field influence.

Even though direct real-time observation of electric motion in the valence shell of atoms or molecules has not been possible before the work presented in this thesis, experiments that demonstrate first steps in electron control have been taken. For example ultrashort light-waveform-controlled laser pulses, comprising only a few optical cycles, as well as polarization and amplitude-shaped light sources, have been proven ideal for accessing and steering the ionization dynamics of atoms [30] and the electronic motion in molecules [31, 32]. Driving electronic motion—which unfolds on an attosecond time scale—with light is a fundamental first step towards the ultimate and systematic coherent electronic control of quantum systems. However, before such control is realized, detailed knowledge of the dynamics that follow excitation, which remain poorly understood due to limited technological capabilities, need to be explored.

Tools capable of granting access to the real-time observation of electronic motion within a control pulse, to study the interaction of the control mechanism, and finally the detection of the unfolding motion after the ultrashort controlled initiation pulse, are needed in order to study and systematically control the fundamental electron dynamics in atomic, molecular and solid state systems.

Development of isolated attosecond light pulses

Advances in laser technology, including the generation of carrier envelope phase (CEP) stabilized pulses, i.e. pulses with field-reproducible waveforms, nowadays nearing a single cycle, enabled the first experiments with attosecond resolution. These advances have led to the generation of single isolated attosecond extreme ultraviolet (XUV) pulses with a duration down to 80 attoseconds (as) [33] and resolution higher than an atomic unit of time. This development has permitted several bench-marking experiments. In its ini-

tial implementations, attosecond streaking spectroscopy has permitted direct access to the vector potential of light fields [34, 35] and the characterization of attosecond XUV pulses [36, 37]. This approach is now known as attosecond streaking spectroscopy and has been implemented for the study of atomic ionization [38] and attosecond spectroscopy in condensed matter [39] which has been investigated and explored theoretically [40, 41], just to name a few of them. Other implementations of attosecond spectroscopy include attosecond pump-probe strategies which have for instance enabled the observation of electron localization following attosecond molecular photoionization [42] and attosecond tunneling spectroscopy, which permitted the real-time observation of electron tunneling [43].

Furthermore, it shall be mentioned that less technologically challenging attosecond experiments can be carried out which utilize trains of attosecond pulses [44, 45, 46]. Those trains of pulses are less flexible for the implementation of two-color pump-probe experiments as it is difficult to disentangle the interaction of individual pulses of the train with the studied system.

Attosecond transient absorption spectroscopy

Over the last few years, an important step in transient absorption spectroscopy has been taken by S. Leone and colleagues. High harmonic pulses generated by multi-cycle laser pulses have been combined with their femtosecond driver pulse to implement femtosecond XUV absorption spectroscopy. Due to the promotion of a core electron to the valence shell by the XUV pulse, XUV absorption spectroscopy offers an impressive sensitivity to processes occurring in the valence shell. However, the temporal resolution offered by femtosecond high-order harmonic transient absorption spectroscopy [23, 24] is insufficient for tracking the attosecond motion of electrons and to resolve sub-cycle dynamics of matter exposed to intense fields in the visible and infrared. Therefore a dramatic extension of this approach is necessary to access these fundamental dynamics.

In this thesis, the potential of combining attosecond resolution with core hole transient absorption spectroscopy is explored experimentally for the first time. We conduct proof-of-concept experiments in which we trace electron and ionization dynamics on a sub-optical cycle time-scale *during* and *after* the quasimonocycle initiation pulse.

- In this work, I present the first experiments in which—in contrast to any demonstration so far—an isolated attosecond extreme ultraviolet pulse is employed as a probe. With such a well confined probe I have been able to acquire snapshots of unfolding ionization dynamics by tracing the ionization of an atom, being triggered by a quasimonocycle pulse, in real time. The non-invasive XUV attosecond probe pulse is transmitted through a medium and records electron dynamics which manifest themselves as modulations on the XUV spectrum as a function of its delay with respect to the laser field.
- Due to the spectral breadth of the attosecond pulse, which spans more than 30 eV, the formation and evolution of dynamics in *several* charge states of the formed ions

can be time resolved. In our experiments, the formation of singly, doubly and triply charged krypton ions within the laser pulse as a function of time has been recorded. This comprises the first time resolved observation of the non-simultaneous formation of different charge states, a fact which was up to now only phenomenologically inferred from time integrated observations. In addition, attosecond transient absorption spectroscopy enabled the temporally resolved detection of saturation in ionization for the singly charged krypton ions at higher intensities. This will allow for the identification of contributing and dominant ionization mechanisms of strong-field ionization of matter, since ionization can now be traced with sub-cycle precision inside the laser pulse. An attempt is made to establish a link between the strength of absorption lines with underlying populations, which is a non-trivial relation in the presence of a strong laser field, intense enough to ionize noble gas atoms.

- Due to their ultrashort nature, the few-cycle laser pulses confine ionization of matter to less than ~ 3.4 fs which, by itself, exclusively enables the efficient superposition of electronic states and the onset of ultrafast wavepacket motion—for example, in ions which evolve for tens of femtosecond after the laser pulse. Furthermore, attosecond transient absorption spectroscopy allowed me to directly trace for the first time valence electron motion (spin-orbit wavepacket dynamics) in real-time, for instance in strong-field singly ionized krypton ions. Careful modeling has enabled the complete reconstruction of the quantum mechanical valence electron motion in Kr^+ ions and to determine its degree of coherence (purity of the quantum wavepacket superposition) in the specimen of the ensemble, which is by itself not accessible by time integrated spectroscopy. Finally, the periodically-varying hole density distribution of the valence shell, with a period of 6.2 fs, can be visualized as a function of time.
- Apart from this simplest prototypical opened system, attosecond transient absorption spectroscopy was furthermore applied to study atomic electron dynamics at the valence shell of more complex systems. In the doubly charged krypton ion, even faster quantum beats were triggered and traced. Due to the confinement of double ionization to a time window shorter than the pulse length (~ 3.4 fs), these quantum beats could be triggered coherently despite the fact that their period is short compared to the pulse duration of the pulses used. Enabled by the state resolved character of transient absorption spectroscopy, their analysis indicates that the strong-field generated population of Kr^{2+} states deviates from those expected by adiabatic tunneling. Multiple quantum beats in different charge states of xenon up to Xe^{3+} and concomitant excited states were configuration-resolved observed which manifest complex multi-electron dynamics. Both experiments promise to shed light on hole-hole and multi-hole correlations in atoms whose theoretical ab-initio modeling is not yet within reach.

The structure of the thesis is arranged as follows: After a short introduction on atomic ionization by intense laser fields, where single and double ionization as well as the generation of high order harmonic generation is introduced in chapter 1, the generation and

metrology of isolated attosecond pulses is described in chapter 2. It includes the basic concepts of the few-cycle phase-stabilized laser frontend. Chapter 3 is devoted to the description of the ultra high vacuum attosecond pump-probe experimental end station. The combination of attosecond technology and XUV transient absorption spectroscopy is then applied in several aspects to atomic systems. The experiments performed in the frame of this work can be separated into two main categories. The first set of experiments focuses on the pump-probe delay regime, where there is no temporal overlap between pump and probe pulse, saying that XUV absorption happens in the absence of strong field influence (chapter 5). In the introduction of this chapter, I also give a general overview of the current theoretical understanding of attosecond transient absorption, which, though it can be found in the literature, facilitates a comprehensive description of the experiments. The second category of experiments is reported in chapter 6, where the pump and probe pulses overlap in time. The ongoing next developments and potential prospects of attosecond transient absorption spectroscopy will be laid out in chapter 7.

List of publications in the context of the work presented in this thesis

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Oral conference contributions of the author

- [C1] A. Wirth et al., 'Sub-optical-cycle waveform light synthesis: Steering and tracing ionization and electron dynamics in real-time', LPHYS'11, July 2011, Sarajevo, Bosnia and Herzegovina (**Invited**)
- [C2] A. Wirth et al., 'Attosecond transient absorption spectroscopy for real-time observation of valence electron motion', ULTRAFast PHENOMENA XVII, July 2010, Snowmass Village, CA, USA (**Highest-ranked contribution**)
- [C3] A. Wirth et al., 'Attosecond transient absorption spectroscopy', ATTOFEL Network Meeting, May 2010, Lund, Sweden
- [C4] A. Wirth et al., 'Attosecond transient absorption spectroscopy', DPG Spring Meeting, March 2010, Hannover, Germany

Chapter 1

Ionization of atoms in intense laser fields: Fundamentals

Enabled by the development of ultra short pulse lasers which permitted for the first time the creation of electric field strengths comparable to the fields which bind electrons inside atoms, many new phenomena have been observed and explored. Modern ultra short pulse laser systems deliver routinely pulses as short as a few femtoseconds (fs) (10^{-15} s) and peak powers in the terrawatt (10^{12} Watt) regime. Advancement of these laser systems has led to the generation of laser pulses in the (near) infrared range which only last a few cycles of the optical field oscillations, yielding pulse durations as short as ~ 4 fs (section 2.2). For controlling further atomic processes, the sweep of the carrier frequency (chirp) and the timing between the maximum of the envelope of the pulse with the electric field oscillation, expressed as a phase related to the central laser period and named carrier envelope phase (CEP) are of enormous importance and can be well characterized and controlled as described in section 2.4.

Based on the interaction of ultrashort pulses with matter, even shorter laser pulses, only lasting several tenth of attoseconds (as) (10^{-18} s) centered in the extreme ultraviolet (XUV) spectral range can be generated. Even though their generation mechanism differs fundamentally from the one of a conventional laser that creates radiation by electronic energy decay inside a laser cavity, all laser relevant properties like temporal and spatial confinement, coherence and propagation are maintained. Both femtosecond and attosecond laser pulses are further utilized within the context of this work in a pump-probe setup to study ultrafast dynamics in atomic light-matter interaction which are triggered by the few-cycle laser pulse and are being observed by the attosecond pulse. Since not only the generation of attosecond laser pulses but also the reported observations of ion formation and their electronic dynamics rely on high-intensity light-matter interactions, the following chapter provides a brief overview of high-intensity light-matter interactions, confined to the experimentally relevant laser intensities ($10^{12} - 10^{15}$ W/cm²).

1.1 The Keldysh parameter: Classification of different ionization regimes

Depending on the atom or molecule, laser pulses in the near infrared or in the visible spectral range start ionizing at around 10^{12} W/cm². The mechanism of ionization depends on the intensity of the laser pulse and the ionization potential I_p of the atomic system. The different regimes with their diverse mechanisms of ionization were first characterized by Keldysh in 1964 [47] by defining an adiabaticity parameter which is also known as Keldysh parameter γ :

$$\gamma = \frac{\omega_L \sqrt{2m_e I_p}}{eE_0} = \sqrt{\frac{I_p}{2U_p}}. \quad (1.1)$$

Here the laser electric field is described as $E(t) = E_0 \cos(\omega_L t)$, e denotes the electron's charge and m_e the mass of the electron. The adiabaticity parameter is the ratio between the estimated tunneling time of an electron through a potential well, referenced to the laser period. The deeper meaning of the Keldysh parameter will become apparent in paragraph 1.3 where the concept of electronic tunneling is introduced. Alternatively the Keldysh parameter can also be expressed by introducing the ponderomotive energy U_p which is the cycle-averaged kinetic energy of an electron in a laser field, being put in relation to the ionization potential of the ionization medium. The ponderomotive energy of a free electron in a laser pulse at an intensity $4 \cdot 10^{14}$ W/cm² centered at a wavelength of 750 nm yields according to the equation $U_p[\text{eV}] = 9.3 \cdot I[10^{14} \text{W/cm}^2] \lambda^2[\mu\text{m}]$ [48] around 21 eV.

For $\gamma \gg 1$ or $E_0 \ll E_{atom}$ where E_{atom} is the electric field inside the atom which is for hydrogen of the order of 10^9 V/cm, the tunneling time is substantially longer than the laser period which shows that ionization is a multi-photon process [47]. The multi-photon ionization (MPI) as being the limit for large γ values, can be accurately described by n -th order perturbation theory as needed to describe an n -photon process [47]. For $\gamma \ll 1$, that is when $E_0 \leq E_{atom}$, tunnel ionization of atomic states dominates the ionization process. Both processes are outlined in the next paragraphs.

1.2 Multi-photon and above threshold ionization

Multi-photon ionization occurs in a strong laser field when the energy of a photon $h\nu$ is not sufficient to overcome the binding energy of the valence electron and γ is substantially larger than 1. The valence electron is excited from the bound state into the continuum by absorbing many photons as schematically depicted by black arrows in Fig. 1.1. This nonlinear response can be described with a n -photon ionization rate Γ_n and can be written as:

$$\Gamma_n = \sigma_n \cdot I^n$$

where σ_n is the n -photon ionization cross-section and I the laser intensity [48].

For higher intensities where E_0 approaches E_{atom} but is still well below the atomic Coulomb

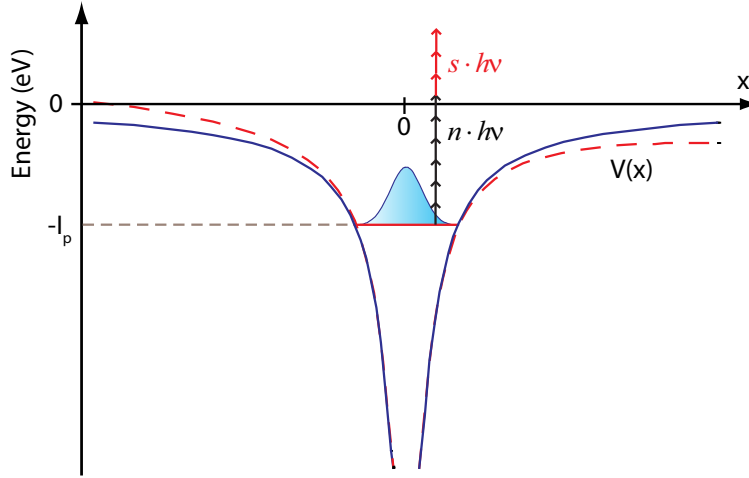


Figure 1.1: Multi-photon ionization by absorption of n photons of energy $h\nu$ and above threshold ionization by absorbing s excess photons. $V(x)$ shows the atomic potential without external field (blue line) and including the laser field (dashed red curve).

field strength, MPI cannot be treated anymore by perturbation theory. The non-perturbative signatures of MPI particularly manifest itself in non-perturbative effects of the above threshold ionization (ATI) [48, 49]. Here, the bound electron absorbs more photons than the minimum required number. The electron which is still influenced by the Coulomb potential can absorb additional excess photons (depicted as red arrows). It is shown in [48] that the ATI-rate originating from the absorption of $n + s$ photons can be expressed as:

$$\Gamma_{n+s} \propto I^{n+s}.$$

The kinetic energy spectrum of ATI photoelectrons exhibits a strong structure consisting mainly of a series of peaks spaced by the photon energy $h\nu$ [49, 50]. ATI effects can be found at intensities where ionization is still well described by perturbation theory and at higher intensities where perturbative descriptions fail. The non-perturbative characteristic of above threshold ionization manifests itself as the disappearance of many expected photoelectron peaks at low kinetic energies in the photoelectron spectrum at high laser intensities. Higher-order processes responsible for the ATI spectrum have gained in weight with respect to lower order ATI peaks [48].

Another approach of understanding the absorption of several additional photons can be obtained by considerations conducted in the time domain. Strong-field ionization launches outgoing photoelectron wavepackets twice per optical period into opposite directions. If the photoelectrons are detected with an electron spectrometer which of course can only detect electrons being emitted along the direction of the detector, the measurement of the wavepacket happens once every laser cycle. Upon interference of the outgoing photoelectron wavepackets, the measured spectra will show peaks separated by the energy $h\nu$ of one photon of the central laser frequency ν [51]. Herein it is even numerically confirmed that

the modulation depth of the ATI peaks is reduced for decreasing laser pulse durations. For laser pulses only consisting of one single-ionization event, the ATI modulation vanishes completely.

1.3 Adiabatic tunnel and barrier suppression ionization

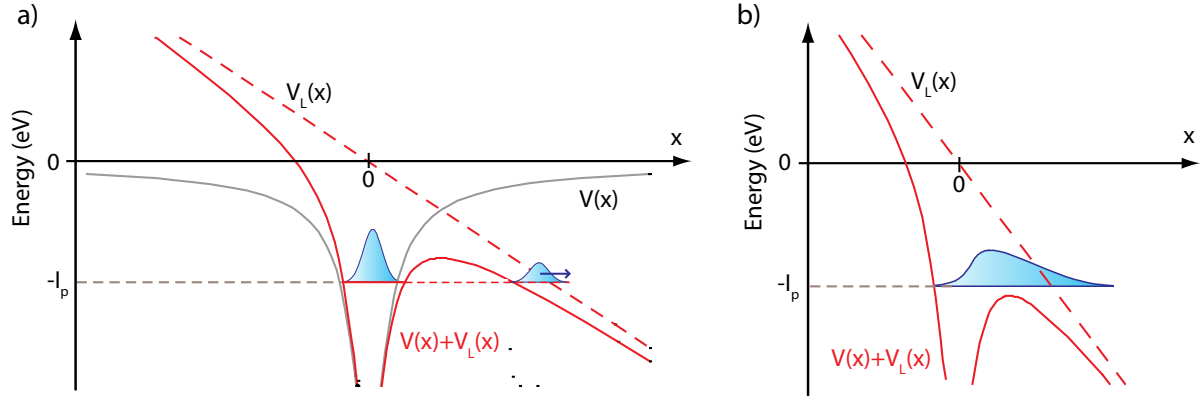


Figure 1.2: Schematic diagram of strong-field photoionization for $\gamma \ll 1$ illustrating tunnel ionization **a)** and Barrier suppression ionization **b)**.

Keldysh realized that strong enough fields $E_0 \lesssim E_{atom}$ distort the atomic Coulomb potential $V(x)$ such that it forms a potential barrier which alternating with the laser frequency is formed on opposite sides of the atom as indicated in Fig. 1.2 a). Now, the electron can tunnel with a non-negligible probability through the potential barrier. This picture applies only if the oscillation period of the external laser field is substantially longer than it takes the wavepacket to tunnel through the barrier (quasi stationary approximation) which is in agreement with $\gamma \ll 1$ (Eq. 1.1).

The cycle averaged ionization rate for tunnel ionization was worked out first by Keldysh [52, 47] and further developed for instance by Perelomov, Popov and Terent'ev [53] (PPT-Model) and Ammosov, Delone and Krainov ('ADK-Theory')[54, 47]. For short and very intense laser pulses fulfilling $\gamma \ll 1$ the ionization rate Γ can be expressed as:

$$\Gamma = N \cdot \exp\left(-\frac{4\sqrt{2m_e}I_p^{3/2}}{3\hbar eE_0}\right), \quad (1.2)$$

where N is a slowly varying function that depends on the cycle averaged field intensity, the ionization potential I_p and quantum numbers describing the wave function from which

ionization is taking place [47, 55]. This analytical expression describes the tunneling rate in a DC electric field with amplitude E_0 in good approximation. In the quasistatic approximation these rates can be applied to oscillating electric fields if the tunneling time is less than the oscillation period ($\gamma \leq 1/2$). It became common to describe the tunnel ionization by using the 'ADK-Theory' and involving the cycle-averaged field intensity instead of the DC field amplitude or even the instantaneous field intensity $E_0 \rightarrow |E(t)|$ [56] where the latter accounts for phase effects of the ionization rate. As expected, the ionization rate strongly peaks at intensity crests confining ionization to a temporally very narrow window around the intensity peaks of the field oscillations.

As the most extreme case of ionization, the regime of barrier suppression ionization (BSI) (or 'over-the-barrier ionization') shall be mentioned for completeness, too. Here the laser electric field exceeds the one of the atomic system and hence the tunnel barrier is reduced down to the point where the ground state is no longer bound and the initial wavepacket is free to escape from the Coulomb atomic potential as sketched in Fig. 1.2 b) [48]. The field which is necessary to trigger the barrier suppression ionization can be expressed as the critical intensity:

$$I_{\text{BSI}}[\text{W}/\text{cm}^2] = 4 \cdot 10^9 (I_p[\text{eV}])^4 Z^2.$$

Here Z denotes the charge state of the atom or ion (for ionization of neutral atoms Z equals one). As an example, an onset of BSI is expected according to the approximative equation for neutral krypton atoms to happen at intensities exceeding $1.3 \cdot 10^{14} \text{ W}/\text{cm}^2$.

1.4 Nonadiabatic tunneling

To describe the formation of ion population as a function of time during a few-cycle NIR laser pulse, the ADK description of the ionization rate is strictly speaking not applicable, since the envelope changes substantially on a sub-cycle timescale and the adiabaticity parameter changes within the pulse. For few-cycle laser pulses of a duration of 4 fs which were utilized for the measurements reported in this dissertation, the Keldysh parameter amounts to ≈ 0.6 for the ionization of krypton at an intensity of $4 \cdot 10^{14} \frac{\text{W}}{\text{cm}^2}$. The intermediate range, where γ is on the order of unity, the assumptions made for deriving the Keldysh-like ionization rate (Eq. 1.2) is not anymore adequate but still being used extensively in nowadays publications, mainly out of computational convenience since simple closed-form analytical expressions for the instantaneous ionization rates of $\gamma \sim 1$ are absent [55].

Yudin and Ivanov have derived a simple expression for the sub-cycle ionization rate in the intermediate γ range for an electric field $E(t) = \mathcal{E}f(t)\cos(\omega_L t + \varphi_0)$ where \mathcal{E} denotes the amplitude, $f(t)$ the envelope function peaked at $t = 0$, $f(0) = 1$ and φ_0 the carrier envelope phase. The time-dependent ionization rate in atomic units can be expressed as:

$$\Gamma(t) = \tilde{N}(t) \cdot \exp \left(-\frac{\mathcal{E}^2 f(t)^2}{\omega_L^3} \Phi(\gamma(t), \theta(t)) \right). \quad (1.3)$$

The adiabaticity parameter $\gamma(t)$ is a function of the envelope $f(t)$ and the function $\theta(t) = \omega_L t + \varphi_0 - \pi k$ where k is an integer chosen such to ensure $-\pi/2 \leq \theta(t) \leq \pi/2$. In view

of the scope of this work it is refrained from showing the complete analytical expressions for $\tilde{N}(t)$ and $\Phi(t)$ since it is reported in detail in [55], but it should be mentioned that the complete phase dependence $\theta(t)$ is contained in the function $\Phi(t)$.

The obtained analytical expression infers - as expected - that for $\gamma \gg 1$ the ionization rate does not depend on $\theta(t)$ whereas a clear phase dependence is reproduced with the analytical expression for $\gamma \ll 1$. In the intermediate regime, tunneling still dominates but multi-photon effects are not negligible and lead to a softening of the temporal ionization window at intensity crests. The Yudin and Ivanov approximation agrees well with a Schrödinger-equation analysis of ionization [56]. To our knowledge, the Yudin Ivanov expression can be seen as being currently the most appropriate analytical expression describing the ionization rate inside a few-cycle laser pulse in the most common intensity regime of nowadays few-cycle laser pulses where γ varies between unity and substantially smaller values. The difference between the Yudin Ivanov approach and instantaneous ADK equation for $\gamma \sim 0.5$ is small as it is compared in [56], however for larger Keldysh parameters the difference significantly increases.

1.5 High-harmonic generation: bursts of coherent XUV light pulses

High-harmonic generation (HHG) is a process where optical light of a certain frequency is frequency converted by a highly nonlinear process which involves in the first place the tunnel ionization of gas atoms. Low-order nonlinear frequency conversion processes (for instance wave-mixing) already take place at sufficiently low laser intensities and do not require ionization of the medium. The interaction in this perturbative regime can be described by a nonlinear optical susceptibility $\chi^{(q)}$ of the order q . The efficiency of perturbative processes is expected to drop rapidly for higher orders [58]. By focusing laser pulses of central frequency ω_L to reach intensities of $10^{14} - 10^{16} \frac{\text{W}}{\text{cm}^2}$ in gases, the relative intensity of individual harmonics of the high-harmonic generation can be described by the simplified schematic spectrum shown in Fig. 1.3a). It is composed of three main parts: low-order harmonics in the perturbative regime can be described by the nonlinear dipole response of the gas medium. The so called plateau-harmonics have all similar efficiency and the cutoff range contains the highest harmonics which are generated.

Most of the features of HHG can be understood by the so called three-step-model which was proposed by Corkum [59]. A linearly polarized laser field ionizes the atom via tunneling through the atomic potential barrier. Once the photoelectron is set free, it is accelerated by the laser field away from the parent ion and is driven backward when the field reverses its direction in the next quarter of the cycle. When the electron returns to the parent ion, there are many possibilities for the interaction with the atomic core, which give rise to subfemtosecond phenomena [57]. The responsible process for HHG is the recombination of the electron with its parent ion which leads to the release of an energetic photon. The whole sequence of tunnel ionization, recollision and emission of a high energy photon hap-

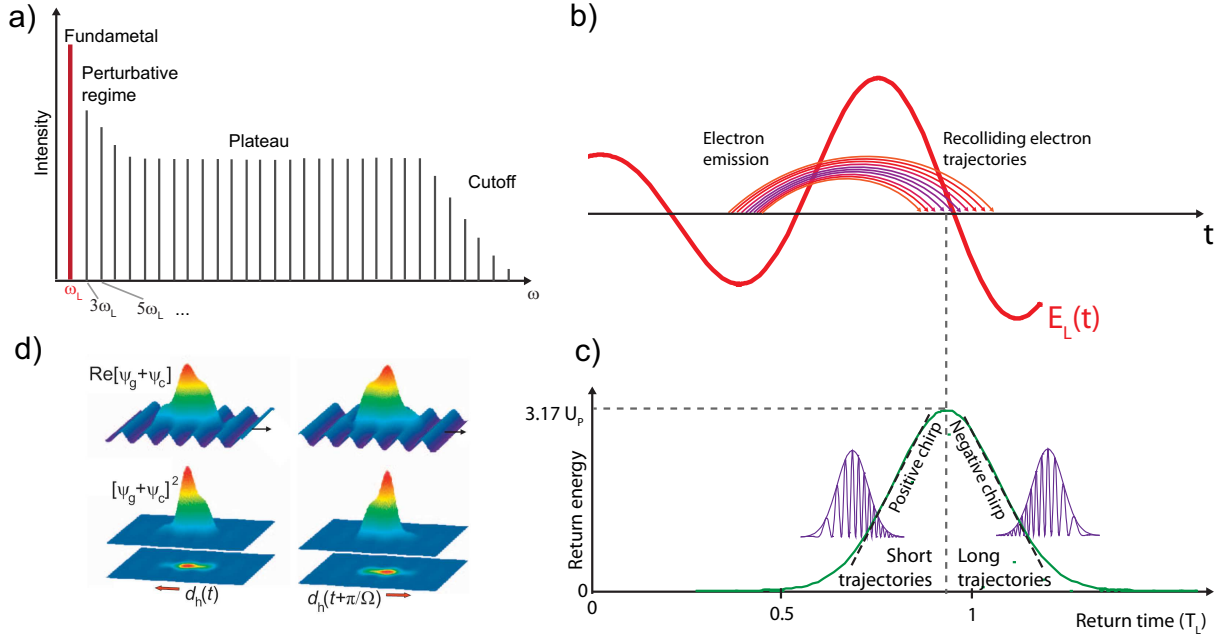


Figure 1.3: **a)** Schematic high-harmonic spectrum with sub-division into perturbative regime, plateau region and the cut-off range which contains the highest photon energy. For an isolated recombination cycle of ionized, accelerated and recombining electrons, trajectories for different times of birth are visualized. The vertical coordinate displays the distance from the parent ion versus the return time in laser cycles T_L . Energy of the returning electrons for different trajectories and their individual return times **c)**. **d)** Quantum mechanical origin of high-order harmonic generation. A spatially and temporally rapidly varying electron density is created by the interference of the returning continuum part of the electron wave function ψ_c with its bound part ψ_g shown for the two reversal points (illustration taken from [57]).

pens once each optical period. But since the emission of photons takes place near every zero-crossing of the electric field, the HHG spectrum of gas harmonics consists of odd harmonics of the fundamental frequency. An isolated recombination event would result in a broad, structureless spectral continuum with no harmonic modulation.

The recombination of the electron with its parent ion can lead to the generation of extreme ultraviolet (XUV) photons. Since the recombination event has a low cross-section, efficiencies of the order of 10^{-6} keep the production yield of XUV photons low. The maximum emitted photon energy $E_{\text{cut-off}}$ would be on first sight the sum consisting of the kinetic return energy of the electron which is intuitively related to the ponderomotive potential U_P and the ionization potential I_P of the gas atom when the electron returns to the ground state of the atom. However, detailed analysis of the electron trajectories for linear polarized laser fields yields a maximum return energy of $3.17 \cdot U_P$ [59]. Figs. 1.3b) and c) illustrate the dependence of the return energy on the electron trajectory. Depending on

the moment of ionization, the electrons encounter the core at different times with different energies. Panel c) shows the corresponding return energy as a function of return time. A detailed analysis gives that electrons have the highest return energy when they are ionized not at the field crest, but rather at a phase $\omega_L \cdot t = 17^\circ$ after the tunnel maximum [59]. Finally, the trajectory with the highest return energy defines the cut-off energy which can be expressed as

$$E_{\text{cut-off}} = 3.17 U_P + I_P. \quad (1.4)$$

Driven by few-cycle laser fields, valence electrons in neon or helium will stay in the ground state up to several times 10^{15} W/cm^2 . Here the emitted photons can reach energies of thousands of electron volts (eV) [57].

Fig. 1.3c) furthermore indicates that recolliding electron trajectories with return times smaller than the excursion time of the trajectory which provides the highest return energy, are called short and the others long trajectories. There is one trajectory in every set along which the electron has acquired the same energy at the time of recombination. XUV bursts being dominated by short (long) trajectories carry positive (negative) chirp¹ [60]. As a consequence, by filtering out the most energetic recombination event, the XUV burst would inherit the least amount of chirp.

The quantum mechanical description of high-order harmonic generation treats the wave function of the photoelectron as being composed of a contribution ψ_g which remains bound and a continuum part ψ_c . When the recolliding photoelectron arrives at its parent ion, the unbound part of its wave function with its fast oscillating phase can interfere with its bound part. This interference leads to a fast oscillation of the electron density and hence results in the harmonic emission. Fig. 1.3d) (taken from [57]) visualizes theoretically the real part of the electron wave function and its concomitant electron density for two adjacent moments in time.

1.6 Double ionization

The formation of doubly charged ions with laser ionization ranges back to the end of the 1970s. Laser pulses with picosecond durations were used to create doubly charged ions via multi-photon ionization [63, 64, 61]. The intensity which is necessary to trigger multiple ionization by absorbing several photons amounts to $> 10^{13} \frac{\text{W}}{\text{cm}^2}$. One of the pioneering experimental results are shown in Fig. 1.4a) (taken from [61]). These findings still inspire experimental and theoretical physicists up to now. The number of detected ions in Xe, created with 50 ps laser pulses at 532.2 nm are shown in a double-logarithmic plot as a function of the intensity. For Xe^{2+} , the indicated slope of 6 ± 0.5 for the variation of Xe^{2+} ions as a function of the intensity corresponds to a 6 photon absorption leading from the ground state of xenon to Xe^{2+} as indicated in Fig. 1.4b). The saturation intensity I_S ,

¹The term positive (negative) linear chirp describes a linear increase (decrease) of the instantaneous frequency along the light pulse from its leading tail to its trailing side.

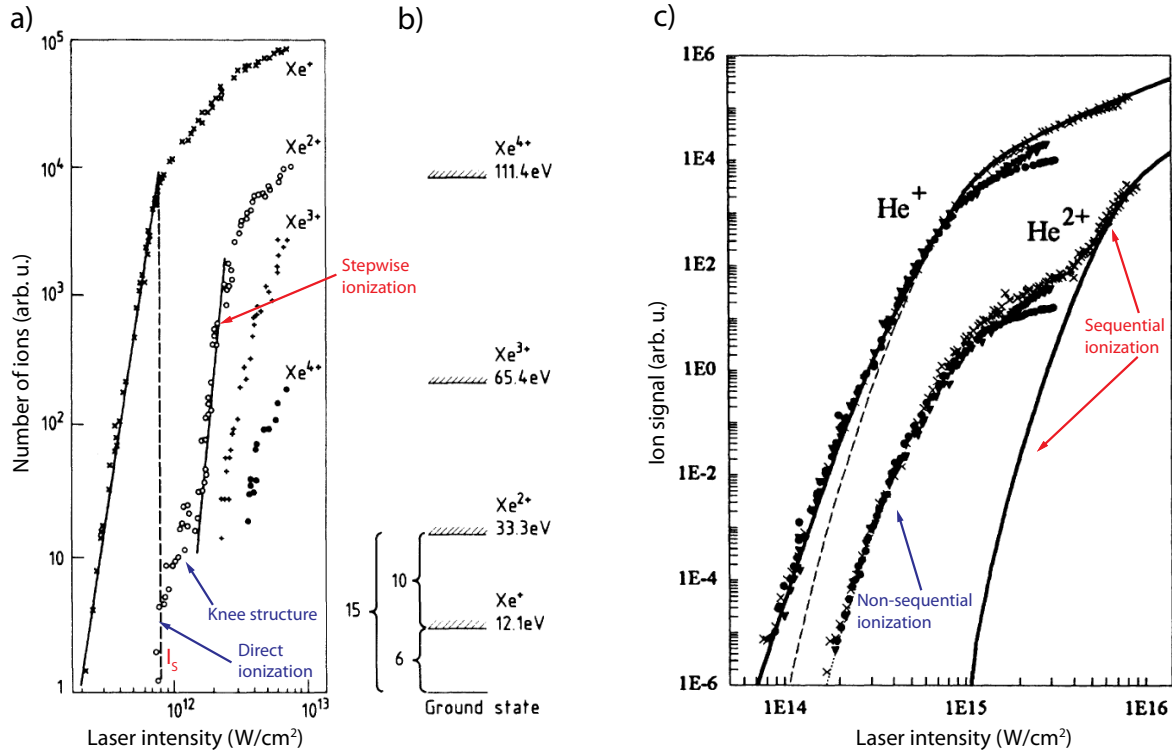


Figure 1.4: **a)** Number of xenon ions formed as a function of laser intensity with pulses of 50 ps and 532.2 nm central wavelength reported in [61]. Already at saturation intensity I_S of the Xe^+ yield, a substantial amount of doubly charged ions is detected. The process of double-ionization has apparently two contributions which result in the so called 'knee-structure' at their crossover from direct 15 photon absorption to a stepwise (sequential) process involving 6+10 photons **b)** [61]. Even though the processes leading to double-ionization are different for ultrashort laser pulses with durations in the femtosecond regime, contributions from non-sequential process dominate the double ionization in the range of the saturation intensity of the single ionization. Ion yield for ionization of helium with 100 fs pulses at 780 nm from [62] precisely indicate the pronounced appearance of the knee-like structure in double ionization even for shorter laser pulses (see text for details and possible non-sequential ionization processes).

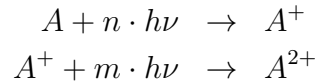
marked as a vertical dashed line, is a typical effect in multiphoton ionization experiments when the ionization probability approaches unity indicating that almost all atoms in the ionization volume are ionized. With increasing intensity the law of variation changes to something less steep since with increasing intensity the ionization volume expands. Looking at the ion yield of Xe^{2+} shows that a so called 'knee-structure' is obtained. Below the saturation intensity of Xe^{2+} , two different processes were suggested and theoretically implemented which lead to doubly charged ions. A direct process in which the Xe^{2+} ions

are formed from neutral atoms by absorption of 15 photons and a stepwise process where first six photons are absorbed for the generation of Xe^+ and afterwards another 10 to create Xe^{2+} (see Fig. 1.4b). The sudden increase of the yield of doubly charged ions right after the knee structure is explained by the stepwise process whereas the direct double ionization process dominates at intensities below I_S [61].

Similar 'knee-structures' for doubly charged ions and higher charged states were also observed with ultrashort laser pulses with durations in the femtosecond regime. Fig. 1.4c) ([62]) shows a high resolution measurement on the single and double ionization of helium with NIR laser pulses and pulse durations of 100 fs. The solid curves show the modeling based on the single active electron approach (SAE) (see next paragraph for details) and for the generation of He^{2+} the extended stepwise yield. Also in these experiments the yield of doubly charged ions below $1 \cdot 10^{15} \frac{W}{cm^2}$ are several orders of magnitude higher than expected from stepwise calculations [65].

1.6.1 Sequential ionization

The number of singly charged ions versus laser intensity and the double ionization yields for laser intensities larger than the appearance of the knee structure are well described by assuming ionization processes which are based on the so called single active electron (SAE) approximation [62, 66, 67]. Within this approximation, the ionization dynamics are dominated by single-electron excitations which lead to sequential (stepwise) production of ionic charge states. Any correlations between electrons in a many-electron atom are only included by the field-free initial state wave function. All other electrons besides the outermost electron, which describes the ionization dynamics, remain in the same state. In general, any sequential process which leads to double ionization can be written for an atom A in the following stepwise way



where n, m are the numbers of absorbed photons. Both emitted electrons tunnel independently from each other at different instances of the laser field. In the simplest approach the double ionization can be calculated as two independent events of single ionization [68]. For example, the 'ADK-formula' (Eq. 1.2) or the nonadiabatic tunneling expression (Eq. 1.3) by Yudin & Ivanov provide estimates for the stepwise ionization rates $\Gamma_{A \rightarrow A^+}$ and $\Gamma_{A^+ \rightarrow A^{2+}}$. Since the 'knee-structure' cannot be explained by any kind of sequential process, it was established in the community to call the ionization process which produces the 'knee-structure' as non-sequential ionization.

1.6.2 Non-sequential ionization

The processes responsible for the experimentally observed enhanced production of doubly charged ions for intensities below the appearance of the knee-like structure are summarized

as non-sequential ionization mechanisms [62]. In the literature several processes which explain the non-sequential double ionization (NSDI) were proposed. All non-sequential processes involve electron correlations. The dynamic of the second electron is influenced by the first electron. Potential processes of non-sequential ionization are:

Shake-off mechanism

The first electron is removed by ionization very quickly ('sudden approximation'). The wave function of the remaining bound electrons relaxes to the new eigenstates of the modified potential. Some of these new states are located in the continuum ('shake-off') or are still bound but excited ('shake-up'), which means that a second electron can be 'shaken off' in the course of the relaxation process [68]. A 'shake-up' electron can be tunnel ionized within the next half-cycle [69, 62]. It becomes the dominant mechanism of double ionization at very high incident photon energies in the keV range [68]. Its importance to non-sequential double ionization by strong-field ionization in the tunneling regime is negligible since the underlying 'sudden approximation' is strictly speaking not fulfilled.

Collective two-electron tunneling

Another possible mechanism for NSDI is the quantum mechanical process in which two electrons tunnel through the potential barrier created by the Coulomb potential and the strong external electric field. This scenario is only possible if the two electrons have the same distance from the nucleus. If not, the delayed electron is recaptured with a high probability [70]. However it was found that this ionization rate on its own cannot explain the high experimentally observed ionization rate. Possibly it is a contributing channel to NSDI but might become dominant for very high field strengths or sub-cycle pulses.

Rescattering mechanism

In experiments where NSDI is observed with ultrashort laser pulses, the importance of tunneling in the non-sequential mechanism is been proven [65]. In the rescattering model, on which also the high-order harmonic generation is based [59], the first electron is tunnel or over the barrier ionized close to an electric field maximum and afterwards accelerated and finally driven back to its parent ion. If the recollision energy is larger than the ionization potential of the singly charged ion, the recolliding electron can directly knock off the second electron (for HHG the recolliding electron recombines). This is known as the recollision-induced direct ionization (RIDI) process. If the return energy of the driven first electron is not sufficient to lead to double ionization, it can collisionally excite a still bound electron to an excited state which then can rapidly field ionize in a so called recollision-induced excitation plus tunneling process (RIET) [62, 71].

In both processes the two electrons in the continuum are correlated with each other and therefore the recollision process is still classified as a non-sequential ionization process. Recollision induced ionization is the dominant process which explains the observed non-sequential doubly charged ion yield which is by orders of magnitude higher than the se-

quential contribution for intensities of 10^{14} to $10^{16} \frac{\text{W}}{\text{cm}^2}$. Recent experiments indicate that the role of the rescattering mechanism for ionization, and any non-sequential ionization is strongly suppressed for intensities between 10^{16} to $10^{18} \frac{\text{W}}{\text{cm}^2}$ [72].

The applicability of the proposed ionization mechanisms and their relative contribution to the final ion yield cannot only be charged upon the integrated measurement of the ion counts after the strong field laser pulse. A technique which measures the momentum of every electron or ion in coincidence, namely measurements addressing electron-electron and electron-ion coincidences which are based on the COLTRIMS (cold target recoil ion momentum spectroscopy) technique have shown to deliver additional insight into the dominant processes responsible for NSDI [65, 73].

The presented attosecond transient absorption spectroscopy in this thesis provides first evidence that it can access ionization dynamics in form of a pure pump-probe experiment in real time and therefore will add the required temporal aspect of the ongoing ionization mechanism. The sub-cycle resolved ionization dynamics, which were up to now only been limited to phenomenological modeling based on a time-integrated detection, might be studied soon for several different atomic systems and parameter regimes very precisely in a time-resolved fashion within the generating laser pulse. First proof-of-principle experiments are reported in chapter 6.

Chapter 2

Generation and metrology of isolated attosecond XUV pulses

2.1 Introduction and requirements

Time-resolved studies of tracking and controlling electron dynamics in the interior of atoms as well as in molecules and solids, require attosecond temporal resolution. Experiments, mainly those which are based on the generation of high-order harmonic radiation are very sensitive to the field waveform rather than the envelope of the driving laser field and therefore have very high demands on the precision, stability and reproducible control of the carrier envelope phase or more generally speaking of the waveform of the laser pulses. With driving pulse durations as short as 1.5 cycles of the carrier field, experiments become even more sensitive to variations of the carrier envelope phase as the interaction is confined to a small fraction of a cycle. Since several highly nonlinear processes are employed to generate isolated attosecond XUV light bursts, the overall generation of those pulses is also very sensitive to intensity fluctuations of the driving laser pulses. Thus, a high degree of shot-to-shot and long term laser pulse stability is essential for the performance of attosecond pump-probe experiments.

This chapter will introduce the state-of-the-art tools for attosecond metrology from the perspective of laser requirements and measurement principles whereas chapter 3 describes in detail the experimental apparatus and implementation of diagnostics specifically tailored for attosecond streaking and for the first attosecond transient absorption experiments reported here.

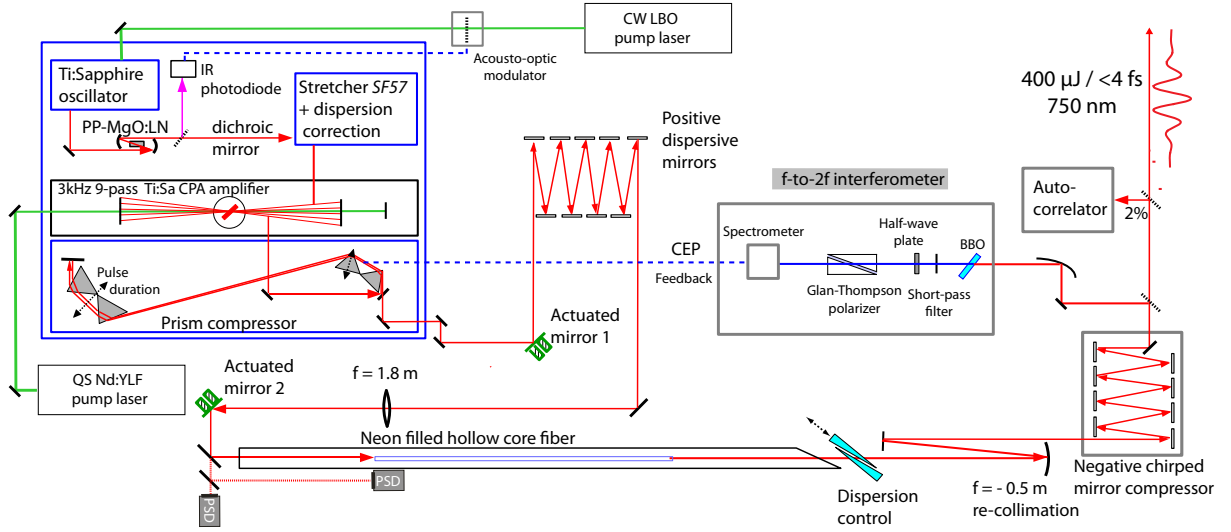


Figure 2.1: Overview of the 3 kHz sub-1.5-cycle laser pulse system for attosecond experiments. It shows the commercially available front end consisting of a Ti:Sa oscillator seeding a 9-pass Ti:Sa amplifier system which was tailored for the special needs of attosecond experiments. Subsequent spectral broadening of the pulses is taking place in a neon filled hollow-core fiber. Pulses are dispersion controlled and compressed by a chirped mirror compressor yielding a pulse duration of sub-4fs laser pulses centered at 750 nm with $330 \mu\text{J}$ pulse energy.

2.2 Phase stabilized, few-cycle laser pulse system

2.2.1 Laser pulse amplification, spectral broadening and compression

Front-end of laser system

To generate the few-cycle NIR driving pulses needed for the generation of single-isolated attosecond pulses, a commercially available chirped-pulse-amplification system (CPA) is used [74] which is modified according to the needs of attosecond experiments as discussed below. An ultra broadband oscillator based on a titanium doped sapphire (Ti:Sa) crystal and pumped by a continuous wave (CW) pump laser, provides the seed pulses for the amplifier system (Fig. 2.1). The oscillator emits pulses of about 6 fs with an output power of 300 mW at 78 MHz [75]. The output of the oscillator is focused into a periodically poled magnesium-oxide-doped lithium niobate (PP-MgO:LN) crystal for further spectral broadening and difference frequency generation which serves as the basis for the CEP stabilization of the oscillator (described in detail in 2.2.2). Before seeding the amplifier (seed pulse energy ~ 1 nJ), the oscillator pulses are dispersively stretched to around 15 ps in a SF57 glass stretcher and higher order chirp is dispersion corrected by chirped mirrors. The

complete train of oscillator pulses is amplified by four passes in the Ti:Sa CPA multi-pass amplifier, pumped by a Q-switched neodymium-doped yttrium lithium fluoride (Nd:YLF) pump laser at 527 nm (~ 20 W), before a Pockels cell reduces the repetition rate to 3 kHz. Another 5 amplification passes through the amplifier crystal raise the pulse energy to 1.3 mJ. Two dielectric filters, installed in the seed beam, modulate the spectrum of the oscillator such that gain narrowing during the amplification process is reduced such that a spectral bandwidth of 64 nm (Fig. 2.2) is maintained after the amplification which is very essential for the next steps where short pulse durations of the amplified pulses is a prerequisite for spectral broadening. The spectral bandwidth supports pulses down to 18 fs pulse duration. Typically pulses with 25 fs have been used here. Subsequent re-compression takes place in a hybrid prism/positive dispersive mirror-compressor. The prism compressor is modified to overcompensate the positive chirp of the amplified pulses to avoid self-phase modulation (SPM) which would narrow and modulate the spectrum and thus hinder the final temporal compression of the pulses. The pulses are compressed by positive-dispersion chirped mirrors yielding sub-25-fs pulses at 850 μJ [76].

Hollow fiber-chirped mirror pulse compressor

The amplified pulses are focused by a thin bi-convex lens ($f = 1.8$ m) into a 1 m long hollow-core fiber (HCF) with an inner diameter of 250 μm which is mounted on a straight rail in a pressure chamber filled with neon at ~ 2.5 bar. The FWHM diameter of the focus is around 230 μm . A 4D beam stabilization system, consisting of two piezo actuated mirrors (actuated mirror 1 and 2 in Fig. 2.1) and two position sensitive detectors (PSD), stabilizes the pointing and steering of the laser beam and therefore ensures a proper coupling into the HCF over several hours. Both entrance and exit windows of the pressure chamber are placed substantially far away from the entrance and end of the HCF to avoid SPM. Non-linear propagation of these pulses in the HCF waveguide results in substantial broadening of their spectrum, primarily due to controlled SPM, self steepening and ionization-induced blue shift [77, 78]. The transmission through the fiber is around 55% yielding a throughput of 450 μJ pulse energy. Dispersion controlled by two fused silica glass wedges, the pulses are compressed by a low-loss chirped mirror compressor optimized for the wavelength range of 500 to 1000 nm to a pulse duration of less than 4 fs [79] what equals less than 1.6 optical cycles in the FWHM pulse width. Their spectral content is displayed in Fig. 2.2. Besides a characterization of the pulses with an autocorrelator or transient grating FROG [80], the pulses were accurately characterized by the attosecond streak camera as exemplarily described in section 2.4. The final pulse energy available for driving high-order harmonic generation amounts to 330 μJ .

2.2.2 Carrier-envelope phase stabilization of laser pulses

For laser pulses that last only a few oscillations of the light field, the actual evolution of the electric field inside the pulse envelope, rather than just the cycle-averaged intensity, becomes relevant to the experiments that include for instance steering the ionization of

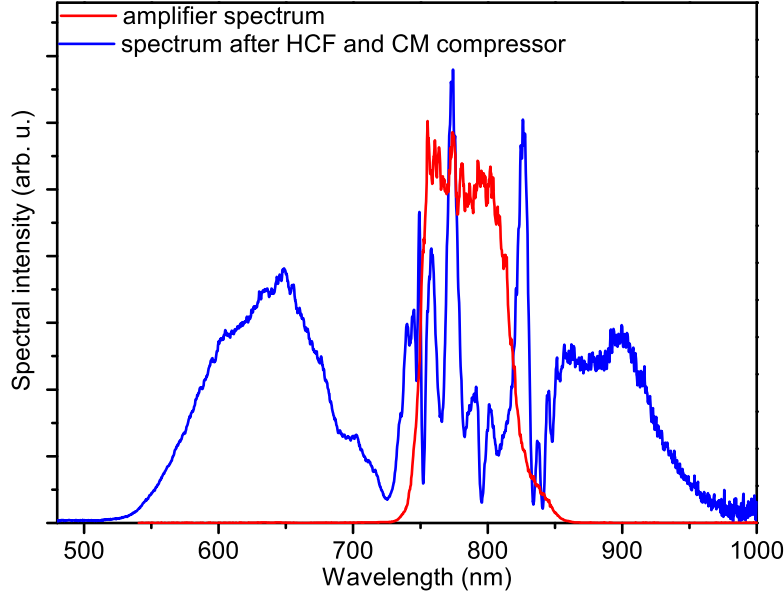


Figure 2.2: Typical laser spectrum after the amplification process and final spectral content of the sub-4fs laser pulses measured after the hollow-core fiber (HCF) and the chirped mirror (CM) compressor.

atoms [30], controlling the electron localization in molecular dissociation [31] and electron dynamics in carbon monoxide [32] as well as steering the near-field enhanced electron acceleration from dielectric nanospheres [81]. Especially for the reliable generation of single isolated attosecond XUV pulses the precise control of the carrier envelope phase is very critical [34, 82, 83, 33]. Thus, the described sub-1.5-optical-cycle pulses delivering laser system has to be carrier phase stabilized such that the electric field of consecutive pulses has the same temporal structure. This requires the carrier envelope phase (CEP) stabilization of the oscillator and of the amplification and pulse broadening process.

Stabilization of laser oscillator: The f-to-zero technique

The electric field of a pulse train can be described as

$$E(t) = \sum_{n=-\infty}^{\infty} A(t - n \nu_R^{-1}) \exp(i\phi_n) + c.c.,$$

where ν_R is the repetition rate of the pulse train and ϕ_n is the CEP of the n th pulse. The function $A(t)$ is the complex electric field amplitude of a single pulse that vanishes for $|t| > \frac{1}{2\nu_R^{-1}}$. It should be noted that the carrier envelope phase ϕ_n has no meaning between individual pulses [84]. The pulse-to-pulse CEP change is described by $\Delta\phi =$

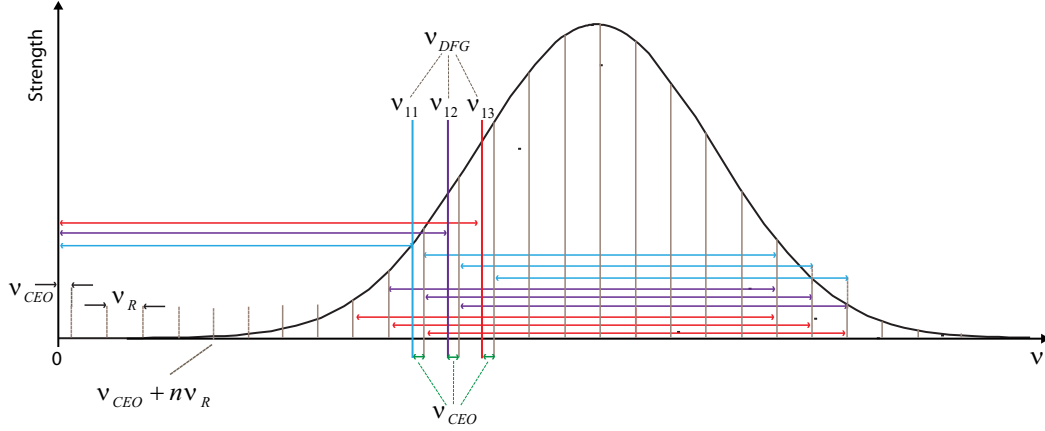


Figure 2.3: F-to-zero measurement scheme used for tracking the offset frequency of the frequency comb. Difference frequency generation between modes from opposite ends of the comb and the subsequent mixing with frequencies from the low-frequency wing of the spectrum result in an interferometric beating at ν_{CEO} .

$\phi_{n+1} - \phi_n = 2\pi \frac{\nu_{CEO}}{\nu_R}$, where ν_{CEO} is the offset frequency of the phase locked comb of laser modes as indicated in Fig. 2.3. For vanishing ν_{CEO} subsequent pulses of the pulse train have an identical carrier-envelope phase. Locking ν_{CEO} for instance to a r th fraction of the repetition rate principally ensures that every r th pulse of the pulse train has the same carrier envelope phase. Picking only those pulses which have the same phase for seeding the amplifier, results in an amplified pulse train whose pulses have the same CEP. In the case of the ultra broadband output of the femtosecond oscillator which ranges from 630 nm to 1015 nm, the so called f-to-zero technique allows access to ν_{CEO} and therefore enables locking the offset frequency of the frequency comb [85]. The output of the laser oscillator is tightly focused into a highly nonlinear periodically poled magnesium-oxide-doped lithium niobate (PP-MgO:LN) crystal which is optimized for type 0 second-harmonic generation (SHG) at 1500 nm. The pulses undergo spectral broadening in form of SPM and difference-frequency generation (DFG). This leads to spectral components of the laser pulses up to 1600 nm. DFG between modes from the high ($\nu_{CEO} + n_{high} \cdot \nu_R$) and low ($\nu_{CEO} + n_{low} \cdot \nu_R$) side of the frequency comb result in DFG frequencies at the long wavelength side of the spectrum according to

$$\nu_{DFG} = (\nu_{CEO} + n_{high} \cdot \nu_R) - (\nu_{CEO} + n_{low} \cdot \nu_R) = (n_{high} - n_{low})\nu_R.$$

Mixing those DFG frequencies spaced by multiple integers of ν_R (schematically shown with blue, violet and red arrows in Fig. 2.2.2), with modes $\nu_{2k} = \nu_{CEO} + k \cdot \nu_R$ from the low-frequency wing as indicated in Fig. 2.3 for which $n_{high} - n_{low} = k$ results in a beat frequency of ν_{CEO} . This beat frequency is imprinted on the pulse train in the spectral range above 1350 nm. A dichroic mirror in combination with a long-pass interference filter isolates the

spectral range of interest and directs the beating signal onto a fast photodiode (Fig. 2.1). Locking electronics in combination with the fast photodiode are used to detect the beat frequency and to generate an error signal proportional to the deviation of ν_{CEO} from the desired value which is set in our case to one fourth of the repetition rate. The derived error signal is used in a closed loop as feedback signal to drive an acousto-optic modulator that is installed in the beam path of the oscillator pump laser and modulates the transmitted pump power (Fig. 2.1). A Pockels cell picks only integer multiples of every fourth pulse of the oscillator output pulse train to ensure amplification of only isolated pulses which should have by definition and in the absence of any thermal/optical fluctuations the same carrier-envelope phase and thus inherit identical waveforms. The stabilization is used to compensate for phase drifts that occur due to instabilities introduced by thermal changes or drifts in the pump laser parameter. Reference [85] provides information about the stability performance of such systems.

Phase stabilization of amplified pulses: The f-to-2f approach

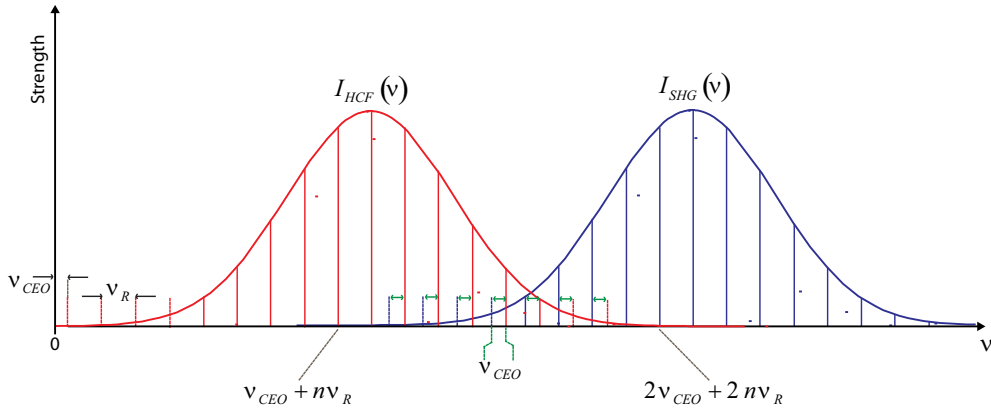


Figure 2.4: F-to-2f measurement scheme used for tracking changes in the carrier envelope phase of amplified pulses. Frequency doubling of the octave-spanning output of the fiber in a BBO crystal and spectral mixing of modes in common area of both pulses leads to the creation of a beat frequency at ν_{CEO} . Analysis of the spectral interferometry between both pulses carries signatures which depend on ν_{CEO} (see Eq. 2.1).

Numerous optical components, an extensive propagation of the pulses through air and SPM in the hollow-core fiber are sources for additional phase noise during and after the amplification process. The slippage of the CEP during propagation has to be tracked and corrected in a second CEP stabilization loop. Making use of the already octave-spanning bandwidth of the spectrum after propagation of the pulses through the HCF, the f-to-2f measurement can be directly implemented. The detection module called f-to-2f interferometer is placed after the HCF and the negative chirped mirror compressor and is seeded with 3% of the pulse energy (Fig. 2.1). The light is focused by a parabolic mirror

into a BBO crystal for second harmonic generation. Since the amplified and broadened pulses cover a spectrum which exceeds one octave, the spectrum of the fundamental pulse $I_{HCF}(\nu)$ overlaps on its high frequency tail with frequencies from the high wavelength side of the frequency doubled spectrum $I_{SHG}(\nu)$ as indicated in Fig. 2.4. A short-pass filter blocks low frequency components and a half-wave plate turns the polarization to be parallel to the blue part of the fundamental spectrum. Beating of the modes $2\nu_{CEO} + 2n_{low} \cdot \nu_R$ with modes $\nu_{CEO} + n_{high} \cdot \nu_R$ gives rise to a beat note at

$$2(\nu_{CEO} + n_{low}\nu_R) - \nu_{CEO} + n_{high}\nu_R = \nu_{CEO}.$$

Additional beat notes arise at $n \cdot \nu_R \pm \nu_{CEO}$ for $n = 1, 2, \dots$ [86]. Experimentally, the signature of the beat frequency is observed in form of an interference pattern in the spectral region where the fundamental and the frequency doubled light overlap. A Glan-Thompson polarizer is used to balance the relative intensity and the interference pattern which carries the information about changes in the carrier envelope phase. The spectral interference is recorded with a fiber spectrometer. Mathematically treated, the spectral interference result $S(\nu)$ between the output of the fiber I_{HCF} and its frequency doubled counterpart I_{SHG} , separated by a time delay τ upon walk-off effects in the BBO and related optics, can be expressed as

$$S(\nu) = (1 - \epsilon)I_{HCF}(\nu) + \epsilon I_{SHG}(\nu) + 2\sqrt{\epsilon(1 - \epsilon)I_{HCF}(\nu)I_{SHG}(\nu)} \cdot \cos(\phi_{SHG}(\nu) - \phi_{HCF}(\nu) + 2\pi\nu\tau + \phi_0) \quad (2.1)$$

where ϵ is the polarizer transmission for the polarization of the SHG light, ϕ_0 the carrier envelope phase and ϕ_{HCF} (ϕ_{SHG}) denotes the spectral phase of the fiber broadened (frequency doubled) pulse [87]. A continuous Fourier analysis of the part of the spectrum containing the interference pattern tracks changes of ϕ_0 . Changes of the spectral phases of the two interfering spectra and especially of the delay between the two interfering pulses can be neglected for an intensity-stable laser system. A standard proportional controller algorithm adjusts the insertion of the prisms in the prism compressor based on the deviation of the fringe phase of the interference pattern from the user defined reference phase (Fig. 2.1). The achieved CEP stability is typically better than 100mrad RMS fluctuations [88].

2.3 Generation of isolated attosecond XUV pulses

As discussed in chapter 1.3 the generation of attosecond light bursts happens every half-cycle of the laser field and leads to the appearance of discrete harmonic spikes in the spectrum of the attosecond pulse train spaced by twice the driving laser frequency corresponding to around 3.1 eV for an 800 nm NIR driving pulse.

In our attosecond experimental setup, single isolated attosecond pulses are generated by making use of the sub-3.6 fs laser pulses in combination with spectral filtering the cut-off range of the HHG. By definition, sub-1.5-cycle pulses arising from the laser setup as

described before lead only to 2-3 major recombination events of the photoelectrons and their parent ion. Fig. 2.5 a,b) show those attosecond light bursts originating from a 3.6 fs driving laser pulse for two different CEP settings in form of schematic visualizations. The sketched height of the violet flashes corresponds to the highest generated photon energy of the recombination event and the area underneath those peaks is a measure of the number of generated XUV photons per recombination event. Their breadth should not be confused with the duration of the emitted pulse. The number of generated photons, namely the amplitude of the launched electron wave packet is defined by the ionization probability at the instance of ionization for the re-combining trajectories. Quantitative ionization probabilities for different laser half-cycles for our laser pulses are presented in [33]. Special ultrathin metal filters, only 100 to 200 nanometer thin, are acting as optical high-pass filters for XUV photons. Commonly used are zirconium, aluminum and palladium (see Fig. A.2 for corresponding filter curves). A combination of the utilized gas for HHG, driving intensity, metal filter and utilized consecutive XUV optics allows the adjustment of the central energy and bandwidth of the attosecond EUV pulse. Thus, the properties of the attosecond light pulse can be specifically modified for individual experimental applications within certain limitations. The inset of Fig. 2.5 a) displays the transmission curve for a 150 nm thin zirconium (Zr) filter which upon interaction with the few XUV bursts spectrally gates only the energetically highest photons which are confined to a single recombination event. The photons transmitted through the filter are the prerequisite for a single isolated attosecond pulse whose spectral content is shaped by the thin metal filter and the reflection properties of subsequent XUV optics which are used to focus and to introduce a delay between the XUV pulse and the driving laser pulse. The panel on the right of Fig. 2.5 a) shows a representative, measured quasi-continuous XUV spectrum. The very minor modulation is originating from a slight leakage of another, energetically lower recombination event of the HHG process. By changing the CEP ϕ_0 from zero to $\frac{\pi}{2}$, two subsequent recombination bursts are generating photons of a similar energy distribution as shown in panel b). But since the amplitude of the launched electron wave packet is weaker for the first of both dominating recombination events, the majority of spectrally gated photons arises from the second pronounced burst of XUV light. Even for this sine-shaped pulse with a duration of sub-4 fs the amount of generated satellite XUV pulse is marginal which can be seen in a light increase of the spectral modulation with respect to the cosine-shaped pulse shown in panel a). For slightly longer pulses, for instance 4.5 fs pulse duration, the CEP had to be kept very close to zero since a sine-shaped electric field right away leads to the emission of two almost identical XUV flashes as indicated in Fig. 2.5 c). In view of the latest achievements of these short driving laser pulses utilizing the described laser system, which actually can deliver after demanding fine tuning pulse durations of 3.3 fs [33], the CEP dictates not anymore the creation of either an isolated attosecond burst or the strong generation of a satellite pulse but rather steers the contrast between the main attosecond pulse and -if applicable at all- the satellite pulse. As shown in panel a) and b), reasonable clean attosecond experiments can be performed at all CEP settings.

Isolated attosecond pulses based on high-order harmonic generation (HHG) have also been generated by different approaches within the scientific community.

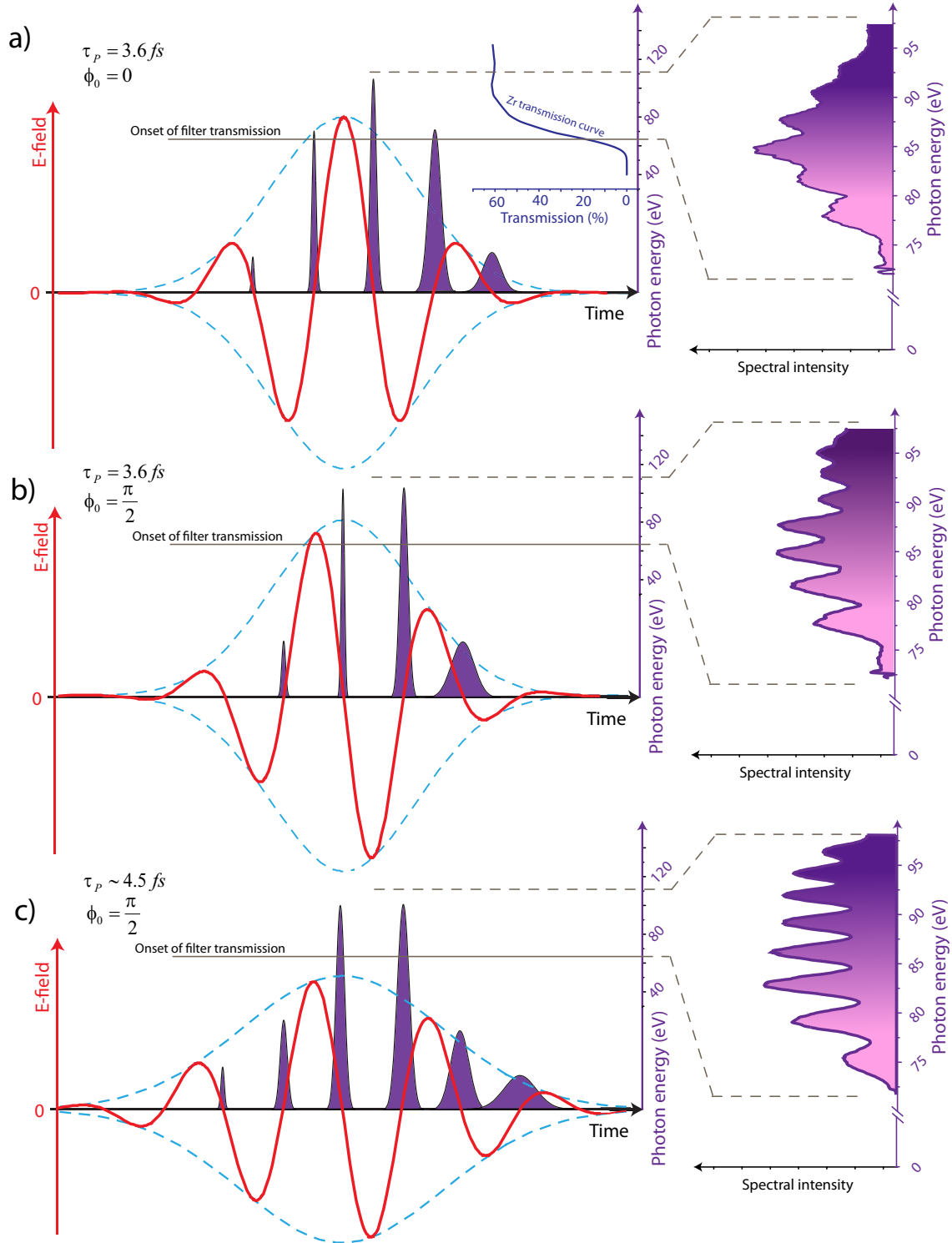


Figure 2.5: Generation of single isolated attosecond light bursts by means of spectral gating. An optical high pass metal filter in combination with a XUV optic spectrally gates only the strongest recombination event for a cosine-shaped ($\phi_0 = 0$) (a) and sine-formed ($\phi_0 = \frac{\pi}{2}$) (b) driving field with a pulse duration of $\tau_p = 3.6 \text{ fs}$. The peaks of the sketched photon bursts (violet) encode the cut-off energy and the enclosed area the number of launched photons. Measured adequate XUV spectra are shown in the graphs on the right hand side. In both cases minor spectral modulations are arising whereas the CEP requirement is less relaxed for slightly longer (4.5 fs, $\phi_0 = \frac{\pi}{2}$) driving pulses (c).

One of those makes use of phase stabilized few-cycle laser pulses in combination with the high sensitivity of high harmonic emission to the ellipticity of the fundamental laser beam. Using birefringent plates [89], few-cycle laser pulses are generated which are only linearly polarized for a narrow time window (the so-called 'polarization-gate'), and elliptically polarized during the other instances of the pulse. Since HHG relies on the recombination of the accelerated electron with its parent ion, any small degree of ellipticity will lead to a strong reduction of the HH yield since the accelerated electron is missing its parent ion and therefore the recombination rate reduces substantially. A disadvantage of the polarization gating approach arises from the situation that this linearly polarized time window is created in fact by delaying two few-cycle laser pulses with perpendicular ellipticity such that the counter-rotating E-vectors of both pulses cancel each other at the temporal overlap of the two pulses [90] which is confined to a fraction of their pulse duration. Since the main pulse has to be split into two pulses, the intensity at the time of the polarization gate is lower than it would have been if the original pulse had been used for HHG and therefore this approach results in a lower cut-off energy or requires higher pulse energies in order to reach the same cut-off energies as in our spectral-selection approach. On the other hand this approach has less stringent requirements on an extreme short and still technologically challenging pulse duration of the driving pulses.

An approach using a generalized polarization-gating method in combination with a two-color driving field relaxes the requirements upon the duration of the driving laser pulse for the generation of single-isolated attosecond laser pulses even further. However the needed interferometric complexity increases again. Utilizing this technique called generalized double optical gating (GDOG), it was shown that multi-optical cycle pulses with durations exceeding 20 fs were able to create isolated XUV flashes centered at 40 eV [91].

A further development which had been recently implemented is based on a combination of CEP stabilized few-optical-cycle pulses, with peak intensities above the saturation intensity of the gas used for HHG and of careful adjustment of the interaction geometry, yielding a substantial increase of the amount of photons per EUV pulse at a central energy of ~ 30 eV [92].

In order to conclude this paragraph it shall be summarized that there are several techniques for generating isolated attosecond light pulses based on gas harmonics. But in order to coherently launch for instance also fastest electron wave-packet motion in atoms and molecules in general, not only an attosecond XUV pulse acting as the probe is necessary but also a very short driving laser pulse is crucial to trigger electron motion on an attosecond time scale with a high degree of fidelity. Experiments presented in this work would not have been able with the reported precision and unambiguousness with longer few-cycle laser pulses as driving laser pulses. Therefore the uniqueness of the sub-1.5-cycle laser pulses in combination with the spectral isolation of attosecond pulses in the spectral cut-off region finally allowed us as the first team to time resolve for instance valence electron motion in ions (chapter 5).

2.4 Attosecond metrology: Characterization of ultrashort laser and XUV pulses

For a complete exploration and interpretation of pump-probe experiments conducted with sub-1.5-cycle NIR and attosecond XUV laser pulses, it is essential to characterize both pulses, not only in terms of pulse duration and intensity, but also with respect to their spectral/temporal phase. Complete description of a laser pulse requires either in the frequency domain the knowledge of

$$\tilde{E}(\omega) = E_A(\omega) \cdot e^{i\phi(\omega)}, \quad (2.2)$$

where $E_A(\omega)$ is the amplitude and $\phi(\omega)$ the spectral phase or in the time domain the determination of the quantity

$$\tilde{E}(t) = E_A(t) \cdot e^{i\phi(t)}, \quad (2.3)$$

where $E_A(t)$ and $\phi(t)$ are the amplitude and temporal phase of the complex electric field in the time domain. $\tilde{E}(t)$ is the Fourier transformation of $\tilde{E}(\omega)$.

In the past years several powerful techniques have been developed to access $\tilde{E}(t)$ or $\tilde{E}(\omega)$ of short optical laser pulses. They can be categorized in two classes. The earlier development was the invention of a spectrally resolved detection of a signal coming from an optically gated autocorrelator. It is known as FROG (Frequency Resolved Optical Gating) [93]. An iterative algorithm retrieves $\tilde{E}(t)$ which gives the best agreement with the measured spectrum as a function of the delay between the two auto-correlated replicas (one acts as a gate in a nonlinear medium) of the original beam. Several related schemes like polarization-gating, three wave mixing (self diffraction), 2nd and 3rd order FROG apparatus have been developed and explored [94].

The spectral phase interferometry for direct electric-field reconstruction (SPIDER) [95] utilizes the interaction of a double pulse in a nonlinear crystal with a stretched pulse. Sum frequency generation (SFG) generates two pulses at twice their fundamental frequency which are slightly shifted in frequency. Recording spectra of the two spectrally interfering pulses allows in combination with an algorithm the determination of the electric field.

But these in principal powerful techniques have also limitations. First, they do not allow the determination of the carrier envelope phase and are not useful for the characterization of few-cycle pulses approaching a duration of 4 fs or less. The latter is due to the fact that nonlinear media do not inherit the capability for a more than octave spanning phase matching condition which would be required to take the full spectral bandwidth of ultrashort laser pulses into account. Second, they are limited to central wavelengths of laser pulses which do not get substantially absorbed in the nonlinear medium and require a pulse intensity which can trigger nonlinear effects herein. Therefore they can not be used for the reliable metrology of attosecond XUV laser pulses and the driving quasi monocycle pulses which are utilized in the presented experiments.

2.4.1 Concept of the attosecond streak camera

The attosecond streak camera proposed in [35] and first realized in [34] is a concept which extrapolates the principle of a classical streak camera into the attosecond time regime which allows for the direct observation of light waveforms of laser pulses. Besides its technologically challenging implementation on its own, it is a powerful tool of modern attosecond pulse metrology which allows direct access to the light waveform $E(t)$ and since it relies on a cross-correlation of the NIR laser pulse with a synchronized attosecond XUV pulse (in fact a photoelectron wavepacket which is a replica of the XUV pulse), a FROG (X-FROG) phase retrieval algorithm enables the determination of the complex electric field of the attosecond laser pulse.

In attosecond streaking experiments neon gas serves as the gating medium between the attosecond XUV pulse and the few-cycle NIR laser pulse. Both beams get spatially and temporally overlapped and focused into a very fine confined stream of neon atoms. Photons of the attosecond XUV pulse centered at 80 eV photoionize 2p valence electrons of neutral neon, leading to unbound electrons with initial kinetic Energy $E(t_0)$ of ~ 60 eV as sketched in Fig. 2.6 a). The synchronized co-propagating NIR laser pulse whose intensity is adjusted such that it can not ionize neon atoms, accelerates or decelerates the free photoelectron wavepacket depending on the instantaneous delay between NIR and XUV pulse. The modified distribution of kinetic energies of the free electron wavepacket is detected with a time-of-flight (TOF) spectrometer, oriented such to be axially aligned with the linear polarization of both laser pulses which inherit the same direction of polarization. While scanning the attosecond XUV pulse through the NIR laser pulse and recording simultaneously the photoelectron distribution, a streaking spectrogram is obtained (Fig. 2.6 b).

2.4.2 Mathematical description of attosecond streaking

The mathematical description of the streaking process will be derived for our experimental parameters and arrangement between laser polarization and detector orientation. Several assumptions have to be made:

- The launched photoelectron wavepacket is a replica of the ionizing attosecond XUV pulse, inferring that the distribution of the photoelectrons carries all the information of the XUV pulse (temporal structure, chirp, etc.). This is fulfilled if photoionization occurs with the same cross-section throughout the entire spectral bandwidth of the XUV pulse and if the corresponding phase of the dipole matrix elements describing the ionization does not vary within the XUV spectrum. In general this requirement is not met by very short XUV pulses, but nevertheless to a good extent in the absence of resonant processes for instance like auto-ionization and Auger effects.
- The photoelectric effect has to be instantaneous.
- Assuming no strong-field induced modifications of the XUV ionization yield.

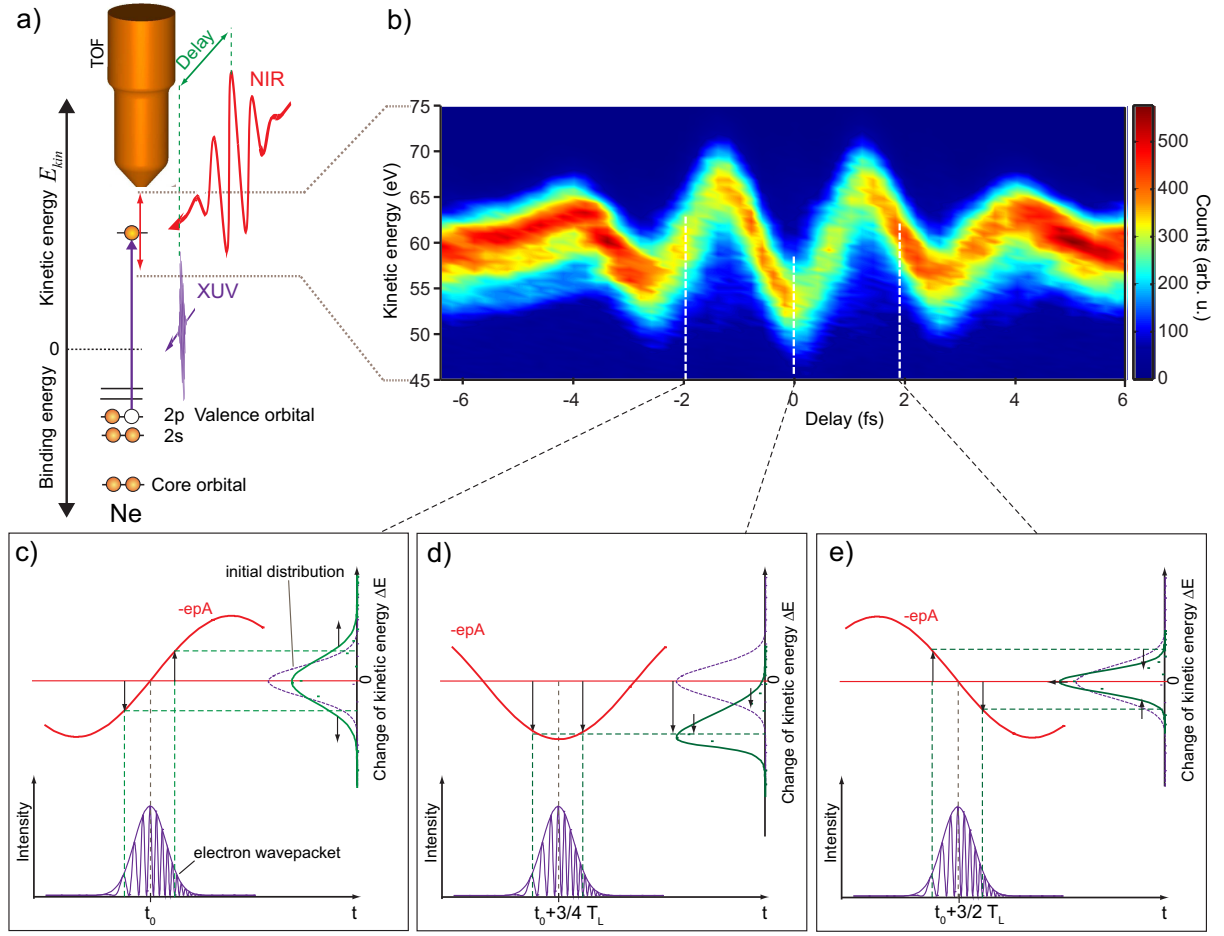


Figure 2.6: Attosecond streak camera. **a)** An XUV pulse photo-ionizes neon atoms and the released photoelectrons are either accelerated or decelerated in the NIR streaking field. A time-of-flight (TOF) spectrometer disperses the photoelectrons. Plotting the electron spectrum as function of the delay results in a streaking spectrogram as shown in **b)**. It shows profound signs of a chirped attosecond XUV pulse which are explained for the most extreme delay-instances in panel **c)** to **e)**. The XUV ionized, free electrons form a bunch with initial momentum distribution displayed as the violet profile. Instance **c)** and **e)** explain the influence of the chirp of the XUV pulse to the resulting final momentum distribution for the two most extreme cases where the electron bunch is being probed by the laser pulse around a zero-crossing of the vector potential. Panel **c)** considers the emission around a laser field oscillation with slope parallel to the chirp, where the term $-epA_L$ (Eq. 2.7) leads to a broadening of the electron momentum distribution which is accompanied by a reduction of the peak of the distribution. The opposite case is depicted in panel **e)**. This is experimentally verified in **b)**. In both cases the center of the distribution is not shifted by the streaking field, whereas the largest collective shift of the electron distribution is observed for local maxima and minima of the vector potential (panel **d)**).

- Both the NIR and XUV laser pulses have the same polarization. Therefore the laser field does not affect the trajectory of the photoelectrons but only their kinetic energy.
- The detection of the photoelectron's momentum change is carried out along the laser polarization axis.

According to Newton's law of motion the acceleration of a free electron with charge $-e$ and mass m_e in an external laser field $E_L(t)$ can be written as

$$\ddot{x}(t) = -\frac{eE_L(t)}{m_e}.$$

Integrating this equation of motion yields

$$\dot{x}(t) - \dot{x}(t_0) = -\frac{e}{m_e} \int_{t_0}^t E_L(t') dt'. \quad (2.4)$$

The velocity of the electron at time t depends on the velocity at time t_0 , which we set as the time instance of ionization, and on the E-field evolution. Since the photoelectron is not able of leaving the area of the focus on the order of the pulse duration of the NIR laser field, the momentum of the electron is modified by the electric field from its instance of ionization to the end of the pulse. Assuming an isolated few-cycle NIR laser pulse with field $E_L(t)$, the final velocity of the photoelectron as detected by the TOF spectrometer can be denoted therefore as $\dot{x}(t = \infty)$. Thus, the definition of the vector potential $A_L(t) = \int_t^\infty E_L(t') dt'$ in the Coulomb gauge can be substituted into Eq. 2.4 and gives for the velocity of the photoelectron after the pulse:

$$\begin{aligned} v(\infty) &= v(t_0) - \frac{e}{m_e} A_L(t_0) \\ \Leftrightarrow p(\infty, t_0) &= p(t_0) - eA_L(t_0) \\ \Leftrightarrow \Delta p(\infty, t_0) &= -eA_L(t_0). \end{aligned} \quad (2.5)$$

The momentum change of a photoelectron Δp released at t_0 is proportional to the vector potential at the time of ionization. The final kinetic energy $E_{kin}(\infty)$ amounts to

$$E_{kin}(\infty, t_0) = \frac{1}{2} m_e \left[\dot{x}(t_0)^2 - \frac{2e}{m_e} A_L(t_0) \dot{x}(t_0) + \left(\frac{e}{m_e} \right)^2 A_L(t_0)^2 \right]. \quad (2.6)$$

In order to meet the requirement that the NIR laser pulse does not lead to ionization of the neon atoms itself, the intensity is kept in the experiments well below $1 \cdot 10^{13} \frac{\text{W}}{\text{cm}^2}$ where the term $(\frac{e}{m_e})^2 A_L(t_0)^2$ can be neglected with respect to $\frac{2e}{m_e} A_L(t_0) \dot{x}(t_0)$. Hence according to Eq. 2.6 the change of the kinetic energy owing to the interaction of the unbound electron with the NIR light results in

$$\begin{aligned} \Delta E_{kin}(\infty, t_0) &\approx -\frac{e}{m_e} A_L(t_0) p(t_0) \\ &\approx -eA_L(t_0) \sqrt{\frac{2}{m_e} (h\nu - I_p)}, \end{aligned} \quad (2.7)$$

where $h\nu$ is the central photon energy of the XUV pulse and I_P the first ionization potential of the atom. A derivation for arbitrary angle of observation is given in [35]. Equation 2.7 shows several important consequences. The streaked electron distribution as given for example in Fig. 2.6 b) is proportional to the vector potential and its streaking amplitude scales linearly with the initial photoelectron momentum and the wavelength of the streaking field since $E_L(t) = -\frac{\partial A_L(t)}{\partial t}$. The latter dependence becomes obvious if the laser field $E_L(t) = E_0(t)\cos(\omega_L t + \phi_0)$ is integrated to calculate the corresponding vector potential. Since the momentum distribution of the XUV pulse and therefore of the photoelectrons is finite, the proper description of the process has to be made by mapping the initial photoelectron distribution $\eta_e(p(t_0), t_0)$ into a final distribution $\sigma(p(\infty, t_0))$ [82] which can be written using Eq. 2.5 as

$$\sigma(p(\infty, t_0)) = \int_{-\infty}^{\infty} \eta_e(p(\infty, t_0) + eA_L(t_0 + t'), (t_0 + t')) dt'.$$

Utilizing Eq. 2.7 in combination with a streaking spectrogram allows direct access to the NIR-electric field if $\Delta E_{kin}(\infty, t_0)$ is extracted for the center of the distribution $\sigma(p(\infty, t_0))$ which is a good approximation for symmetrically shaped momentum distributions as it is the case for our attosecond XUV pulses:

$$E_L(t_0) \approx \frac{\sqrt{m_e}}{e\sqrt{2(h\nu - I_P)}} \cdot \frac{\partial \Delta E_{kin}(t_0)}{\partial t_0}. \quad (2.8)$$

Besides the extractable vector potential which completely describes the NIR laser waveform, the streaking spectrogram is sensitive to a chirp in the XUV pulse. The spectrogram shown in Fig. 2.6 b) comprises 32 individual spectra taken at a delay step size of 200 as. It was measured with a positively chirped XUV pulse. Information about the phase and reflectivity of the utilized XUV optic are given in Fig. A.1. The indications imprinted on the streaking spectrogram are schematically explained in Fig. 2.6 c) - e) for three different delays between XUV and NIR laser pulse. The attosecond XUV pulse photo-ionizes a rare gas sample and the released electrons form a bunch with initial momentum distribution displayed as the violet profile in Fig. 2.6 c) - e). The chirp of the XUV pulse is transferred to the chirp of the photoelectrons. Instants c) and e) show the influence of the chirp on the resulting final momentum distribution for the two most extreme cases where the electron bunch is being probed by the laser pulse at a zero-crossing of the vector potential. Panel c) considers the emission around a laser field oscillation with slope parallel to the chirp. Here the term $-epA_L$ (according to Eq. 2.7) leads to a broadening of the electron momentum distribution which is accompanied by a reduction of the peak of the distribution. For the opposite case depicted in panel e), namely when the slope of the term $-epA_L$ is anti-parallel to the chirp, the final momentum distribution is compressed which in turn leads to a rise of the counts at the center of the kinetic energy distribution. This is clearly observed in the experimental streaking trace in panel b). In both cases the center of the distribution is not shifted by the streaking field, whereas the largest collective shift of the electron distribution can be observed for local maxima and minima of the vector potential

(panel d). Furthermore the curvature of the vector potential leads to an asymmetrization of the distribution at those instances.

2.4.3 FROG retrieval of an attosecond XUV pulse

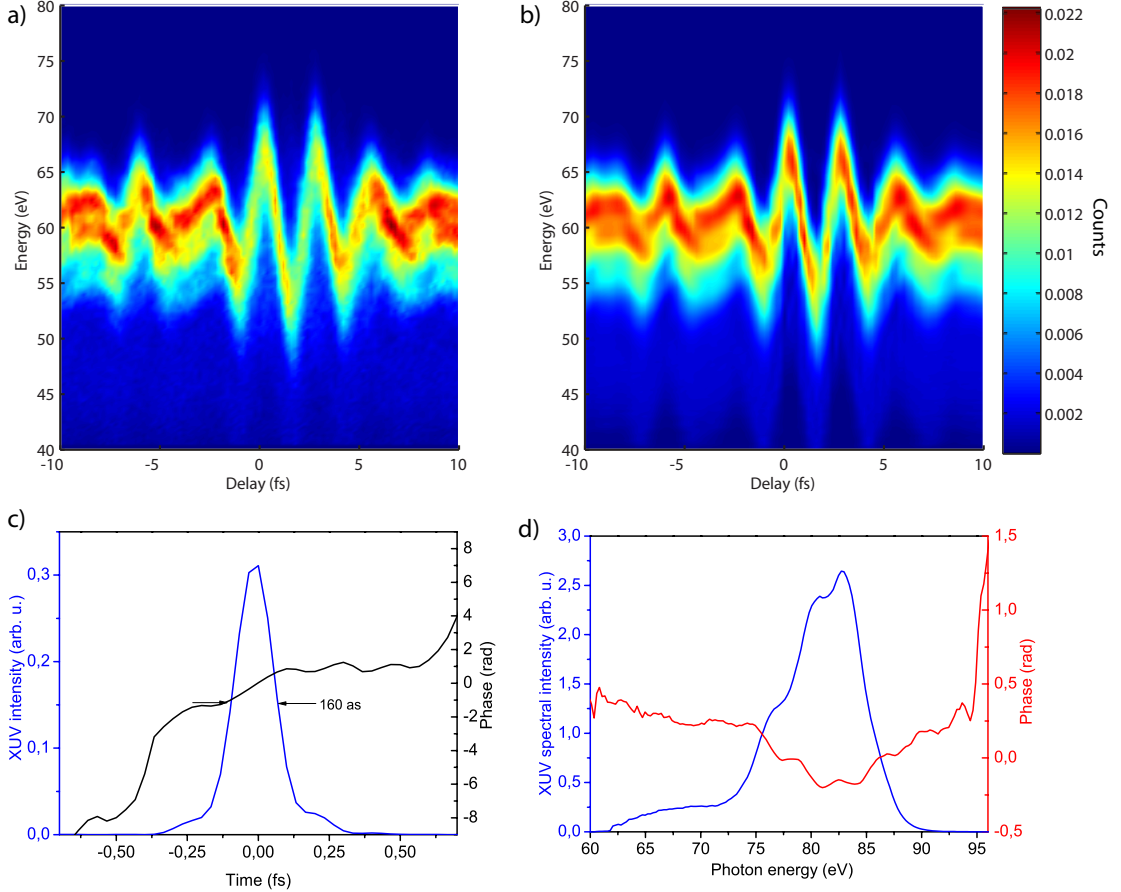


Figure 2.7: Phase reconstruction based on the measured streaking spectrogram given in **a)** and the FROG-like algorithm described in [96]. **b)** shows reconstructed spectrogram. Retrieved phase and amplitude of the XUV pulse in the time **(c)** and frequency **(d)** domain. The linear chirp amounts to 4500 as^2 and the bandwidth limited duration to 120 as.

An analysis along the lines of a FROG phase retrieval allows the precise reconstruction of the temporal structure of the attosecond pulse, including its temporal and spectral phase [37, 96]. Based on the algorithm described in [96] the retrieved characteristics of the XUV pulse manifesting the spectrogram shown in Fig. 2.6 b) are obtained. Fig. 2.7 a) shows the complete measured streaking spectrogram and panel b) the reconstructed spectrogram. Subsequent panels c) and d) display the retrieved temporal intensity profile and spectral

phase of the XUV pulse. The retrieval supports the earlier observation of the positive chirp and yields a quantitative group delay dispersion (GDD) of the XUV emission of $GDD = \frac{\partial^2 \varphi(\omega)}{\partial \omega^2} \approx 4500 \text{ as}^2$, resulting in a XUV pulse duration of 160 as. The spectral phase is denoted as $\varphi(\omega)$. The bandwidth limited duration is 120 as.

Streaking experiments enable the temporal characterization of the attosecond burst in the high harmonic process when performed on electrons liberated from only one specific atomic state [34, 83]. Recent developments to shape the XUV emission specifically for experimental needs enabled the study of multiple photoemission lines [38]. There it was found that emission of electrons from the 2s shell of neon precedes the liberation of these from the 2p shell by about 20 attoseconds. This demonstrates the power of the attosecond streaking metrology in tracking ultrafast electron dynamics. It can characterize the streaking light waveforms without any lower limit on its pulse duration, retrieves the concomitant XUV pulse and grants access into subtle timing features in photoemission processes.

Chapter 3

Apparatus for attosecond pump-probe experiments and metrology

There are two critical prerequisites which have to be met for a setup capable of performing attosecond pump-probe experiments, including XUV pulse metrology (attosecond streaking) and attosecond transient absorption spectroscopy. First, a significant amount of generated XUV high-harmonic photons will be re-absorbed if the partial pressure exceeds 10^{-3} mbar [97]. Therefore, and in view of multi-channel plate (MCP) based detector units as well as specially coated XUV optics, the complete experimental setup, excluding the HHG section, has to be located in a good high-vacuum (HV) or even ultra high vacuum (UHV) chamber arrangement. Second, since a duration of 100 attoseconds corresponds to 30 nm of spatial displacement, special attention has to be paid to the correct implementation of vibration damping for isolating the most sensitive units from external mechanical noise sources.

In order to meet these requirements, optical breadboards inside the vacuum vessels are mounted on separate pedestals which are directly attached on the optical table which itself carries the laser system. To ensure vacuum tightness, those posts are connected to the bottom of the chamber and the walls by soft edge welded bellows. This construction suppresses to an acceptable extent the unavoidable propagation of vibrations originating from turbo- and pre-vacuum pumps to optics located on breadboards. The beamline consists of several chambers which are connected by tubes along the beam propagation axis. In the HHG chamber the pressure is close to the pressure where re-absorption is taking place. Since this pressure is not low enough for attosecond experiments in the gas phase, the gas load originating from the HHG target, is subsequently reduced by differential pumping stages along the beam propagation direction, until the pressure conditions fulfill (U)HV. At this point, the main experimental chamber is placed in which isolated attosecond laser pulsed as short as 80 as [33] are being applied for pump-probe experiments (Fig. 3.1 b).

3.1 High-order harmonic generation section

Few-cycle NIR driving laser pulses are focused by a concave mirror with a radius of curvature (ROC) of -1200 mm through a 1 mm thick fused silica Brewster window into the first vacuum chamber of the beamline. Gas harmonics are generated by placing a quasi-static gas cell into the focus of the incident radiation in the HHG chamber (Fig. 3.1 b). This HHG target consists of a thin nickel tube which is filled with neon and is kept at a constant backing pressure. First exposure of the tube to the focused beam results in the generation of two holes in the target tube. The optimum pressure for the HH generation depends in general on several pulse- and target- specific parameters. Optimum yields are achieved for pressures varying between 180 to 320 mbar. For sub-4 fs driver pulses with 300 μJ pulse energy and pulse intensity of around $4 \cdot 10^{14} \frac{\text{W}}{\text{cm}^2}$ at a focus diameter of 150 μm , optimum XUV flux in the spectral range of 70 - 130 eV are achieved with tubes of an inner diameter of ~ 2 mm and by placing the target slightly after the actual focus of the laser beam. The physics of high-harmonic generation has been described in section 1.3. Two hybrid turbo pumps maintain during the operation of the gas target a pressure below 10^{-2} mbar inside the chamber. Neon exhibits the optimum combination between ionization potential and absorption cross-section for high-harmonic emission of isolated pulses in the energy range of interest 70 - 130 eV [98]. The generated XUV radiation is mainly emitted within a small divergence angle as compared to the driving laser pulse. This follows from the short wavelength of the generated light, together with the coherence between the emission process and the electric field of the driving laser pulse. The difference in beam divergence between the NIR and XUV laser pulse is used for a spatial separation between pump and probe pulse (Fig. 3.1 a). As shown in Fig. 3.1 b), the vacuum chamber hosting the generation target is followed by two differential pumping stages to reduce the parasitic gas load down to pressure values where MCPs can be safely operated.

Between the two differential pumping stages an ionization based detector for measuring the flux of high-harmonics is implemented (the so called HH-Meter). A conductive wire along the tube with a small applied voltage collects the generated ions and electrons that are created by the ionization of the residual gas and the corresponding current is in good approximation proportional to the number of electrons and ions created by absorption of XUV photons. In agreement with its working principle, we observe that it is a good measure for the overall created flux of harmonic photons but less accurate for optimizing the number of photons in the spectral range of the cut-off since it can not spectrally resolve the detected fragments. The advantage of the HH-Meter is, that it conveniently tracks fluctuations of the harmonic signal and very reliable monitors overall slow drifts during the acquisition of data in attosecond experiments. The harmonic photon flux stability recorded with the HH detector is better than 2.5% NRMSD (normalized root mean square deviation).

In the second differential pumping stage, the pressure is further reduced to 10^{-7} mbar. Here, a motorized iris module can control the intensity of the NIR laser pulse and is furthermore used on the daily basis as a reference for aligning the direction of the XUV and NIR radiation.

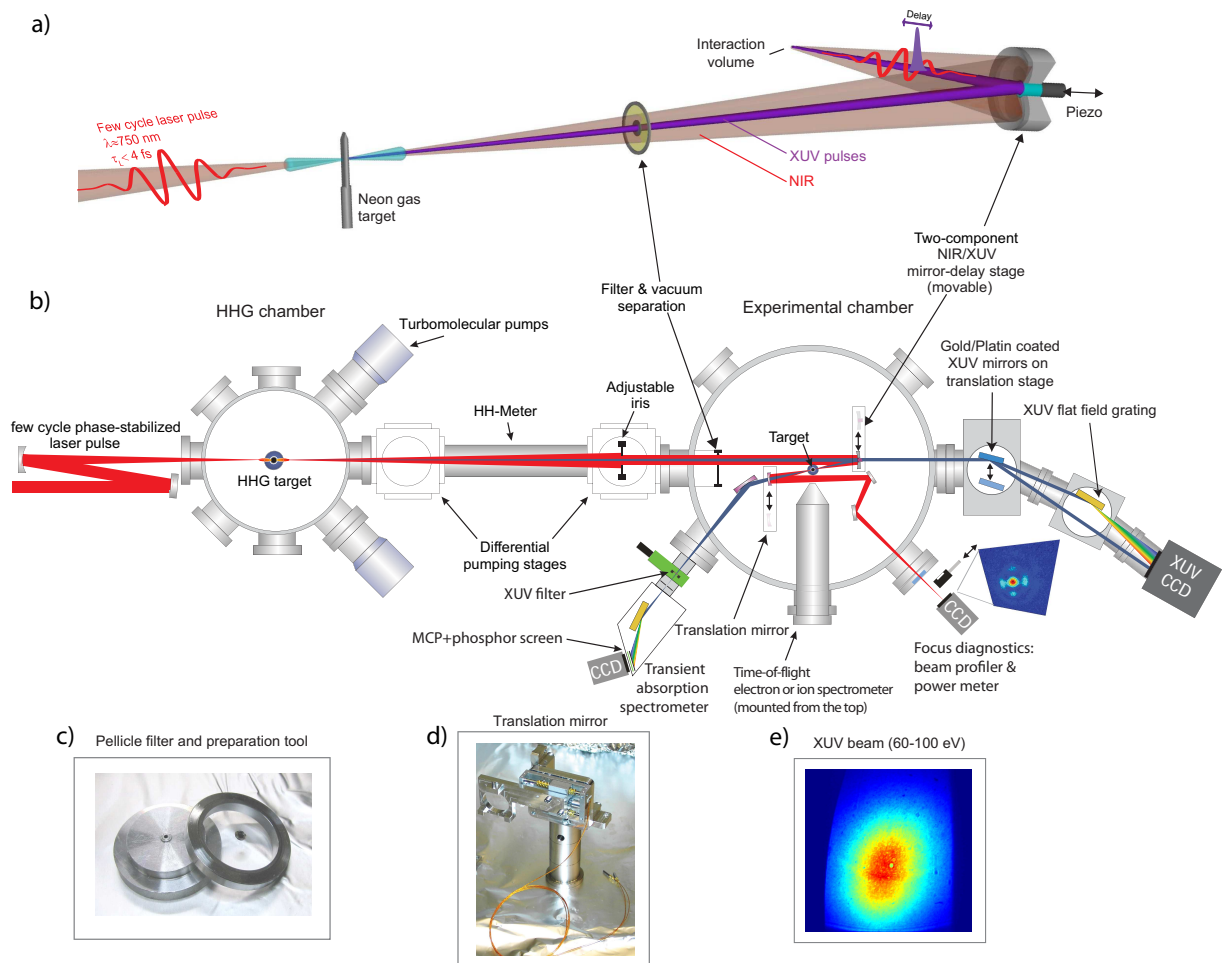


Figure 3.1: Apparatus for attosecond pump-probe experiments. The schematic view in **a)** displays the separation between NIR and XUV pulses which is based on a different divergence between the two beams and a special pellicle filter (**c**). A two-component delay mirror module, consisting of an XUV-core mirror and an outer silver mirror, introduces a delay by geometric displacement and focuses both beams into the interaction volume. The necessary vacuum arrangement and diagnostic tools for performing attosecond streaking and attosecond transient absorption experiments are shown in **b)**. In order to maintain ultra high vacuum in the experimental chamber, all kinematic stages and elements have to be designed and manufactured with care to avoid any virtual leaks. Representative for those requirements, a home-built translation mirror (**d**) which is motorized by a linear inertia-driven piezo motor, is displayed. Panel **e**) shows the XUV beam profile (60-100 eV) recorded with the XUV sensitive camera by bypassing the flat field grating in the XUV spectrometer at the end of the target chamber. Typical XUV spectra recorded with the commercial high resolution XUV spectrometer in attosecond transient absorption experiments are presented in Fig. 4.1 b).

3.2 Attosecond end station

The high vacuum attosecond experimental chamber hosts the setup by which isolated attosecond laser pulses are generated from high-order harmonic radiation, are delayed with respect to the NIR driving laser pulse and are characterized. Finally they are used in attosecond transient absorption experiments.

At the entrance of the attosecond end station, the two collinear beams pass a variable filter setup that permits separation of the beams into the central, low divergence XUV part and the NIR driving laser pulse as shown in Fig. 3.1 a)-c). The uncoated laser grade pellicles have an effective optical diameter of 30 mm and therefore support the complete NIR laser beam. Small rings made of stainless steel or super invar are glued in the middle of the pellicle and host a free-standing metallic filter (~ 150 nm thickness) to block the NIR radiation in the central part of the beam. The filter material is chosen such that it blocks the NIR light, has a high transmission in the spectral range of the generated XUV cut-off and also acts as a high-pass filter for the high-order harmonics. In the conducted experiments zirconium (Zr) has been chosen since its transmittance characteristics match the spectral bandwidth required for the experiment. After the filtering, both beams impinge on a two component delay mirror assembly shown in Fig. 3.1 a). The mirror assembly consists of a core and an outer mirror which has a hole in its center that is marginally larger than the inner mirror to allow for a slight displacement of the inner and outer one along the beam axis. This displacement along the normal of the mirror surface introduces the delay between the XUV and NIR by means of a closed loop controlled piezo stage that allows translation of the core mirror with a resolution better than 2 nm setting the ultimate limit for the smallest possible delay step to the equivalent of ~ 14 as. The inner mirror is coated by a multilayer (molybdenum/silicon) structure designed for high reflectivity in the XUV range. Adjusting the relative layer thickness, the sequence of materials and the number of layers, the spectral response as well as the reflectance of the XUV optic can be tuned [99, 38, 100]. Recently even chirped mirrors for soft X-ray radiation have been demonstrated [101]. Appropriate selection of thin foils along with multilayer mirrors can isolate a desired spectral band for experiments and are therefore the prerequisite for the generation of isolated attosecond laser pulses. The outer mirror is coated by silver. Both mirrors are produced out of the same one inch substrate which has a ROC of -250 mm. Both beams get spatially and temporally focused under a narrow angle ($< 5^\circ$) into the interaction volume, such that the focus is located several millimeter to the side of the incoming beams (Fig. 3.1 a). The astigmatism and the waveform distortion resulting from the aberration are small enough not to influence the experiments. For pump-probe experiments a spatial overlap of the XUV and NIR focus is very essential. In order to overlap both foci, the outer mirror features two independently adjustable angles to precisely position the focus of the NIR on top of the focus of the XUV. By removing the pellicle filter, both inner and outer mirror are illuminated with NIR radiation and a subsequent imaging of the two foci by means of an imaging system based on a biconvex lens ($f=15$ cm) magnifies (factor 3.35) and images both foci onto a beam profiler. Fine-adjusting the outer mirror such that both beam profiles overlap on the CCD camera also ensures spatial overlap of the XUV and

NIR beam in the interaction volume. Due to the shorter wavelength of the XUV radiation, the focus of the XUV pulse is safely smaller than the laser focus. A typical XUV flux attainable in an isolated pulse on target was estimated to yield $5 \cdot 10^8$ photons per second. A single pulse therefore contains on average 10^5 photons [102].

For the optimization of the XUV source, the direct observation of the direction and spectral distribution of the beam is essential. Therefore an imaging spectrometer based on a grazing-incidence flat field grating and a back-illuminated CCD camera are located in the home-built XUV spectrometer after the exit of the experimental chamber. By moving a translation stage - which carries the double-mirror assembly - out of the beam path, the XUV beam is released and leaves the chamber to impinge on one of the two plane gold/platinum coated bending mirrors. By means of a translation stage, the bending mirrors are moved into the beam, where the one steers the XUV radiation such that it passes by the grating and directly impinges onto CCD chip. The number of counts recorded with the camera serve as a quantity for the daily optimization procedure of the harmonic yield in the cutoff range. An XUV beam profile is displayed in Fig. 3.1 e) which is limited to the spectral range of 60 to 100 eV since a Zr filter is used in front of the XUV camera to prevent saturation and damage of the sensitive CCD chip. The other XUV bending mirror redirects the beam under almost grazing incidence onto the flat field corrected grating which disperses the photons onto the CCD camera. Monitoring the spectrum for instance supports the adjustment of the high-order harmonic cut-off. A 500 μm thick zirconium foil in front of the camera avoids damage of the chip.

For attosecond streaking experiments, which characterize the NIR and the attosecond XUV laser pulse, a carbon-coated and grounded glass nozzle (for minimizing charging effects) with a tip diameter of $\sim 20 \mu\text{m}$ (installed perpendicular to the laser beams), approaches the focus very closely from the side. The effusive gas cone is well suitable for streaking experiments since the pressure in the focus close to the tip of the nozzle can be very high without deteriorating the vacuum conditions over an extended region. This approach limits the interaction of the attosecond and laser pulses to within a fraction of the focal volume and minimizes spatial averaging effects that might be related to spatiotemporal effects (Guoy phase shifts) or non-uniform intensity distributions. In close proximity to the interaction volume, the entrance of an electron time-of-flight (TOF) spectrometer is placed which spectrally disperses launched photoelectrons. The resolution of $\sim 1 \%$ of the electron kinetic energy is satisfactory for streaking experiments, even though it sets a limit to the potentially observed fine-structure in the recorded streaking spectrograms. The accuracy for determining the central energy of a detected photoelectron distribution or induced asymmetries like the ones associated with the chirp is substantially better than 1 %. In the TOF spectrometer the electrons pass a magnetic shielded drift tube after which they undergo acceleration. The post acceleration ensures a uniform response of the microchannel plate, irrespective of the electrons kinetic energy. In order to enhance the count rate and reduce the necessary integration time for recording an electron TOF spectrum, an electrostatic lens is incorporated at the entrance of the flight tube. It increases the acceptance angle of electrons within a certain range of kinetic energies and thus en-

hances the count rate up to around $2 \cdot 10^3$ electron counts per second. A typical electron time-of-flight spectrum in neon was shown and analyzed in chapter 2. Streaking measurements are generally performed with an intensity of $\sim 1 \cdot 10^{12} \frac{\text{W}}{\text{cm}^2}$. Higher field strength would lead to several complications. First, the electrostatic lens would not cover the very large momentum shift of the photoelectron wave-packet. Second, electrons originating from above-threshold ionization (ATI) would overlap energetically with electrons being released by the XUV photons. In addition to unavoidable space-charge effects, streaking traces obtained under those conditions would lose a substantial amount of their clear structure which originates from the launched electron wave-packet. This would exacerbate the retrieval of pulse characteristics.

For attosecond transient absorption spectroscopy (ATAS) which is the forefront of this thesis, a second XUV spectrometer enables the observation of the spectrum of attosecond pulses after their transmission through an ensemble of atoms within a confined interaction volume as depicted in Fig. 3.1 b). In this class of experiments, the NIR pulse serves as the pump and the attosecond XUV pulse probes the atomic ensemble and can therefore explore ultrafast transient phenomena of the target atoms which are encoded as delay-dependent absorption features in its spectrum. For good signal to noise ratios, ATAS experiments require, besides even higher laser stabilities, also a gas target which can provide a higher interaction gas density than the one used for attosecond streaking experiments. A quasi static gas target, similar to the one used for high-order harmonic generation, is used instead of a diffusive gas nozzle. The inner diameter of the gas cell which amounts to 1 mm confines the interaction volume between the NIR pump and attosecond probe pulse since the gas pressure exponentially decays outside of the nickel tube. Depending on the position of a movable mirror (see Fig. 3.1 b, c) the beam is either redirected into the imaging system or onto a concave (ROC= -340 mm) multilayer broadband coated XUV optic whose reflectivity is optimized for an angle of incidence of 67° (reflectivity depicted in Fig. A.5). This concave optic creates a line focus in the plane of the entrance slit of the spectrometer. A suitable thin metal filter (here zirconium with a thickness of 150 nm) placed in front of the entrance slit suppresses a substantial amount of the main part of the co-propagating NIR radiation. During operation of the transient absorption quasi static gas cell, the pressure in the experimental chamber increases up to $3 \cdot 10^{-3}$ mbar. The zirconium filter which blocks the NIR radiation in front of the spectrometer further serves as a very essential pressure separator between the experimental chamber and the ultra high vacuum unit of the XUV spectrometer and supports a pressure of $2 \cdot 10^{-6}$ mbar in the separately pumped commercially available Rowland-circle based spectrometer. We use a concave grating with 2400 grooves per millimeter. The detection of XUV photons is realized by means of a microchannel plate in combination with a phosphor screen and fiber-coupled Peltier/water cooled CCD camera. Typical XUV spectra recorded with the XUV spectrometer in attosecond transient absorption experiments are shown in Fig. 4.1 b). The experimentally achieved resolution amounts to 0.35 eV (FWHM value of Gaussian spectrometer response function). Compared to an XUV sensitive CCD camera, this detection scheme is more superior for ATAS experiments because it inherits a heavily reduced sensitivity to leaking

and scattered parasitic NIR light which can not be completely blocked by the 150 nm thin zirconium filter.

More details about ATAS experiments are provided in the following chapter, especially in section 4.2. In sharp contrast to utilized intensities in streaking experiments, transient absorption experiments generally are aiming at the observation of multiply charged states. This requires preferably the focusing of a larger portion of the beam. In turn, this increases the thermal load on the crucial pellicle filter which leads to rapidly damaged pellicles even after exposure times of a couple of hours. We observe that damaged pellicles develop an almost opaque white area around the metal ring. In an earlier damage state, the beam profile of the NIR radiation changes, which is accompanied by a drop in the peak intensity. Since it is very time consuming to prepare pellicle filters, we were working on an expansion of the life time of the pellicle during laser irradiation. An increase of the pellicle thickness from 5 μm to 15 μm and approaching smallest possible ring sizes ($d_o = 3.0\text{ mm}$, $d_i = 2.5\text{ mm}$) made of stainless steel to increase the transmitted NIR light power, helped to improve the lifetime of those delicate pellicle filter stacks. Developed preparation tools, assisting the filter preparation, reduced preparation times necessary for the pellicle/filter assembly (Fig. 3.1 d). For completeness it shall be mentioned that our recently published technical paper which describes this attosecond beamline AS1 at the Max Planck Institute of Quantum Optics [80] provides in addition to an overview of other performed experiments at this beamline also information about commercial suppliers and item specifications on a more technical perspective which would exceed the scope of this work.

3.3 Beam characterization and determination of pump intensity

In streaking experiments which are conducted at substantial lower intensity, the intensity can be inferred from the streaking trace itself. But due to higher intensity values used in ATAS experiments, a new approach of determining the intensity has to be considered. The beam profiler placed at the end of the imaging system of the attosecond beamline as shown in Fig. 3.1 b) in combination with an absolute power meter and the knowledge of the pulse duration allow the estimation of the peak intensity in the focus created by the NIR pump beam. The determination of the intensity in ATAS measurements is a key-parameter for investigating the physical mechanisms and ab-initio simulations supporting the experiment.

Beam profiles of the NIR pump beam at experimental conditions were recorded as a function of laser power. The latter was adjusted by increasing the radius of the beam. The power losses introduced by the imaging system have been taken into account by measuring the power drop between the input and the exit of the imaging system. Once calibrated by the power transfer function of the imaging system, the external power head provided the power in the interaction area. Fig. 3.2 shows a representative beam profile. The axis were calibrated by taking the magnification factor of 3.35 of our imaging system and the pixel

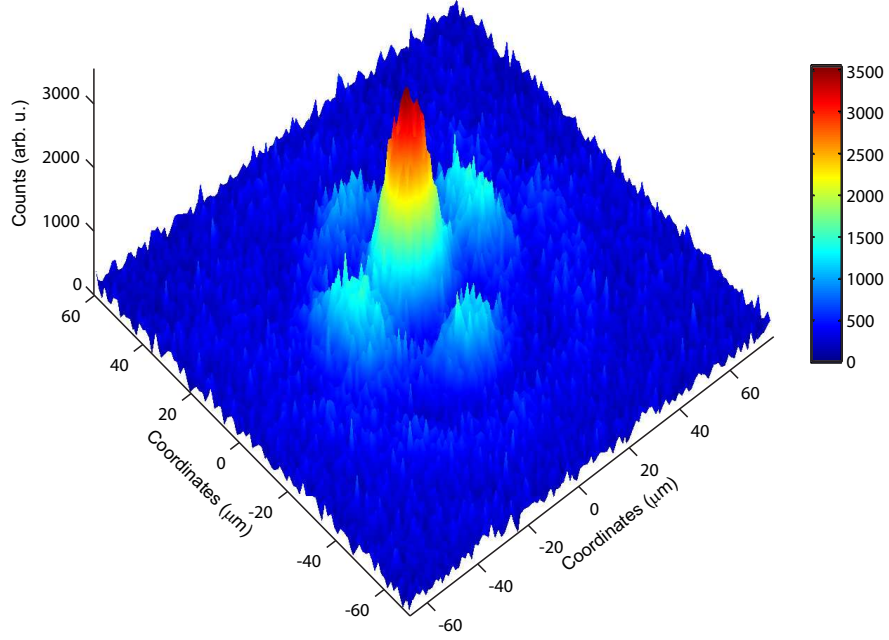


Figure 3.2: Beam profile of the NIR beam at its focus (interaction area) after being reflected from the outer silver mirror where the inner part of the beam is blocked by the zirconium filter seated on the pellicle as explained in Fig. 3.1 a). Cylindrical diffraction rings are originating from perforation of the beam center and accumulated astigmatism leads to the breaking of the cylindrical symmetry which manifests itself in the appearance of four lobes. Dimensions are given in μm .

dimensions of the CCD camera ($4.4 \times 4.4 \mu\text{m}^2$) into account. The given axes dimensions denote the real dimension of the beam focus. Cylindrical diffraction rings are expected to originate from the focusing of a Bessel beam whose center spot is blocked. In our system, the round metal filter of 3 mm diameter which is mounted on the pellicle as depicted in Fig. 3.1 a) blocks the inner part of the NIR beam and therefore the focus inherits the cylindrical symmetric diffraction rings. Astigmatism persisting in the beam and accumulated in the laser system breaks the cylindrical symmetry and produces four side lobes in the beam profile. Due to the substantially smaller XUV focus, pump probe experiments only probe processes in the main peak of the intensity distribution in Fig. 3.2. A Gaussian fit to the central peak reveals a FWHM focal spot diameter of $(18.4 \pm 1.2) \mu\text{m}$. This corresponds to a beam waist radius w_0 of $(13.1 \pm 0.9) \mu\text{m}$ taken at a width of $1/e^2$ the peak intensity. In order to determine the peak intensity in the central peak of the focus, it has to be taken into account that a very substantial fraction of the pulse energy is stored in the diffraction lobes and rings. Integrating the detected power in the main intensity peak and compar-

ing the number to the energy contained in the ring- and lobe structure reveals that the central intensity peak contains $\sim 29\%$ of the overall pulse energy. This percentage slightly increases to 34% for the maximum achievable intensity / iris opening. The changes on the beam profile as a function of iris opening are very minor. Furthermore, we included in the intensity calculation the presence of a temporal pre/post pulse structure which had been investigated by earlier streaking measurements. By considering several streaking curves we evaluated the energy which was stored in the leading / trailing pulse structures to $\sim 20\%$ of the overall pulse energy. Utilizing the optical intensity distribution of a Gaussian pulse as given by the following textbook equation

$$I(\rho, z) = \frac{2P}{\pi w(z)^2} \cdot e^{-2(\rho/w(z))^2},$$

where ρ and z denote the radial and axial coordinates of the beam, P the total power and $w(z)$ the beam radius, the on-axis temporal peak intensity average can be calculated. Considering a NIR laser pulse duration of (3.8 ± 0.2) fs and assuming that within this time all the pulse energy passes the beam cross-section, yields a temporal on axis peak intensity average of $(2.3 \pm 0.37)10^{14} \frac{\text{W}}{\text{cm}^2}$ for the beamprofile shown in Fig. 3.2. Pump intensities up to $(6.8 \pm 1.1)10^{14} \frac{\text{W}}{\text{cm}^2}$ can be achieved with the current beamline design.

3.4 Dual target module

As mentioned earlier, attosecond streaking measurements for the field characterization necessitate a substantially lower intensity and different gas target design than transient absorption experiments. In the following it will be distinguished between the streaking and the transient absorption gas target. One of the limitations of the presented first attosecond transient absorption experiments (see chapter 4) was the fact that the pulses could not be characterized when the transient absorption target was installed. A tedious re-build was necessary to replace one target with the other. Here, not only the replacement itself was time consuming, but the correct placement of the target in the foci required several hours work of optimization. Motivated by the unique benefits of a future combination of attosecond streaking with attosecond transient absorption experiments a new gas target unit providing the possibility to change within minutes from streaking to absorption measurements was designed. Its implementation allows precise characterization of the electric field which is used after its measurement for transient absorption experiments. In this context, one of the latest upgrades of the described beamline was the design and installation of a closed-loop encoded dual target module which had not been available for any of the presented proof-of-concept studies at that time. First tests have proven its power in combining streaking and transient absorption experiments by opening the door for changing the targets completely reliable in-situ within few minutes without the need of opening the chamber or running through any optimization routines.

Both target types are mounted on a three-axis closed-loop controlled micro-translation stage assembly such that the targets are in close proximity to the focus of the beam as

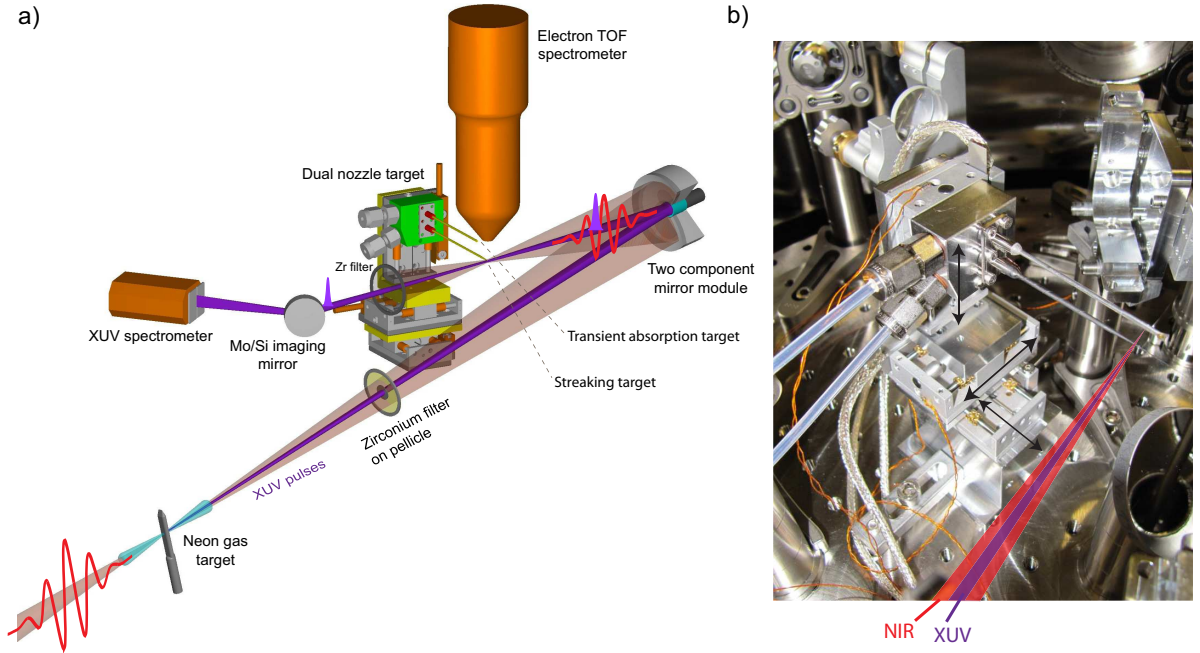


Figure 3.3: Schematic implementation of a dual target module for further advances in attosecond science **a)** and its realization and implementation in the experimental chamber shown in **b)**, allowing the combination of attosecond streaking and attosecond transient absorption experiments. The composed light-waveform can be determined within minutes before or after its application in transient absorption studies.

sketched in Fig. 3.3 a). Having once found the correct coordinates for both targets, it is possible to move to the other target within seconds. Since the positioning of the targets with respect to the focus is very sensitive in both types of experiments, a high resolution and bi-directional reproducibility of the stage movement is required. Infrared laser based optical encoding of the three degrees of freedom meets the requirements and results in a resolution better than 300 nm. Both targets are connected by flexible Teflon tubes to fine dosing valves which allow for an independent fine adjustment of the backing pressure in the targets. Both targets are mounted independently from each other onto the base socket (shown in green in Fig. 3.3 a). This allows the replacement of one of the targets while not having to move the other target. A logic algorithm (implemented in the software control) avoids the fragile targets from being damaged by crashing them against the entrance of the TOF which has to be placed very close to the focus and target itself. Fig. 3.3 b) shows the dual target unit including the two targets after its realization and fabrication. Due to the high resolution of the utilized translation stages, it is in addition possible to determine beam diameters by means of the knife-edge method. A small but sharp edge, additionally installed besides the two gas targets, can clip the beam for such a measurement. This finalized dual target module will open the door for an ultimate combination of

the attosecond streak camera and the powerful tool of transient absorption (see section 4) to provide for instance real-time insight into sub-cycle atomic ionization dynamics which can be related to the triggered temporal NIR strong field distribution.

Chapter 4

Attosecond transient absorption spectroscopy

A first combination of modern attosecond technology and the well-known tool of transient absorption spectroscopy will be introduced permitting access into electron dynamics and merges the advantages of attosecond chronoscopy with those of transient absorption spectroscopy. The attosecond XUV pulse will serve as the probe pulse and therefore it is referred to the new tool as attosecond transient absorption spectroscopy. Some of its obvious profits are the gentle probing owing to the absence of strong fields, the capacity to study processes within atomic, molecular and condensed matter systems, and a wide applicability to materials with arbitrary ionization potentials. Thus, this approach is ideal for attosecond real-time observation of electronic and concomitant processes in atoms, molecules and solids.

4.1 Methods

Fig. 4.1 a) illustrates the attosecond probing concept using the example of our first proof-of-concept experiment, where a sub-4-fs near-infrared (NIR) laser pulse liberates electrons from the valence shell of atoms ($4p$ subshell in krypton atoms) to generate singly charged $4p^{-1}$, doubly charged $4p^{-2}$ and even triply charged $4p^{-3}$ ions in the $4p^{-1}$, $4p^{-2}$ and $4p^{-3}$ manifolds of quantum states for krypton by means of optical field ionization (indicated by red arrows). Conventional spectroscopy [103] shows that the ions are created in manifolds of states depicted by green boxes and denoted by nl^{-i} , indicating that, relative to the ground-state configuration of the atom, i electrons are missing from the nl subshell. An attosecond XUV pulse carried at a photon energy of ≈ 80 eV (depicted in violet) promotes the krypton ions created in their $4p^{-i}$ manifolds to the $3d^{-1} 4p^{-(i-1)}$ core-hole states (as indicated by the violet arrows). Transient XUV absorption spectra are acquired by recording the attosecond XUV pulse spectrum transmitted through the ionized gas target as a function of pump-probe delay with an XUV spectrometer. The spectral intensity distribution of the relevant part of the broadband attosecond probe pulse is shown in Fig.4.1b) and the schematic

of the experimental set-up in Fig.4.1c). As a blue curve, Fig.4.1b) displays the spectrum of the attosecond pulse transmitted through an ensemble of krypton atoms before their ionization and as the red curve the spectrum of the attosecond pulse after the ionization of the gas target atoms by a NIR laser pulse with a peak intensity of up to $7 \cdot 10^{14} \frac{\text{W}}{\text{cm}^2}$. The XUV transitions lead to absorption dips in the spectrum of the broadband XUV radiation transmitted through the ionized atomic ensemble, revealing populations and coherences on an attosecond-femtosecond timescale being imprinted onto the time-dependent absorption lines. Details concerning the experimental realization are provided in the next section, including information about the several optical elements shown in Fig.4.1c).

4.2 Experimental details

Carrier-envelope-phase-controlled, sub-4-fs, 0.3 mJ NIR laser pulses carried at a wavelength of ~ 750 nm and delivered at a repetition rate of 3 kHz are focused into a neon-filled tube to generate XUV pulses by means of high-harmonic generation (Fig. 4.1 c). The achieved CEP stability amounts to a standard deviation of ~ 100 mrad. On their way towards a two-component, concentric mirror module, the collinear NIR and XUV beams pass through a filter assembly consisting of a 150 nm-thick zirconium foil (transmission characteristics are shown in A.2) and an ultrathin 15 μm pellicle. The small-divergence XUV beam is transmitted through the zirconium filter covering a circular spot ~ 3 mm in diameter, whereas the NIR beam is efficiently blocked by this filter. The outer part of the (more divergent) NIR beam is transmitted by the pellicle carrying the zirconium foil. The XUV beam transmitted through the circular zirconium filter has a diameter of ~ 3 mm when hitting the internal part of the double mirror assembly. This inner mirror is covered with a molybdenum-silicon multilayer with a peak reflectance of ~ 2.5 % over a 28 eV (full-width at half-maximum) band centered at ~ 80 eV [33]. In these experiments, spectral filtering and the intensity of the driving field yield pulses with ~ 15 eV bandwidth. The NIR beam is reflected by the outer part of the mirror assembly, which is coated with silver. Both mirrors are deposited on a super-polished substrate with a radius of curvature of 25 cm and are focused in a quasistatic gas cell formed by a nickel tube, containing the krypton gas at a pressure of about 80 mbar. The effective interaction length in the krypton gas target is 1.0 mm. The XUV pulses hitting the target have a duration of less than 150 as as verified by attosecond streak-camera measurements. It is delayed with respect to the laser pulse by the focusing molybdenum-silicon mirror mounted on a piezo-controlled translation stage. A motorized aperture installed downstream of the source adjusts the on-axis NIR intensity on the target (not shown) between zero and $7 \cdot 10^{14} \frac{\text{W}}{\text{cm}^2}$. A second zirconium foil, installed behind the krypton gas cell, prevents the NIR light from entering the XUV spectrometer. A broadband molybdenum-silicon multilayer mirror (reflectivity curve given in Fig. A.5), images in one transverse dimension, the transmitted XUV beam from the krypton gas target to the entrance slit of an XUV spectrometer, used for measuring the spectral intensity distribution of the attosecond XUV beam transmitted through the ionized target.

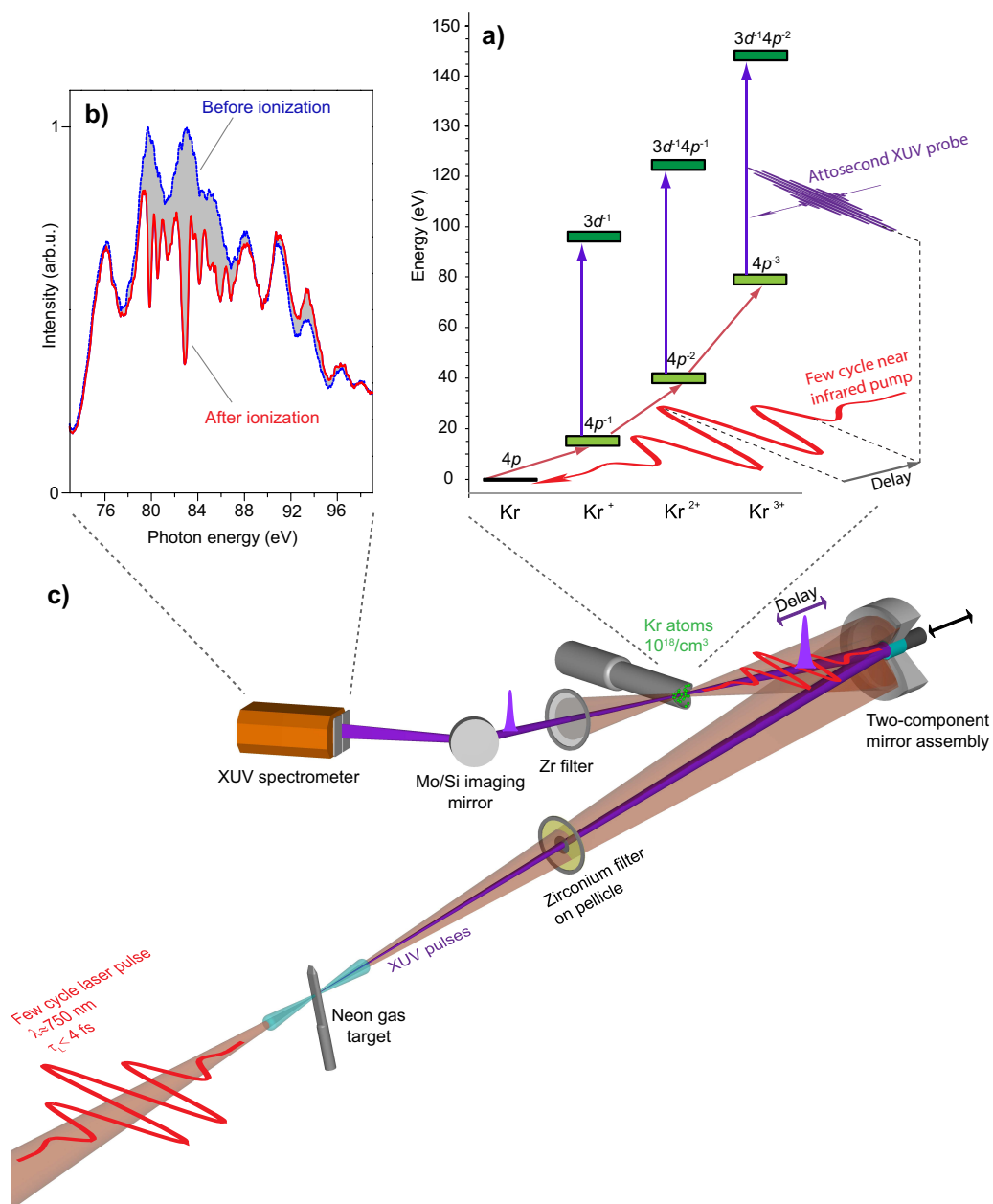


Figure 4.1: **a)** The strong electric field of a sub-4-fs near-infrared (NIR) laser pulse (in red) liberates electrons from the valence subshell of atoms (4p shell in krypton atoms) to generate singly charged $4p^{-1}$, doubly charged $4p^{-2}$ or triply charged $4p^{-3}$ ions in the $4p^{-1}$, $4p^{-2}$ and $4p^{-3}$ manifolds of quantum states for krypton. An attosecond XUV pulse (in violet) is passed through the ions and promotes them to core-hole excited-state manifolds (as indicated by the violet arrows). **b), c)** Transient XUV absorption spectra are acquired by recording the attosecond XUV pulse spectrum transmitted through the ionized gas target as a function of pump-probe delay with an XUV spectrometer. Spectral intensity distribution of the relevant part of the broadband attosecond probe pulse (**b**) and schematic of the experimental set-up (**c**). The pulse is transmitted through an ensemble of krypton atoms before their ionization (blue curve) and after their ionization (red curve) by the laser pulse with a peak intensity of up to $7 \cdot 10^{14} \frac{\text{W}}{\text{cm}^2}$. Arb.u., arbitrary units.

4.3 Overview of performed experiments

Several experiments utilizing attosecond transient absorption spectroscopy were performed which can be separated into two categories.

The first class of experiments focuses at the pump-probe delay regime where there is no temporal overlap between pump and probe pulse, that is the probe pulse probes the system after the strong field perturbation has ended (section 5). After a general theoretical description of the absorption of pump pulses and the special case for ions, experimental observations obtained in krypton and xenon atoms, including their ions, are presented. In the proof-of-concept study we observed for the first time in real time valence electron motion in Kr^+ ions. Theoretical modeling and careful analysis of the experimental data allows for the complete reconstruction of hole density motion in strong-field created Kr^+ ions. Apart from this simplest prototypical open system, further experiments were carried out in more complex quantum systems, where electron motion was observed in multiply charged ions of krypton (section 5.5) and xenon (section 5.6). In these more complex systems for instance hole-hole correlations might modify the multiple-hole density motion.

The second category of experiments is devoted to the pump-probe delay regime where the pump and probe pulse overlap in time and therefore probing of the atomic system is performed in the presence of a strong NIR light field. Here we focus at the real-time observation of atomic ionization (chapter 6) and despite the enormous theoretical challenges, an attempt is made to connect the strength of absorption lines with the underlying populations, which is a non-trivial relation in the presence of a strong laser field.

Chapter 5

Attosecond transient absorption studies I: Real-time observation of valence electron motion

5.1 Theory of transient absorption spectroscopy

Since transient absorption spectroscopy in combination with appropriate theoretical modeling allows access to the reduced density matrix elements it is essential to describe the absorption process of the probe pulse after the pump pulse has modified the electronic system. It should be pointed out that for the convenience of the reader and of its importance for analyzing some of the acquired experimental data sets, the theoretical modeling will be discussed in the scope of the thesis even though the main outcomes were separately worked out and published by our collaboration partners [104], being specialized in the theoretical treatment of light-matter interactions.

The discussed approach treats the pump step in a completely nonperturbative fashion and the probe pulse is assumed to have no temporal overlap with the pump pulse. The derivation of the single photon susceptibility is kept as general as possible and therefore independent of pulse durations and the electronic structure problem of the absorbing system. Finally, the resonant absorption is explicitly described for laser-generated atomic ions and in the short probe pulse approximation.

5.1.1 Atomic response

Fig. 5.1 a) shows a rather general layout of a pump-probe experiment, where both pulses are propagating at vacuum speed of light c along the x axis of the lab frame Σ . The time of the lab frame is t_Σ . The peak of the pump (probe) pulse $E_{pu}(x, t_{pu})$ ($E_{pr}(x, t_{pr})$) is centered at its local time $t_{pr} = 0$ ($t_{pu} = 0$). A more systematic description is shown in Fig. 5.1 b)

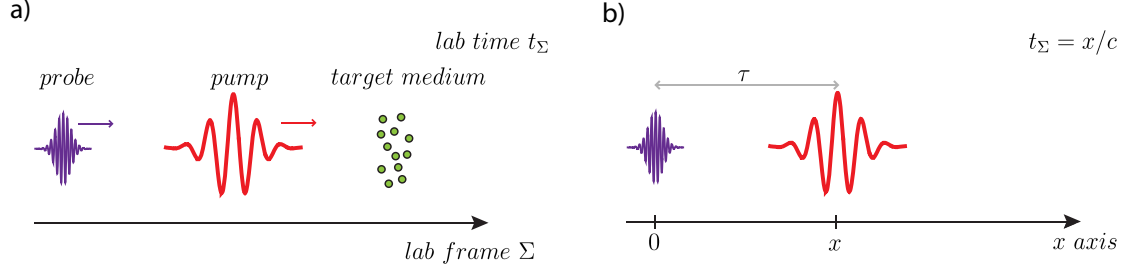


Figure 5.1: General layout of a pump-probe experiment in lab frame Σ at lab time t_Σ is shown in **a)** and specific arrangement of the problem as used for theoretical investigation where both pump and probe pulses are propagating along the x axis in panel **b)**. The delay is introduced as $\tau = x/c$ (see main text for details).

for the time instance $t_\Sigma = \frac{x}{c}$. The probe pulse is spatially centered at $x = 0$ and a target atom is located at x . In this representation the delay τ between the two pulses amounts to $\frac{x}{c}$, such that the pump is centered at the position x of the atom. The pump pulse can be written at the position x as $E_{pu}(x, t_\Sigma - \frac{x}{c})$ and the probe pulse as $E_{pr}(x, t_\Sigma)$. For the atom at position x , it is convenient to introduce the local time $t = t_\Sigma - \frac{x}{c}$ [104].

For the semiclassical description of the interaction of the pump and probe pulse with the atoms in the target gas, the following simplifications are made:

1. The experimental interaction length of the gas cell is substantially shorter than the Rayleigh length. Hence, both pulses can be described by transverse, infinite plane waves propagation along the x axis and being linearly polarized along the z axis.
2. The pump pulse undergoes no significant modifications as it propagates through the pump-modified target medium.
3. Temporal structure changes of the probe pulse are only due to the absorption process.
4. Harmonic generation driven by the pump pulse in the target medium does not spectrally overlap with the spectral content of the probe pulse.
5. Before interaction of the electronic structure of the target medium with the pump pulse, the electronic system is in its groundstate $|\Psi_0\rangle$.
6. The probe pulse is weaker than the pump pulse and thus fulfills the requirements for a noninvasive probe process.

Simplifications 1), 4) and 6) are experimentally verified in the scope of the presented results. Pulse propagation calculations for the experimental intensities have yielded only weak distortions of the pump beam upon its propagation through the gas target. This

proves that assumption 2) is a good approximation. The validity of assumption 3) is numerically verified in [104] for the experimental conditions of the presented results.

In order to describe the absorption of the probe pulse and therefore the polarization response of the electronic structure it is necessary to solve the time-dependent Schrödinger equation (atomic units are used throughout this section)

$$i \frac{\partial}{\partial t} |\Psi(t)\rangle = \hat{\mathcal{H}}(t) |\Psi(t)\rangle \quad (5.1)$$

where the time-dependent Hamiltonian in the electric dipole approximation reads

$$\hat{\mathcal{H}}(t) = \hat{\mathcal{H}}_0 - E_0 - E_{pu}(t) \hat{\mathcal{Z}} - E_{pr}(x, t_\Sigma) \hat{\mathcal{Z}}. \quad (5.2)$$

Here, $\hat{\mathcal{H}}_0$ is the Hamiltonian of the unperturbed problem, E_0 the energy of the atomic ground state and $\hat{\mathcal{Z}}$ represents the z component of the electric dipole operator. For calculating and interpreting the polarization response $P(x, t_\Sigma) = \langle \Psi(t) | \hat{\mathcal{Z}} | \Psi(t) \rangle$, it is necessary to obtain first an expression for $|\Psi(t)\rangle$ as a function of $E_{pr}(x, t_\Sigma)$.

Let $\hat{\mathcal{U}}_{pu}(t, -\infty)$ be the time evolution operator of the solution for the pump-only problem. Therefore,

$$|\Psi_{pu}(t)\rangle = \hat{\mathcal{U}}_{pu}(t, -\infty) |\Psi_0\rangle \quad (5.3)$$

is a solution of Eq. 5.1 for vanishing $E_{pr}(x, t_\Sigma)$. $|\Psi_0\rangle$ is the initial state of the atom which is assumed to be the ground state. Employing standard perturbation theory allows the derivation of the influence of the weak probe field on the wave function. Substituting the ansatz $|\Psi(t)\rangle = |\Psi_{pu}(t)\rangle + |\Psi(t)\rangle^{(1)}$ into equation Eq. 5.1 and utilizing the Hamiltonian of Eq. 5.2 yields

$$i \frac{\partial}{\partial t} |\Psi(t)\rangle^{(1)} = \left[\hat{\mathcal{H}}_0 - E_0 - E_{pu}(t) \hat{\mathcal{Z}} \right] |\Psi(t)\rangle^{(1)} - E_{pr}(x, t_\Sigma) \hat{\mathcal{Z}} |\Psi_{pu}(t)\rangle - E_{pr}(x, t_\Sigma) \hat{\mathcal{Z}} |\Psi(t)\rangle^{(1)} \quad (5.4)$$

Considering only a perturbation in the first order of E_{pr} allows for dropping the last term in Eq. 5.4 and results in the following integral expression for $|\Psi(t)\rangle^{(1)}$:

$$|\Psi(t)\rangle^{(1)} = i \int_{-\infty}^t \hat{\mathcal{U}}_{pu}(t, t') \hat{\mathcal{Z}} E_{pr}(x, t' + x/c) |\Psi_{pu}(t')\rangle dt' \quad (5.5)$$

with $\hat{\mathcal{U}}_{pu}(t, t') = \hat{\mathcal{U}}_{pu}(t, -\infty) \hat{\mathcal{U}}_{pu}^\dagger(t', -\infty)$. Based on this integral solution for the first order perturbation approach, the polarization response per atomic absorber can be written in the following way, where n_0 is the number density of atomic absorbers:

$$P(x, t_\Sigma) = n_0 \{ \langle \Psi_{pu}(t) | \hat{\mathcal{Z}} | \Psi_{pu}(t) \rangle + \langle \Psi_{pu}(t) | \hat{\mathcal{Z}} | \Psi(t)^{(1)} \rangle + \langle \Psi(t)^{(1)} | \hat{\mathcal{Z}} | \Psi_{pu}(t) \rangle + \langle \Psi(t)^{(1)} | \hat{\mathcal{Z}} | \Psi(t)^{(1)} \rangle \}. \quad (5.6)$$

The first term describes harmonic generation driven by the pump field. The second and third term are the first-order components of the polarization response. The fourth term

is quadratic in the probe field and therefore of the second order of the weak perturbation. For describing the absorbance of the probe field, only the terms which are of first-order in E_{pr} shall be taken into account. As stated earlier, we assume that harmonics, generated by the pump field, do not spectrally overlap with the spectral content of the probe pulse. Thus, the polarization response which is caused by absorbing part of the probe pulse of first order in E_{pr} can be written using Eq. 5.5 in the following way:

$$\begin{aligned} P^{(1)}(x, t_\Sigma) &= n_0 \langle \Psi_{pu}(t) | \hat{\mathcal{Z}} | \Psi(t)^{(1)} \rangle + c.c. \\ &= in_0 \int_{-\infty}^t E_{pr}(x, t' + x/c) \langle \Psi_{pu}(t) | \hat{\mathcal{Z}} \hat{\mathcal{U}}_{pu}(t, t') \hat{\mathcal{Z}} | \Psi_{pu}(t') \rangle dt' + c.c. \end{aligned} \quad (5.7)$$

This important equation which was derived for arbitrary pump intensities will serve as the key equation for further calculations. This equation rigorously shows that the polarization response induced by the probe pulse does not only depend on atomic properties at the instant of the EUV pulse, but also on atomic properties after the probe pulse has passed the target medium. This will become more obvious if the probe field is assumed to be a delta function centered at $t' = \tau$: $E_{pr}(x, t' + x/c) \propto \delta(t' - \tau)$. Under this simplification Eq. 5.7 yields for $t > \tau$:

$$\begin{aligned} P^{(1)}(x, t + x/c) &\propto in_0 \int_{-\infty}^t \delta(t' - \tau) \langle \Psi_{pu}(t) | \hat{\mathcal{Z}} \hat{\mathcal{U}}_{pu}(t, t') \hat{\mathcal{Z}} | \Psi_{pu}(t') \rangle dt' + c.c. \\ &\propto \langle \Psi_{pu}(t) | \hat{\mathcal{Z}} \hat{\mathcal{U}}_{pu}(t, \tau) \hat{\mathcal{Z}} | \Psi_{pu}(\tau) \rangle + c.c. \end{aligned} \quad (5.8)$$

This explicitly shows that the polarization response does not only depend on $|\Psi_{pu}\rangle$ at the time of the probe pulse τ , but also on the wave function $\langle \Psi_{pu}(t) |$ and the propagation operator $\hat{\mathcal{U}}(t, \tau)$ for $t > \tau$. This important finding is not contained in previous theoretical transient absorption investigations described in [105].

5.1.2 Propagation of probe pulse through the absorbing medium

In this section the propagation of the probe pulse through the target medium shall be addressed, under the assumption that the probe field reaches the target after the pump field. Thus, no modification of the electronic states populated by photoabsorption of the probe pulse has to be taken into account. Therefore, the time evolution operator can be written as $\hat{\mathcal{U}}_{pu}(t, t') = e^{-i(\hat{H}_0 - E_0)(t - t')}$. Furthermore, the state of the electronic structure after the interaction with the pump field can be expanded in eigenstates $|\varphi_i\rangle$ with corresponding eigenenergies E_i and time-independent expansion coefficients α_i :

$$|\Psi_{pu}(t)\rangle = \sum_i \alpha_i e^{-i(E_i - E_0)t} |\varphi_i\rangle$$

Following the derivation shown in [104], Eq. 5.7 goes over into

$$P^{(1)}(x, t + x/c) = in_0 \sum_{i,i'} \alpha_i^* \alpha_{i'} \sum_f \langle \varphi_i | \hat{\mathcal{Z}} | f \rangle \langle f | \hat{\mathcal{Z}} | \varphi_{i'} \rangle \cdot \int_{-\infty}^t E_{pr}(x, t' + x/c) e^{-i(E_f - E_i)(t-t') + i(E_i - E_{i'})t'} dt' + c.c. \quad (5.9)$$

with $|f\rangle$ denoting eigenstates of $\hat{\mathcal{H}}_0$ with energies E_f . In order to address the propagation of E_{pr} , the wave equation has to be solved:

$$\left(\frac{\partial^2}{\partial x^2} - \frac{\partial^2}{c^2 \partial t_\Sigma^2} \right) E_{pr}(x, t_\Sigma) = \frac{4\pi}{c^2} \frac{\partial^2}{\partial t_\Sigma^2} (P^{(L)}(x, t_\Sigma) + P^{(NL)}(x, t_\Sigma)). \quad (5.10)$$

Since the probe field is assumed to be weak, induced nonlinear polarization terms $P^{(NL)}(x, t_\Sigma)$ can be neglected and the linear polarization response $P^{(L)}(x, t_\Sigma)$ equals in good approximation $P^{(1)}(x, t_\Sigma)$, shown in Eq. 5.9. The wave equation can be solved easier in its Fourier representation. Thus, the Fourier descriptions of $E_{pr}(x, t_\Sigma)$ and $P^{(1)}(x, t_\Sigma)$ are:

$$E_{pr}(x, t_\Sigma) = \frac{1}{2\pi} \int_0^\infty \tilde{E}_{pr}(x, \omega) e^{-i\omega(t_\Sigma - x/c)} + c.c. d\omega \quad (5.11)$$

$$P^{(1)}(x, t_\Sigma) = \frac{1}{2\pi} \int_0^\infty \tilde{P}^{(1)}(x, \omega) e^{-i\omega(t_\Sigma - x/c)} + c.c. d\omega \quad (5.12)$$

and after Fourier transformation the wave equation Eq. 5.10 converts into

$$\frac{\partial^2}{\partial x^2} \tilde{E}_{pr}(x, \omega) + \frac{2i\omega}{c} \frac{\partial}{\partial x} \tilde{E}_{pr}(x, \omega) = -\frac{4\pi\omega^2}{c^2} \tilde{P}^{(1)}(x, \omega), \quad (5.13)$$

where the first term on the left-hand side can be neglected if we employ the slowly varying amplitude approximation.

The wave equation can be analytically solved if the polarization response $\tilde{P}^{(1)}(x, \omega)$ is proportional to the probe field $\tilde{E}_{pr}(x, \omega)$ and therefore the introduction of a linear susceptibility $\chi(x, \omega)$ is justified. In order to proof the applicability of a linear susceptibility, it is necessary to explicitly calculate $\tilde{P}^{(1)}(x, \omega)$. Here, it is sufficient to limit the Fourier transformed result to positive frequencies since $\tilde{P}^{(1)}(x, -\omega) = \tilde{P}^{(1)}(x, \omega)^*$ and to assume a certain lifetime and corresponding decay rate Γ_f of the final state $|f\rangle$. The polarization response in the Fourier domain yields:

$$\tilde{P}^{(1)}(x, \omega > 0) = in_0 \sum_{i,i'} \alpha_i^* \alpha_{i'} \sum_f \langle \varphi_i | \hat{\mathcal{Z}} | f \rangle \langle f | \hat{\mathcal{Z}} | \varphi_{i'} \rangle \cdot \left[\frac{1}{E_{i'} - E_f - i\Gamma_f/2 - \omega} \right] \tilde{E}_{pr}(x, \omega + E_i - E_{i'}) \quad (5.14)$$

This shows that the polarization response is not proportional to the probe field and therefore in general an introduction of a linear susceptibility is not possible and hence the wave

equation has to be solved numerically. However, under certain circumstances it is still possible to have a linear relation between the polarization response and the electric field. In order to understand those cases in which we can assume that $\tilde{E}_{pr}(x, \omega + E_i - E_{i'}) \approx \tilde{E}_{pr}(x, \omega)$, the physical meaning of Eq. 5.14 will be discussed.

Fig. 5.2 shows a typical Λ -scheme where the states $|\varphi_i\rangle$ and $|\varphi_{i'}\rangle$ are coherently populated. The polarization response $\tilde{P}(x, \omega_2)$ at frequency ω_2 does not only depend on $\tilde{E}_{pr}(x, \omega_2)$ but also on $\tilde{E}_{pr}(x, \omega_1)$ since the states $|\varphi_i\rangle$ and $|\varphi_{i'}\rangle$ are in a coherent superposition and the wavepacket undergoes a periodic modulation with the period T_{wp} which is direct proportional to the energy spacing ΔE between the coherently populated states. If the time scale

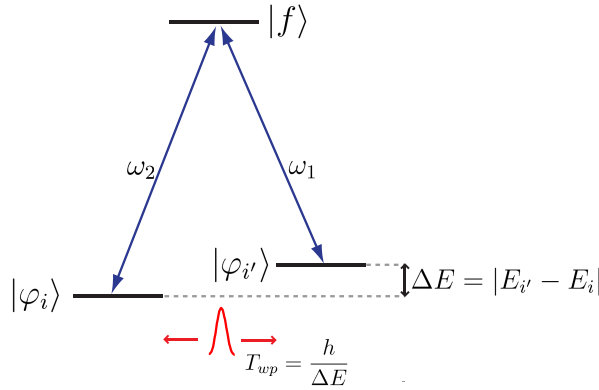


Figure 5.2: Explanation of the $\tilde{E}_{pr}(x, \omega + E_i - E_{i'})$ -dependence of the polarization response (see Eq. 5.14). Assuming that the states $|\varphi_i\rangle$ and $|\varphi_{i'}\rangle$ are coherently coupled, the polarization response of the system at ω_2 does depend on the probe field at ω_2 and ω_1 .

of the absorption process is substantially shorter than T_{wp} (the pulse duration τ_{pr} of E_{pr} is significantly shorter than T_{wp}) or in the short probe pulse limit, where the probe field can be described as a Dirac pulse, this effect can be neglected.

In view of the conducted experiments where the pulse duration of the probe pulse was less than 200 asec, the approximation of the probe field as a delta function centered at $t = \tau$ is justified. In the frequency-domain this yields:

$$\tilde{E}_{pr}(x, \omega - E_{i'} + E_i) = \tilde{E}_0(x) e^{i(\omega - E_{i'} + E_i)t} \quad (5.15)$$

and applying the short pulse approximation, Eq. 5.14 can be written as

$$\tilde{P}^{(1)}(x, \omega > 0, \tau) = in_0 \sum_{i, i'} \alpha_i^*(\tau) \alpha_{i'}(\tau) \sum_f \frac{\langle \varphi_i | \hat{\mathcal{Z}} | f \rangle \langle f | \hat{\mathcal{Z}} | \varphi_{i'} \rangle}{E_{i'} - E_f - i\Gamma_f/2 - \omega} \cdot \tilde{E}_0(x) e^{i\omega\tau} \quad (5.16)$$

where $\alpha_i(\tau)$ are the time-dependent expansion coefficients. Now the linear susceptibility $\chi^{(1)}$ can be introduced and reads:

$$\begin{aligned}\chi^{(1)}(\omega > 0) &= \frac{\tilde{P}^{(1)}(x, \omega)}{\tilde{E}_{pr}(x, \omega)} \\ &= n_0 \sum_{i, i'} \alpha_i^*(\tau) \alpha_{i'}(\tau) \sum_f \frac{\langle \varphi_i | \hat{Z} | f \rangle \langle f | \hat{Z} | \varphi_{i'} \rangle}{E_{i'} - E_f - i\Gamma_f/2 - \omega}.\end{aligned}\quad (5.17)$$

Utilizing the validity of the introduction of a susceptibility, the wave equation (see Eq. 5.10) can be solved analytically if the slowly varying amplitude approximation is employed. The solution is:

$$\tilde{E}_{pr}(x, \omega) = \tilde{E}_{pr}(x_0, \omega) e^{2\pi i \omega / c \int_{x_0}^x \chi^{(1)}(x', \omega) dx'}.\quad (5.18)$$

Expressing the solution in terms of the experimentally relevant intensity $\tilde{I}_{pr}(x, \omega)$ of the probe field yields

$$\tilde{I}_{pr}(L, \omega) = \tilde{I}_{pr}(0, \omega) e^{-4\pi \omega / c \int_0^L \text{Im}[\chi^{(1)}(x', \omega)] dx'},\quad (5.19)$$

where L is the length of the interaction volume. For a homogeneous target medium and the introduction of the single-photon absorption cross section

$$\sigma^{(1)}(\omega) = 4\pi\omega / (c n_0) \text{Im}[\chi^{(1)}(\omega)],\quad (5.20)$$

Eq. 5.19 results in the well-known Lambert Beer's law. At this point it should be mentioned that the validity of Lambert Beer's law relies on the condition that in the presence of a coherently populated ensemble of state the probing time (pulse duration of the probe pulse) is substantially shorter than the coherent electronic dynamics which evolve within the electronic structure of the target medium.

5.1.3 Absorption by laser generated ions - the density matrix description

In view of the availability of short and powerful laser pulses which can be used as the probe pulse, the creation of higher charged states in the atomic ensemble is very likely. In this case neutral atoms as well as the created ions will encode strong characteristic absorption features onto the spectrum of the probe pulse. For electronic systems which undergo an ionization upon the interaction with a strong pump laser field, the description of the polarization response can be described in terms of Slater determinants and the mean-field model [104], [106]. For the general description of the electronic structure problem, the ansatz $|\Psi_{pu}(t)\rangle = \sum_i \alpha_i e^{-i(E_i - E_0)t} |\varphi_i\rangle$ was utilized. Expressing $|\Psi_{pu}(t)\rangle$ in terms of Slater determinants gives:

$$|\Psi_{pu}(t)\rangle = \alpha_0 |\Phi_0\rangle + \sum_i \sum_a \alpha_i^a e^{i(E_a - E_i)t} |\Phi_i^a\rangle\quad (5.21)$$

where $|\Phi_0\rangle$ is the ground state determinant and all particle hole configurations $|\Phi_i^a\rangle$ which are obtained by exciting or ionizing an electron from spin orbital i (hole orbital) to an unoccupied spin orbital a (particle). The energies of the spin orbitals are denoted by E_i and E_a . Substituting ansatz Eq. 5.21 into Eq. 5.7 and following the same steps of the earlier shown derivation gives an expression for the polarization response which consists of several terms that describe the absorption of E_{pr} by neutral ground state atoms and strong field created ions. An explicit display of this polarization response would exceed the scope of this work. However, an exemplary description of the polarization response - especially in view of the conducted experiments - of a gas target where the probe pulse only undergoes absorption by singly charged ions will be given. Furthermore it shall be assumed that the probe pulse only triggers hole-hole transitions which means that a core shell electron is excited into the vacancy in the valence shell of the singly charged atomic species A^+ .

The NIR generated photoelectrons (particles) can be either slightly bound or in the continuum. If they are free photoelectrons they cannot absorb EUV photons. If they still feel the ionic potential, they can absorb EUV photons. However the cross-section for this process is very low and therefore it is a good approximation to assume that the pump field generated photoelectrons do not interact with the probe field. In the particle-hole terminology this would translate into the disregard of EUV initiated particle-particle transitions.

Since the electron excited or ionized by the pump pulse is a spectator of the hole-hole transition of the ion core, it is very convenient to describe the A^+ ions with a reduced density matrix formalism [106]:

$$\rho_{ii'}^{(A^+)}(t) = e^{i(E_i - E_{i'})t} \sum_a \alpha_i^a \alpha_{i'}^{a*} = e^{i(E_i - E_{i'})t} \tilde{\rho}_{ii'}^{(A^+)}. \quad (5.22)$$

The diagonal elements of the density matrix $\tilde{\rho}_{ii}$ are the probabilities of the corresponding ionic states. The non-zero off-diagonal elements are related to the possibility of observing quantum beats; therefore we will refer to them as coherences.

Considering the temporal regime where pump and probe pulse do not temporally overlap, the matrix $\tilde{\rho}_{ii'}^{(A^+)}$ can be considered as time independent. This results in the following polarization response:

$$\tilde{P}^{(1,A^+)}(x, \omega > 0) = n_0 \sum_{i,i'} \tilde{\rho}_{ii'}^{(A^+)} \sum_f \frac{\mu_{fi'} \mu_{if}}{E_{i'} - E_f - i\Gamma_f/2 - \omega} \cdot \tilde{E}_{pr}(x, \omega + E_i - E_{i'}). \quad (5.23)$$

The dipole matrix element μ_{if} describes the filling of a hole in spin orbital i with an electron from spin orbital f and $\mu_{fi'}$ depicts the process which fills the hole created in f with an electron from orbital i' . Finally the general linear susceptibility shown in Eq. 5.17 yields for singly charged ionic absorbers A^+ , the validity of the short pulse approximation and considering only hole-hole transitions in the reduced density matrix formalism:

$$\chi^{(1,A^+)}(\omega > 0, \tau) = n_0 \sum_{i,i'} \tilde{\rho}_{ii'}^{(A^+)}(\tau) \sum_f \frac{\mu_{fi'} \mu_{if}}{E_{i'} - E_f - i\Gamma_f/2 - \omega}. \quad (5.24)$$

It should be emphasized that the wavefunction $|\Psi_{pu}(t)\rangle$ (Eq. 5.21), which describes the electronic structure problem after interaction with the pump laser pulse, is composed of the wavefunctions of the bound and free electrons, whereas the description of the problem with a reduced density matrix allows to describe a coherent superposition of ionic states without explicitly considering the free electrons. This is in fact the reason for naming it *reduced* density matrix formalism.

In the next section an explicit description of the single-photon absorption cross section of krypton singly-charged ions will be given, to describe one of the performed attosecond transient absorption experiments where a few cycle NIR laser pulse was used as the pump pulse and a delayed attosecond XUV pulse probed the strong field created ionic ensemble.

5.2 Real-time observation of valence electron motion in Kr^+

5.2.1 Theoretical modeling of XUV absorption by Kr^+ ions

Several reported experiments document that strong-field ionization of neutral gas atoms by short laser pulses populates not only the ground state but also excited electronic states of the emerging ions. For instance, experiments detecting photoelectrons after the multi-photon ionization of xenon atoms proof the creation of Xe^+ ions in the $^2P_{3/2}$ ground and $^2P_{1/2}$ excited state [107]. Further experiments, carried out at substantially higher laser

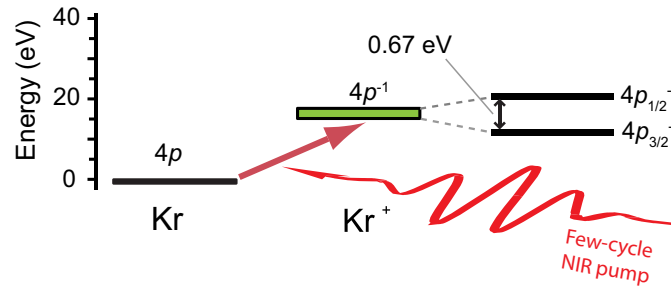


Figure 5.3: The exposure of Kr atoms to a strong, low-frequency laser field creates singly charged ions in their ground and first excited manifold.

intensities where ion yields of highly charged krypton ions are observed, show indications of this claim [72]. Also investigations addressing the state-resolved detection of ions by photoabsorption of x-ray pulses in Kr^+ [22] or of EUV radiation in Xe^+ [23] provide clear evidence for the simultaneous population of ground and excited states of strong-field generated atomic ions. A demonstrative explanation for this observation would be that an ultrashort strong laser pulse at sufficient intensity tunnel-ionizes all noble gas atoms (excluding He) by pulling an electron out of the valence p_z orbital, where z indicates the

laser polarization axis. Such a noble-gas ion which inherits a hole in the valence p_z orbital is not anymore in an eigenstate but rather in a superposition of different quantum states [106]. For instance, exposure of Kr atoms to a strong, low-frequency laser field is expected to generate Kr^+ ions predominantly in their $4p_{j=3/2}^{-1}$ ground-state manifold and the $4p_{j=3/2}^{-1}$ excited-state manifold, comprising four ($m_{j=3/2} = \pm 3/2, \pm 1/2$) and two ($m_{j=1/2} = \pm 1/2$) states, respectively (j denotes the total angular momentum; m_j denotes its projection on the z axis) as shown in Fig. 5.3. The fine-structure (or spin-orbit) energy splitting between the two manifolds is $\Delta E_{SO} = 0.67$ eV [108]. However, the critical and very exciting question is whether they can be populated coherently during strong-field ionization as to allow the creation of subsequent wavepacket motion in the valence shell [109]. This important question is addressed in the next paragraph.

The reduced density matrix of interest for Kr^+

In order to address the question posed above, the strong field ionization has been numerically modeled [104]. As introduced in section 5.1.3, the description of this underlying problem can be described very conveniently by utilizing the reduced density matrix approach which allows the description of a coherent superposition of ionic states without explicitly considering the free electrons. Let us denote a stationary ionic state $\psi_\lambda^{(bound)}$, where the index λ incorporates all the quantum numbers specifying the state. The free-electron wave that corresponds to this state will be denoted by $\psi_\lambda^{(free)}$. While the interaction between the bound and free electrons becomes negligible shortly after the ionization, the correlation, in general, remains. This makes it impossible to disregard free electrons in the wave function description. Instead, a wave function describing a coherent superposition of ionic states should be written as $|\Psi(t)\rangle = \sum_\lambda |\psi_\lambda^{(bound)}, \psi_\lambda^{(free)}(t)\rangle e^{-iE_\lambda t}$, where E_λ is the energy of the state $\psi_\lambda^{(bound)}$. In section 5.1.3 the polarization response based on the absorption of a probe pulse was expressed by using the density matrix. In order to show that the density matrix indirectly describes a quantity which is related solely to the free electrons, the dipole response should be written down for the wave function $|\Psi(t)\rangle$. The dipole response $d(t)$ of a single ion can be written as

$$d(t) = \langle \Psi(t) | \hat{\mathcal{Z}} | \Psi(t) \rangle = \sum_{\lambda, \mu} \langle \psi_\mu^{(bound)}, \psi_\mu^{(free)}(t) | \hat{\mathcal{Z}} | \psi_\lambda^{(bound)}, \psi_\lambda^{(free)}(t) \rangle e^{-i(E_\lambda - E_\mu)t}.$$

In the case of resonant absorption, the dipole operator $\hat{\mathcal{Z}}$ only acts on bound electrons. Hence, the last expression can be written as:

$$d(t) = \sum_{\lambda, \mu} \rho_{\lambda\mu}(t) \langle \psi_\mu^{(bound)} | \hat{\mathcal{Z}} | \psi_\lambda^{(bound)} \rangle.$$

Therefore the elements of the reduced density matrix can also be viewed as a scalar product of the free-electron wave functions:

$$\rho_{\lambda\mu}(t) = \langle \psi_\mu^{(free)}(t) | \psi_\lambda^{(free)}(t) \rangle e^{-i(E_\lambda - E_\mu)t}. \quad (5.25)$$

Eq. 5.25 leads to two important consequences. In the conducted experiment, the ion density matrix must be diagonal with respect to M_{ion} , which is the projection of the ion angular momentum on the laser polarization. Indeed, a krypton atom in its ground state has $M = 0$, where M is the projection quantum number of the total angular momentum, and this number is conserved during the interaction with the linearly-polarized NIR pulse. As a consequence, $M_{ion} = -m_{free}$ for each ionization channel, where m_{free} is the angular momentum projection quantum number of the free electron. This leads to a second consequence. Since any two wave functions with different m_{free} values are orthogonal to each other, $\rho_{\lambda\mu}(t)$ can only be non-zero if the states denoted by the indices λ and μ have the same value of M_{ion} .

The reduced density matrix $\hat{\rho}$ of interest for the Kr^+ description is a 6-by-6 matrix. This is because there are six ion states that are of relevance. The individual elements will be denoted as $\rho_{j,j'}^{(m_j)}$. The diagonal matrix elements $\rho_{j,j}^{(m_j)}$ denote the population of the individual quantum states and the off-diagonal matrix elements are referred to as coherences if they are non-vanishing.

Quantities related to the reduced density matrix

Several definitions based on the density matrix elements will be frequently used and are introduced at this point.

The quantity $C(t)$

$$C(t) = \sqrt{\rho_{3/2,3/2}^{(1/2)}(t) \cdot \rho_{1/2,1/2}^{(1/2)}(t)}$$

is referred to as the **pure state coherence**, which means that if the superposition is in a pure state, then the absolute value of the off-diagonal matrix element of the reduced density matrix $\rho_{3/2,1/2}^{(1/2)}$ would equal the pure state coherence C . It is the maximum achievable coherence.

In order to describe quantitatively the degree to which this maximum is reached, the **degree of coherence** $\gamma(t)$ is defined, which normalizes $|\rho_{3/2,1/2}^{(1/2)}|$ to the pure state coherence:

$$\gamma(t) = \frac{|\rho_{3/2,1/2}^{(1/2)}(t)|}{\sqrt{\rho_{3/2,3/2}^{(1/2)}(t) \cdot \rho_{1/2,1/2}^{(1/2)}(t)}}.$$

Perfect coherence corresponds to $\gamma=1$, whereas incoherent superpositions yield $\gamma=0$.

The **alignment** Θ is defined by the following asymmetry parameter

$$\Theta = \frac{\rho_{3/2,3/2}^{(1/2)} - \rho_{3/2,3/2}^{(3/2)}}{\rho_{3/2,3/2}^{(1/2)} + \rho_{3/2,3/2}^{(3/2)}}.$$

If the alignment equals zero, the populations of the two states are the same and the hole density is spherical. For non-vanishing alignment, the hole density is non-spherical, even if averaging over the fast electron dynamics for a non-zero coherence is taken into account.

Ab-initio modeling of strong-field ionization

The interaction of Kr atoms with a strong laser field was ab-initio modeled as described in detail in [106]. Solving the time-dependent Schrödinger equation for a few-cycle ionizing NIR field, linearly polarized along the quantization axis, yields the evolution of the density matrix elements as depicted in Fig. 5.4 a).

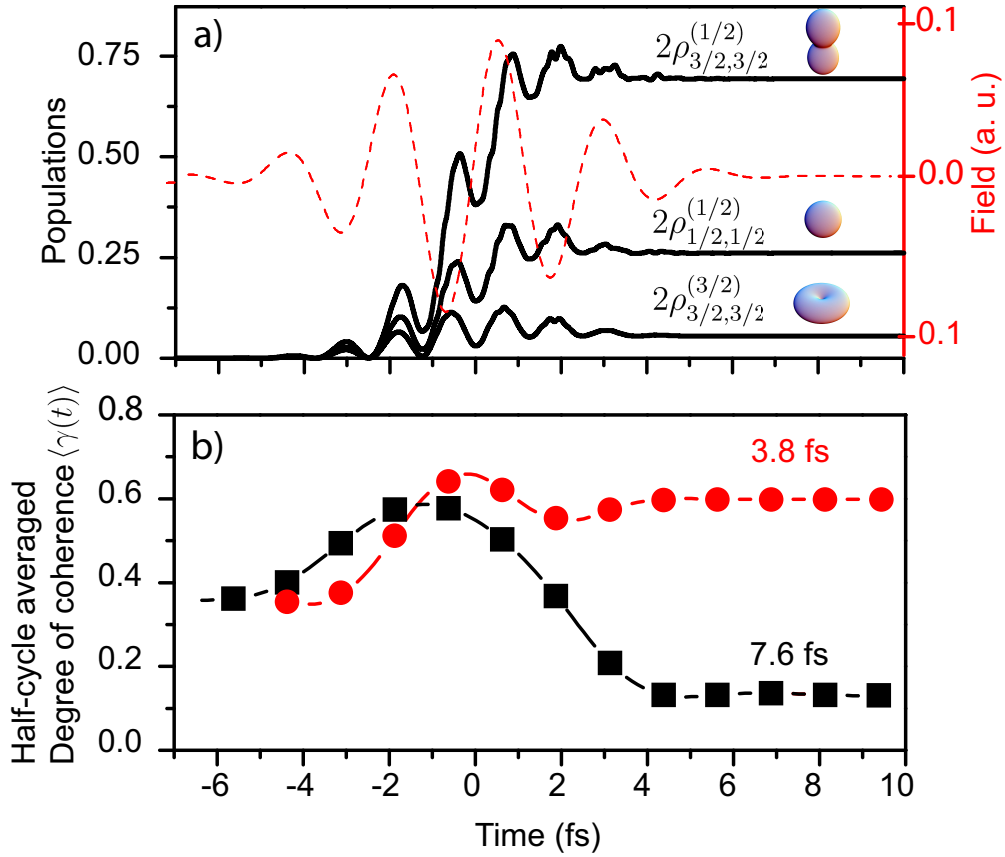


Figure 5.4: Build-up of the electronic coherence in Kr^+ produced by optical field ionization (theory). **a)**, Temporal evolution of the diagonal elements of the reduced density matrix of Kr^+ in the presence of a 750 nm, 3.8 fs laser pulse with a peak intensity of $\sim 3 \cdot 10^{14} \text{ W/cm}^2$ and a sinusoidal waveform (dashed line). The notation of the matrix elements is explained in the text. Hole density distributions of the corresponding orbitals of the $4p$ subshell are also depicted. **b)**, The degree of coherence, $\gamma(t)$, averaged over time intervals of the laser half-cycle (~ 1.25 fs), is shown with red dots for the 3.8 fs driving laser pulse. Squares show the half-cycle-averaged degree of coherence for an ionizing laser pulse with a duration of 7.6 fs at the same peak intensity.

By the end of the laser pulse ($t > 3$ fs), $\sim 30\%$ of the atoms are ionized, with a hole emerging in the $(4p_j, m_j)$ or $(4p_j, -m_j)$ orbital with a relative population of $\rho_{3/2,3/2}^{(1/2)} + \rho_{3/2,3/2}^{(-1/2)} = 2\rho_{3/2,3/2}^{(1/2)} = 0.69$, $\rho_{1/2,1/2}^{(1/2)} + \rho_{1/2,1/2}^{(-1/2)} = 2\rho_{1/2,1/2}^{(1/2)} = 0.26$ and $\rho_{3/2,3/2}^{(3/2)} + \rho_{3/2,3/2}^{(-3/2)} = 2\rho_{3/2,3/2}^{(3/2)} = 0.05$. The populations have been normalized such that the trace of the reduced density matrix at $\tau=10$ fs equals one. The hole populations increase in subfemtosecond steps near the oscillation peaks of the ionizing laser field as depicted by the dashed line. As mentioned earlier, it follows from Eq. 5.25, that only states with the same value of m_j can form a coherent superposition state characterized by a non-zero value of the corresponding off-diagonal element of the density matrix. In the current case, this condition is fulfilled by the $(4p_{3/2}^{-1}, m_j = \pm 1/2)$ and $(4p_{1/2}^{-1}, m_j = \pm 1/2)$ states [106]. In Fig. 5.4 b) the half-cycle-averaged $\gamma(t)$ for pulse durations of 3.8 fs and 7.6 fs (FWHM of the intensity envelope) are plotted. The evolution of coherence shown in Fig. 5.4 b) can be understood intuitively. At every intense wave crest, a fraction of the atoms is ionized and a hole spin-orbit wavepacket is launched in the $4p^{-1}$ valence subshell by populating the $4p^{-1}$ manifold. Spin-orbit wavepackets launched in ions that are generated at a given wave crest have a fairly well-defined phase with respect to the wave crest and evolve with a half-period of 3.1 fs. As a consequence, their phase has changed by 0.4π by the time the next wave crest arrives (after one half of the laser period, $T_L/2 = 1.25$ fs), such that ions produced at this wave crest are phase-shifted with respect to the ions generated previously. In the case of a 3.8-fs pulse, ionization is confined to two to three wave crests, that is, to within a single laser period. Therefore, the final population of the $4p^{-1}$ manifold builds up within less than the 3.1-fs half-period, ensuring that the ions produced at the individual wave crests are substantially in phase. This gives rise to a final ion ensemble with a high degree of coherence ($\gamma \approx 0.6$). By contrast, in the 7.6 fs-pulse, the build-up of $4p^{-1}$ population takes longer, leading to a wider distribution of relative phases among the ions created and, hence, to a strongly reduced degree of coherence of the ion ensemble ($\gamma \approx 0.13$). The detailed behavior of the degree of coherence during ion formation is not yet understood. So far, our ab-initio simulations reveal that in the absence of a tunable excitation period, the creation of a persisting electronic coherence critically relies on the confinement of excitation to a time interval that is comparable to the characteristic timescale of the resultant wavepacket motion. These simulations also reveal that field ionization by multicycle pulses [29] generally creates incoherent ion ensembles.

Analytical expression for XUV absorption

When a coherent broadband XUV probe promotes the system from the components of its superposition state into a common final state, quantum interference leads to a temporal modulation of the transition probability: its depth is indicative for the degree of coherence of the probed superposition state, and its variation with pump-probe delay reveals the temporal evolution of the system. In our case, strong-field ionization is predicted to create a hole superposition in the $4p_{j=3/2}^{-1}$ ground-state manifold and the $4p_{j=1/2}^{-1}$ excited-state manifold of Kr^+ ions (Fig. 5.5). A broadband pulse carried at a central frequency of

~ 80 eV promotes the ions from these states—by means of dipole allowed transitions—into the $3d_{3/2}^{-1}$ manifold by creating a core-level vacancy. A transition from the $4p_{j=3/2}^{-1}$ state to the $3d_{5/2}^{-1}$ state is also possible, but the $4p_{1/2}^{-1} \rightarrow 3d_{5/2}^{-1}$ transition is forbidden by electric dipole selection rules.

Based on the expression for $\chi^{(1)}(\omega)$ for ions (Eq. 5.24), the definition of the single-photon XUV absorption $\sigma^{(1)}(\omega)$ (Eq. 5.20), the electric dipole allowed transitions shown in Fig. 5.5 and by only considering hole-hole transitions and limiting the interaction between the XUV probe pulse and the target ions to delays, where the XUV pulse interacts with the ions after the NIR pulse has passed the target medium, an analytical expression for the expected single-photon absorption cross-section of the Kr^+ ions can be derived, which is limited to states relevant for the experiment and utilizes the short pulse approximation:

$$\begin{aligned} \sigma^{(1,Kr^+)}(\omega, \tau) = 4\pi \frac{\omega}{c} \text{Im} \left\{ \frac{|\langle 4p_{3/2}^{-1} || \mathcal{D} || 3d_{5/2}^{-1} \rangle|^2}{\Delta E_{(4p_{3/2}^{-1} \rightarrow 3d_{5/2}^{-1})} - i\frac{\Gamma_{3d}}{2} - \omega} \left(\rho_{3/2,3/2}^{(3/2)} \frac{2}{15} + \rho_{3/2,3/2}^{(1/2)} \frac{1}{5} \right) + \right. \\ \frac{|\langle 4p_{3/2}^{-1} || \mathcal{D} || 3d_{3/2}^{-1} \rangle|^2}{\Delta E_{(4p_{3/2}^{-1} \rightarrow 3d_{3/2}^{-1})} - i\frac{\Gamma_{3d}}{2} - \omega} \left(\rho_{3/2,3/2}^{(3/2)} \frac{3}{10} + \rho_{3/2,3/2}^{(1/2)} \frac{1}{30} \right) + \\ \frac{|\langle 4p_{1/2}^{-1} || \mathcal{D} || 3d_{3/2}^{-1} \rangle|^2}{\Delta E_{(4p_{1/2}^{-1} \rightarrow 3d_{3/2}^{-1})} - i\frac{\Gamma_{3d}}{2} - \omega} \cdot \rho_{1/2,1/2}^{(1/2)} \frac{1}{3} + \\ \frac{\langle 4p_{3/2}^{-1} || \mathcal{D} || 3d_{3/2}^{-1} \rangle \langle 4p_{1/2}^{-1} || \mathcal{D} || 3d_{3/2}^{-1} \rangle}{3\sqrt{10}} \cdot \\ \left. \left(\frac{\rho_{3/2,1/2}^{(1/2)}(\tau)}{\Delta E_{(4p_{1/2}^{-1} \rightarrow 3d_{3/2}^{-1})} - i\frac{\Gamma_{3d}}{2} - \omega} + \frac{\rho_{3/2,1/2}^{(1/2)}(\tau)^*}{\Delta E_{(4p_{3/2}^{-1} \rightarrow 3d_{3/2}^{-1})} - i\frac{\Gamma_{3d}}{2} - \omega} \right) \right\}. \quad (5.26) \end{aligned}$$

Here, the delay between the NIR and XUV pulse is denoted by τ , the transition energies of the dipole allowed transitions by $\Delta E_{(4p_j^{-1} \rightarrow 3d_{j'}^{-1})}$ that can be calculated using the multiconfiguration Dirac-Fock program package GRASP92 [110] or the COWAN atomic structure code [111] (introduced in chapter 5.6.1) which yield $\Delta E_{(4p_{3/2}^{-1} \rightarrow 3d_{5/2}^{-1})} = 79.8$ eV, $\Delta E_{(4p_{3/2}^{-1} \rightarrow 3d_{3/2}^{-1})} = 81.1$ eV and $\Delta E_{(4p_{1/2}^{-1} \rightarrow 3d_{3/2}^{-1})} = 80.4$ eV.

Furthermore, the transition matrix elements are determined and yield $|\langle 4p_{3/2}^{-1} || \mathcal{D} || 3d_{5/2}^{-1} \rangle|^2 = 0.119$ a.u., $|\langle 4p_{3/2}^{-1} || \mathcal{D} || 3d_{3/2}^{-1} \rangle|^2 = 0.0126$ a.u., $|\langle 4p_{1/2}^{-1} || \mathcal{D} || 3d_{3/2}^{-1} \rangle|^2 = 0.0695$ a.u. and $\langle 4p_{3/2}^{-1} || \mathcal{D} || 3d_{3/2}^{-1} \rangle \langle 4p_{1/2}^{-1} || \mathcal{D} || 3d_{3/2}^{-1} \rangle = -0.0296$. The j -independent decay width of the $3d$ hole is $\Gamma_{3d} = 88$ meV [112]. Since only delays are considered where the XUV pulse proceeds the NIR field, the diagonal matrix elements of the density matrix do not depend on the delay since their population is formed only within the NIR pulse and stay unchanged until the XUV probe pulse arrives. Fractional coefficients like $\frac{2}{15}, \frac{1}{5}, \dots$ are originating from Clebsch-Gordan coupling coefficients of quantum mechanical angular momenta.

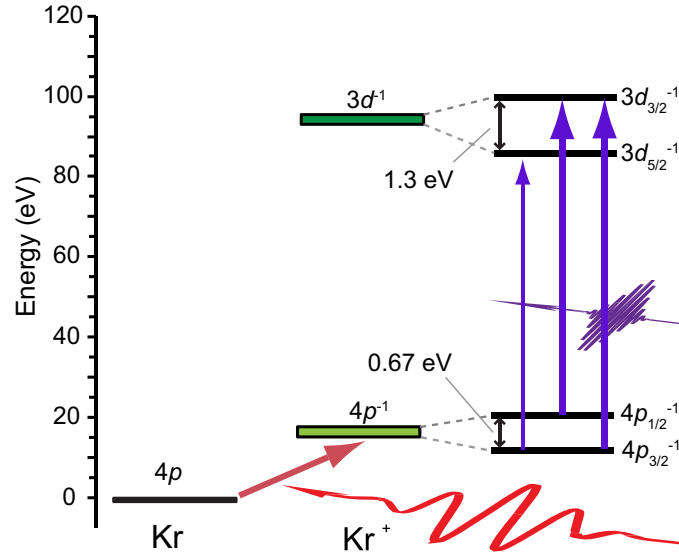


Figure 5.5: Energy-level diagram showing the spin-orbit splitting of the $4p$ and $3d$ subshells in Kr^+ . A sub-4-fs NIR laser pulse (red wave) liberates an electron from the $4p$ subshell and leaves the ensemble of ions in a coherent superposition of $4p_{3/2}^{-1}$ and $4p_{1/2}^{-1}$ states. Single-photon XUV absorption promotes the ions from these states to the core-excited $3d_{3/2}^{-1}$ state.

Simulated attosecond absorption spectrogram

Based on the derived single-photon XUV absorption cross-section as a function of pump-probe delay (Eq. 5.26) and the evolution of the density matrix elements shown in Fig. 5.4, the expected absorption cross-section of Kr^+ as a function of pump-probe delay is presented in Fig. 5.6 a) for the simulation parameters given in Fig. 5.4. The high degree of coherence of $\gamma=0.6$ between the $4p_{1/2}^{-1}$ and $4p_{3/2}^{-1}$ states is predicted to translate into a modulation of the absorption cross-sections as a function of pump-probe delay for the $4p_{3/2}^{-1} \rightarrow 3d_{3/2}^{-1}$ and $4p_{1/2}^{-1} \rightarrow 3d_{3/2}^{-1}$ transitions owing to a temporal variation of the relative phase between the $4p_{1/2}^{-1}$ and $4p_{3/2}^{-1}$ states. The periodicity of the modulation of 6.2 fs originates from the LS splitting which amounts to 0.67 eV as mentioned earlier. The modulation is most pronounced in the weaker $4p_{3/2}^{-1} \rightarrow 3d_{3/2}^{-1}$ and is absent from the $4p_{3/2}^{-1} \rightarrow 3d_{5/2}^{-1}$ transition, which is insensitive to the quantum superposition since the $4p_{1/2}^{-1} \rightarrow 3d_{5/2}^{-1}$ transition is electric dipole forbidden.

Visualization of hole-density dynamics after the NIR laser pulse

It was shown that the spin-orbit wavepacket motion is expected to translate into a conspicuous modulation of the absorption cross-section of the $4p_{3/2}^{-1} \rightarrow 3d_{3/2}^{-1}$ and $4p_{1/2}^{-1} \rightarrow 3d_{3/2}^{-1}$ transitions as shown in Fig. 5.6 a). An interesting question, which can be raised, is how

the spatial propagation of the launched wavepacket evolves in time after the NIR pulse has triggered the motion. Theoretical investigation of this issue by our co-workers [106] has shown that the hole density $\mathcal{Q}(\vec{r}, \tau)$ as a function of delay τ has a radially and angularly varying contribution:

$$\mathcal{Q}(\vec{r}, \tau) = R(r) \cdot h(\theta, \varphi, \tau)$$

Since the radial contribution is isotropic and does not depend on the delay, only the second part can be considered to show the angular hole-density distribution which can be expressed in terms of density matrix elements [106] and yields

$$\begin{aligned} h(\theta, \varphi, \tau) = & \frac{1}{2}\rho_{3/2,3/2}^{(3/2)}\sin^2(\theta) + \frac{1}{2}\rho_{3/2,3/2}^{(1/2)}\left(\cos^2(\theta) + \frac{1}{3}\right) + \frac{1}{3}\rho_{1/2,1/2}^{(1/2)} \\ & + \sqrt{2}|\rho_{3/2,1/2}^{(1/2)}|\cos\left(2\pi\frac{\tau}{T_{(SO)}} + \delta\right)\left(\frac{1}{3} - \cos^2(\theta)\right) \end{aligned} \quad (5.27)$$

where $T_{(SO)}$ is the spin-orbit period and δ a phase offset at $\tau = 0$ of the quantum phase between the $4p_{3/2}^{-1}$ and $4p_{1/2}^{-1}$ states. Strictly speaking, the hole density which is defined here, depends only on the time τ and on the angle θ , which is the polar angle with respect to the laser polarization axis. Therefore, the hole density is azimuthally symmetric with respect to the polarization vector of the NIR pump field. A three dimensional visualization of the hole density motion will be shown in section 5.3.2 together with the experimental absorption trace.

5.2.2 Attosecond transient absorption spectrograms addressing Kr^+

Performing an attosecond transient absorption measurement as described before and utilizing the experimental setup presented in section 4.2 and Fig. 4.1 c) we created Kr^+ ions with sub 4-fs NIR waveform controlled laser pulses at a central wavelength of around 750 nm. The utilized laser pulse intensity of $3 \cdot 10^{14} \frac{\text{W}}{\text{cm}^2}$ leads to the creation of ions and electronic dynamics within the valence subshell of the Kr ions which we probed with isolated sub-150 as XUV pulses carried at 80 eV. The target density of krypton atoms is 10^{18} cm^{-3} . The experimental data shown in Fig. 5.6 b) comprises 40 transient absorption spectra recorded at delays increased in steps of 1 fs. Absorbance is defined as

$$A(\omega, \tau) = \ln(I_0(\omega, \tau)/I_{trans}(\omega, \tau)) \quad (5.28)$$

where $I_0(\omega, \tau)$ is the spectral density recorded at a negative delay of -6 fs, that is, the attosecond probe precedes the ionizing laser pulse by 6 fs in the atomic sample, and $I_{trans}(\omega, \tau)$ the spectral density recorded at a pump-probe delay τ . The absorption spectrum plotted in the background is taken at a delay of 30 fs. The linewidths are determined by the ~ 0.45 eV resolution of our XUV spectrometer. Fig. 5.6 b) clearly shows the predicted consequences of the wavepacket motion described by Eq. 5.26, including the deep amplitude modulation of the $4p_{3/2}^{-1} \rightarrow 3d_{3/2}^{-1}$ absorption line as well as the energy

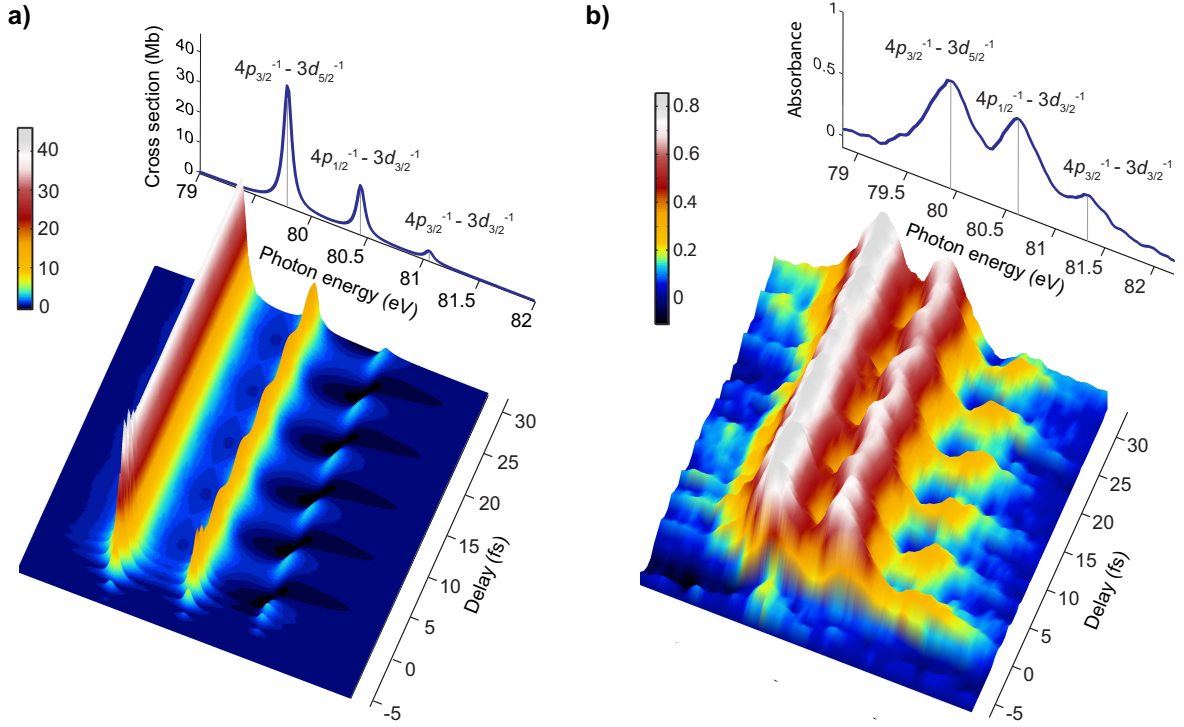


Figure 5.6: **a)** Ab-initio-simulated transient XUV absorption spectra reveal characteristic modulations present in two of the three transitions of Kr^+ as functions of pump-probe delay. The modulation depth is highly sensitive to the degree of coherence γ . **b)** False-color plot of a measured attosecond absorption spectrogram in Kr^+ reveals characteristic modulations present in the $4p_{3/2}^{-1} \rightarrow 3d_{3/2}^{-1}$ and $4p_{1/2}^{-1} \rightarrow 3d_{3/2}^{-1}$ transitions which are a direct observation of valence electron motion - being in good agreement with theoretical predictions shown in panel a).

modulation of the lines, with the latter resulting from absorptive and dispersive terms in the transient absorption cross-section. Fig. 5.6 a) shows the expected ab-initio simulated absorption spectrum obtained for experimental parameters.

The lower modulation depth in our experimental data set of the $4p_{1/2}^{-1} \rightarrow 3d_{3/2}^{-1}$ transition relative to the calculation shown in panel a) of Fig. 5.6 is a result of the spectral resolution being limited in comparison with the ~ 88 meV natural linewidth of the studied transitions. The zero of the delay scale is set to coincide with the instant when the main $4p_{3/2}^{-1} \rightarrow 3d_{5/2}^{-1}$ absorption line reaches 95 % of its quasistationary value.

5.3 Complete reconstruction of quantum mechanical motion in Kr^+

In the following section the reconstruction of quantum mechanical motion based on the measured attosecond transient absorption spectrograms is addressed. The first step is to determine the experimental underlying density matrix elements which describe the atomic ensemble. The rigorous determination of those parameters will allow the calculation and visualization of the dynamics of the angular hole density motion as a function of elapsed time along the measured transient absorption signal.

In the last part of this section, the experimental values will be compared to results of ab-initio modeling.

5.3.1 Determination of density matrix elements

To retrieve the Kr^+ ion quantum state distributions and the degree of coherence of the spin-orbit wavepacket, a two-dimensional fit of the experimental data shown in Fig. 5.6 b) to Eq. 5.26 is performed. Since Eq. 5.26 rigorously defines the transient absorption signal only in the absence of the NIR laser pulse, the fit is performed over the time delay interval of 3 - 33 fs only. Keeping in mind that the absorbance $A(\omega, \tau)$ of the sample is determined via its measured transmission in the experiment, the transmission function computed from Eq. 5.26 is convolved with a normalized Gaussian function to account for the finite XUV spectrometer resolution. Hence, the experimental transient absorption spectrum is fit to the function

$$A(\omega, \tau) = -\ln \left[e^{-N\sigma(\omega, \tau)} \circledast \sqrt{\frac{4 \ln 2}{\pi \Delta^2}} e^{-\frac{4 \ln 2 (\omega - \omega_0)^2}{\Delta^2}} \right] + A_0 \quad (5.29)$$

where N is a normalization constant for the retrieved quantum state distribution, $\sigma(\omega, \tau)$ is given by Eq. 5.26, Δ is a FWHM quantity that characterizes the spectrometer resolution (a fit variable in this case), and $\omega_0 = 80.25$ eV is the central photon energy for the range over which the fit is performed (78.5 - 82 eV). In order to account for some small non-resonant absorption signal which does not depend on the time delay τ , an additional offset value A_0 is added which is not a fit value. A_0 is defined as the mean absorbance in a photon energy band (78.5 - 78.8 eV) located at the low energy side of the $4p_{3/2}^{-1} \rightarrow 3d_{5/2}^{-1}$ absorption line and therefore accounts -if necessary- for a small, but spectrally broad non-resonant absorption background. Since the theoretical modeling assumes the absence of the NIR laser field, the reconstruction has to be limited to time delays where the influence of the NIR pulse on the ionic ensemble can be neglected. Here, two simplifications can be implemented when substituting $\sigma(\omega, \tau)$ into Eq. 5.29:

- the quantum-state populations $2\rho_{j,j}^m$ are delay independent,
- the complex non-vanishing off-diagonal matrix element $\rho_{3/2, 1/2}^{(1/2)}(\tau)$, which describes

the coherence, can be written as $\left| \rho_{3/2, 1/2}^{(1/2)} \right| e^{i\phi_{SO}(\tau)} = \left| \rho_{3/2, 1/2}^{(1/2)} \right| e^{i\left(\frac{2\pi}{T_{SO}}\tau + \delta\right)}$, where ϕ_{SO} represents the relative quantum phase between the coherently populated states and δ an overall phase offset:

$$\phi_{SO}(\tau) = (E_{|4p, j=1/2\rangle} - E_{|4p, j=3/2\rangle}) \tau + \delta = \Delta E_{SO} \tau + \delta = \frac{2\pi}{T_{SO}} \tau + \delta. \quad (5.30)$$

It should be noted that N and the density matrix elements contained in $\sigma(\omega, \tau)$ depend on each other since N can be considered as an overall scaling of the density matrix elements and hence a fitting routine will not be able of distinguishing between N and the density matrix elements. Therefore, the fit is carried out by skipping the fit parameter N . In order to allow for a comparison of the extracted fit parameter to theoretical predictions afterwards, the retrieved matrix elements are scaled to 100 % fractional ionization of Kr^+ ($2 \sum \rho_{j,j}^m \stackrel{!}{=} 1$).

Finally, Eq. 5.29 inherits ten fit parameters:

Δ for the finite XUV spectrometer resolution (FWHM), $\Delta E_{(4p_{3/2}^{-1} \rightarrow 3d_{5/2}^{-1})}$, $\Delta E_{(4p_{3/2}^{-1} \rightarrow 3d_{3/2}^{-1})}$ and $\Delta E_{(4p_{1/2}^{-1} \rightarrow 3d_{3/2}^{-1})}$ for the central photon energies of the three absorption lines of Kr^+ , $\rho_{3/2, 3/2}^{(1/2)}$, $\rho_{3/2, 3/2}^{(3/2)}$, $\rho_{1/2, 1/2}^{(1/2)}$ and $\rho_{3/2, 1/2}^{(1/2)}(\tau)$, which includes T_{SO} and δ for the complete description of the density matrix.

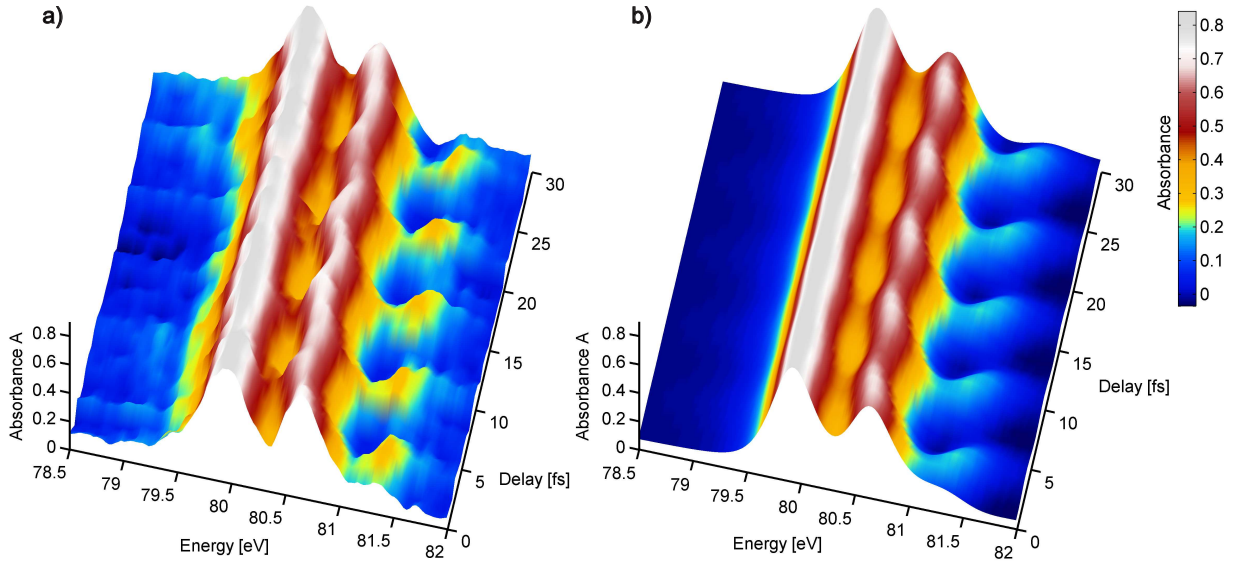


Figure 5.7: Representative attosecond transient absorption spectrogram and its reconstruction. **a)** Part of the NIR field free XUV experimental transient absorption spectrogram (limited to $\tau > 0$) which is fit by Eq. 5.29 to determine quantum populations and the coherence. **b)** Least-square fit to **a)** shown for best fit parameters.

A representative measurement and its fit curve is shown in Fig. 5.7. The determined fit parameters are listed in Table 5.1 and 5.2, respectively. To demonstrate overall reproducibility of the real time observation of quantum coherence in the valence shell of krypton, several other data sets and their fit curves, as shown in Fig. A.4, were analyzed and their fit parameters are listed in the previously mentioned tables. Error bars represent 95 % confidence intervals. All analyzed data sets were taken with NIR laser pulses ≤ 4 fs and XUV pulse durations of less than 150 as. The standard deviation of the carrier envelope phase stability had been better than 150 mrad.

Table 5.1: Best fit values for five different attosecond transient absorption data sets as shown in Appendix Fig. A.3, A.4. (Δ : spectrometer resolution; T_{SO} : spin orbit wavepacket period; $\rho_{j,j'}^m$: density matrix elements). Errors depict 95 % confidence interval. Parameters determined based on the fit shown in Fig. 5.7 are listed in the first row. Further data sets and corresponding fit surfaces are shown in Appendix Fig. A.3, A.4.

Data set	Δ eV	T_{SO} fs	$\rho_{3/2, 3/2}^{(3/2)}$	$\rho_{3/2, 3/2}^{(1/2)}$	$\rho_{1/2, 1/2}^{(1/2)}$	$ \rho_{3/2, 1/2}^{(1/2)} $
020209 49-56	0.432 ± 0.003	6.312 ± 0.029	0.111 ± 0.031	0.207 ± 0.027	0.183 ± 0.011	0.122 ± 0.029
020209 43-48	0.447 ± 0.003	6.205 ± 0.039	0.112 ± 0.0395	0.220 ± 0.037	0.168 ± 0.0154	0.074 ± 0.029
020209 59-63	0.457 ± 0.002	6.337 ± 0.026	0.107 ± 0.025	0.210 ± 0.022	0.1828 ± 0.0093	0.103 ± 0.019
020209 64-66	0.499 ± 0.003	6.381 ± 0.050	0.164 ± 0.034	0.166 ± 0.030	0.170 ± 0.0121	0.083 ± 0.025
121408 110- 137	0.369 ± 0.005	6.38 ± 0.13	0.093 ± 0.037	0.283 ± 0.030	0.1234 ± 0.0078	0.068 ± 0.028

Since the spectrometer resolution Δ strongly depends on the daily alignment and imaging conditions of the XUV beam in the XUV spectrometer, an overall small variation of the resolution as seen in Table 5.1 is observable. The mean spin-orbit period, calculated from several independently measured data sets, amounts to 6.32 ± 0.05 fs which agrees well with the period of 6.22 fs that was calculated based on the reported underlying energy spacing ΔE_{SO} [108]. Besides the density matrix elements, Table 5.2 lists experimental ionization peak intensities and calculated values for the pure state coherence, degree of coherence and alignment. The depth of modulation of the $4p_{3/2}^{-1} \rightarrow 3d_{3/2}^{-1}$ transition probability is indicative of the degree of coherence of the probed superposition state.

In Table 5.2 approximate absolute CE phases are listed for completeness which are based on discrete relative changes of the CE phase on top of an assumably initial close to cosinusoidal electric field. (The cosine pulse is supposed to deliver the smallest amount of XUV satellite pulse which is one of the optimization criteria at the daily startup of these experiments). Small modulations, present in the spectra of the attosecond pulse and dependent

on the CE phase infer, that the amount of satellite pulse can be considered—even for CE phase settings which result in a slightly higher modulation of the XUV pulse spectrum—as being weak compared to the main attosecond XUV pulse.

Table 5.2: Extension of Table 5.1. (I : Peak intensity; CEP: estimated absolute CE phase; C : Pure state coherence, γ : Degree of coherence, Θ : Alignment).

Data set	$\frac{I}{10^{14}\text{W/cm}^2}$	CEP	C	γ	Θ
020209 49-56	3.1 ± 0.5	~ 0	0.194 ± 0.025	0.63 ± 0.13	0.30 ± 0.14
020209 43-48	2.9 ± 0.5	$\sim \pi/2$	0.192 ± 0.018	0.38 ± 0.16	0.32 ± 0.17
020209 59-63	3.1 ± 0.5	~ 0	0.196 ± 0.011	0.53 ± 0.10	0.32 ± 0.11
020209 64-66	4.2 ± 0.5	~ 0	0.168 ± 0.016	0.49 ± 0.16	0.00 ± 0.15
121408 110-137	4.0 ± 0.5	$\sim \pi/2$	0.187 ± 0.011	0.36 ± 0.16	0.50 ± 0.15

The comparison of the retrieved density matrix elements to theoretical ab-initio modeling will be discussed in section 5.3.3.

5.3.2 Snapshots of the hole density motion

The complete characterization of the quantum mechanical electron motion based on the observed attosecond transient absorption spectrogram enables—along with appropriate modeling—the visualization of the electron motion inside the Kr^+ valence shell. As mentioned earlier, theoretical modeling is performed in the hole picture of the atomic ion. Since Kr^+ consists of 35 remaining electrons, the modulation of the overall electron density due to the quantum superposition in the valence shell, will be very weak. In order to show the periodic arrangement of the electronic charge, the charge density motion will be shown in terms of a hole density motion.

Fig. 5.8 displays the mean optical density of the $4p_{3/2}^{-1} \rightarrow 3d_{3/2}^{-1}$ absorption line as a function of pump-probe delay over the energy range 81.20 - 81.45 eV (black dots) of data set 020209 49-56 which is itself shown in Fig. 5.7 a) in comparison with the prediction of our model with the fit parameters given in Tab. 5.1 (red line). To reconstruct the quantum mechanical motion of the electron wavepacket, the temporal evolution of the quantum phase $\phi_{SO}(\tau)$ defined by Eq. 5.30 must also be retrieved. Attosecond absorption spectroscopy allows this retrieval over a multifemtosecond time interval with attosecond resolution (Fig. 5.8 b). The uncertainty in the obtained values of the quantum phase (of $\pi/5$) translates—using Eq. 5.30—into a temporal resolution of 0.6 fs. In Fig. 5.8 b), the evolution of the quantum phase versus the time elapsed since the main absorption line of Kr^+ reached 95 % of its stationary value is shown. The inset of Fig. 5.8 c) shows the underlying coordinate system of the hole-density motion, where the tunnel-ionizing NIR laser pulse is polarized along the axis z which is used in the theoretical description as the quantization axis. The hole density distribution can be reconstructed using Eq. 5.27 at any instant after the ionizing laser pulse with subfemtosecond accuracy. Results of this reconstruction at a few selected instants separated by 1 fs are plotted in Fig. 5.8 c) by substituting the

experimentally measured values of the density matrix into Eq. 5.27. This diagram shows ensemble-averaged angular components of the hole density distributions in the $4p$ subshell of Kr^+ . The radial component is time independent and is therefore not included in the presented visualization. The isotropic symmetry of the initially neutral Kr atoms (perfect sphere) is broken upon ionization by a linearly polarized laser field by tunnel ionization. After ionization, the combined system has perfect cylindrical symmetry, and therefore all instances of the positive charge density distributions show a cylindrical symmetry along the polarization axis. Within one beating period, the hole distribution evolves from a prolate two lobe-distribution, corresponding to a maximum in the XUV absorption cross section, to an oblate positive charge distribution which results after $t = T_{SO}/2$ in a pronounced minimum of the XUV oscillator strength and back again. At this point, a demonstrative explanation shall be offered in order to explain why the prolate charge density results in a local maximum in the $4p_{3/2}^{-1} \rightarrow 3d_{3/2}^{-1}$ absorption cross-section and not in a minimum:

The XUV probe pulse excites electrons from the $3d$ shell into electronic vacancies in the $4p$ shell and therefore its absorbance monitors the $3d \rightarrow 4p$ transition probability. The overall distribution of charge, consisting of all core electrons up to the completely occupied $3d$ and $4s$ subshell, is isotropic. In contrast to this, the electronic density of the $4p$ valence shell, where a wavepacket motion was launched is varying in time. Here it shall be repeated that the XUV pulse is linearly polarized along the z direction (like the NIR laser pulse). At the instance at which the hole density is in the two lobe distribution and aligned with the quantization axis y and the XUV polarization vector, the transition probability is higher for a transition from the $3d$ to a $4p$ valence shell vacancy, because the electronic vacancies (holes) in the $4p$ shell are aligned in the direction of the absorbed XUV photons and vice versa for the connection between the minimum in the absorbance and the oblate hole density distribution. Revisiting such an experiment with a XUV pulse whose polarization vector is rotated by 90° with respect to the one of the NIR ionizing laser pulse, will yield a local minimum of the absorbance for the prolate distribution and respectively.

To emphasize the importance of launching the wavepacket motion with sub-4 fs NIR pulses which confine the ionization window to a time span being shorter than the spin-orbit wavepacket period of ~ 6.2 fs, Fig. 5.8 d) displays the expected hole density distribution for an initiation pulse of 7.6 fs duration as it was investigated theoretically in section 5.2.1 (Fig. 5.4 b). It was shown that it will trigger the quantum beat with a degree of coherence of only 0.12. The corresponding modulation of the hole density distribution is expected to be almost totally suppressed as shown in Fig. 5.8 d).

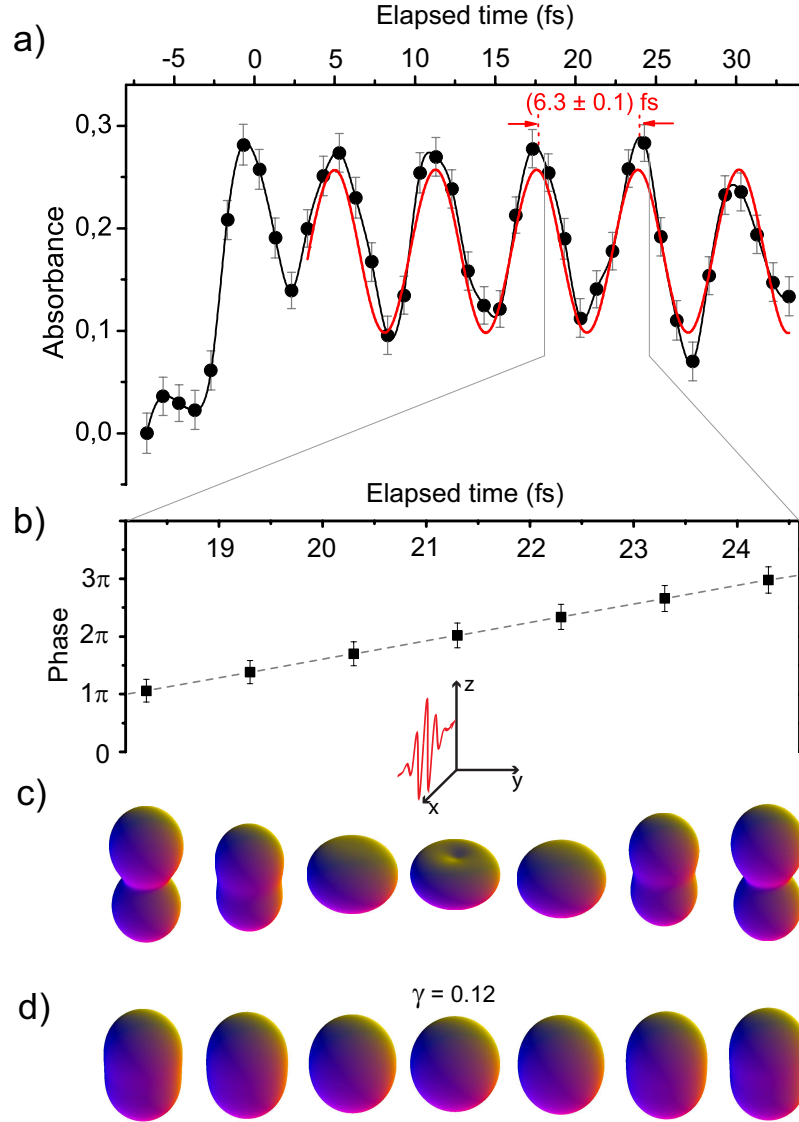


Figure 5.8: Reconstruction of valence-shell electron wavepacket motion. **a)** Absorbance (dots) averaged over the photon energy range 81.20 - 81.45 eV corresponding to the $4p_{3/2}^{-1} \rightarrow 3d_{3/2}^{-1}$ transition, as a function of time elapsed since zero as defined in the text. The full line shows the result of the modeling for the values of the fit parameters given in Tab.5.1. The modulation occurs with a period of $6.312 \pm 0.029 \text{ fs}$. Error bars depict the standard error of the values extracted from several scans recorded under identical experimental conditions as shown in Fig. 5.6 b). **b)** Quantum phase of the $4p$ superposition state $\phi_{SO}(t)$ (see Eq. 5.30), as retrieved from the measured attosecond absorption spectrogram shown in Fig. 5.6 b). **c)** depicts ensemble-averaged hole density distributions (according to Eq. 5.27) in the $4p$ subshell of Kr^+ reconstructed from the measured $\phi_{SO}(t)$ and the measured components of the density matrix, at instants separated by 1 fs, within an interval of 17 - 25 fs following ionization. **d)** Expected hole density distribution for same instances as above but for a degree of coherence of $\gamma=0.12$, as it is expected by triggering the wavepacket motion with a 7.6 fs pulse (Fig. 5.4 b).

5.3.3 Comparison to theoretical predictions and conclusion

Due to the experimental complexity of the performed experiment, the requirements on the laser performance (in terms of intensity stability, CEP fluctuations, e.t.c) are even more demanding than for attosecond streaking investigations. The laser performance, especially the stability of the laser pulse energy and of the short- and longterm CEP locking, can be subject to strong fluctuations in those cutting edge experiments which involve highly nonlinear processes. As indicated by several additional data sets (Fig. A.3, A.4), taken on different days where the laser performance was exceeding the performance of other experimental days, weeks and sometimes month, differences in the signal to noise ratio between the best data sets are visible. The degree of confidence of the extracted values obviously increases with increasing signal to noise ratio of the transient absorption spectrogram. The comparison between experimental and theoretical results focuses mainly on quantities extracted from the spectrogram which yielded the highest signal to noise contrast. This is justified since all data sets give similar values within their error bars. The data set of highest fidelity itself had been shown in Fig. 5.6, 5.7 and its fit values are listed in the first line of both Table 5.1 and 5.2. Table 5.3 summarizes experimental and theoretically predicted parameters for comparison.

Table 5.3: Comparison between experimental best fit parameters and quantities predicted by ab-initio simulation based on experimental laser parameters (summary)

	Experiment	Theory
$\rho_{3/2, 3/2}^{(3/2)}$	0.111 ± 0.031	0.025
$\rho_{3/2, 3/2}^{(1/2)}$	0.207 ± 0.027	0.345
$\rho_{1/2, 1/2}^{(1/2)}$	0.183 ± 0.011	0.13
$ \rho_{3/2, 1/2}^{(1/2)} $	0.122 ± 0.029	0.13
γ	0.63 ± 0.13	0.61
Θ	0.30 ± 0.14	0.86

The ratio between the population of the $j = \frac{1}{2}$ and $j = \frac{3}{2}$ level is comparable between experiment and theory. The resulting degree of coherence γ agrees well with the prediction, verifying that few-cycle ionization is capable of creating robust electronic coherence. However, a discrepancy can be found for the alignment Θ . Here, the experiment suggests a much smaller alignment than theory. In order to shed light on the observed disagreement, the validity of Lambert Beer's law, which was used to determine the density matrix elements from the experimental absorption spectra, was checked numerically [104] by our co-workers. Without the assumption that different frequency components of the XUV pulse propagate independently, the wave equation (Eq. 5.13) has to be solved numerically. Repeating the determination of the density matrix without the approximation of Beer's law for the experimental data set and the theoretically predicted one by Beer's law, gives very similar values for the density matrix as obtained by assuming Beer's law [104]. This

indicates that Beer's law is a good approximation for extracting electronic structure information from attosecond transient absorption data sets. A failure of the Lambert Beer's law cannot account for the observed discrepancy in the ion alignment. We propose that the discrepancy most probably has to be attributed to multi-electron effects beyond the utilized multichannel theory used so far.

Theoretical investigation has already shown that the pulse duration of the initiating laser pulse by itself has a significant impact on the created degree of coherence as displayed in Fig. 5.4 b). An exciting question is whether the control of the driving NIR waveform allows for coherent control of electron motion in the valence shell of ions. In the conducted experiments the waveform can be efficiently controlled by changing the CEP. Two data sets have been taken with a $\pi/2$ shifted CE phase (Table 5.2). They tend to yield the lowest observed degrees of coherence. But in view of the large error bar, any conclusion has to be handled with care. Furthermore, one has to take into account that changes in the CE phase can also slightly influence the temporal structure of the XUV probing field. Thus, CEP shifts of $\pi/2$ might result in a small amount of satellite pulse which can influence the probing process and therefore the extracted density matrix. Further experiments with improved statistics and therefore smaller error bars and investigations of the probing process in view of a potential small XUV satellite pulse have to be performed before a conclusion can be drawn about the potential coherent control of electron motion in the valence shell of Kr^+ ions with the current laser performance. Chapter 7 provides an outlook about ongoing technological developments which will pave the road towards a first coherent control of valence electron motion in atoms where single isolated attosecond probe pulses are available for several extraordinary NIR driving light waveforms.

In this first proof-of-concept experiment it was shown that attosecond transient absorption spectroscopy allows the real-time observation and the complete reconstruction of valence electron motion of strong-field ionized, singly charged krypton ions.

Accessing the populations of the ionic quantum states in strong-field ionized atomic ensembles is also possible with conventional time-integrated spectroscopy [23] and is therefore not of our main experimental interest. The requirement for turning on electron motion in the valence shell of atomic systems is a very short initiation pulse which confines ionization to less than the wavepacket period. Reading out and completely reconstructing the electron wavepacket motion requires the determination of the coherence of the launched wavepacket system which requires a sufficiently high temporal resolution that can only be achieved by utilizing single isolated attosecond probe pulses as it was done for the first time in the reported experiment. As shown here, attosecond transient absorption spectroscopy is able not only of qualitatively granting access to valence shell electron dynamics but also allows the quantitative characterization of the coherence which was not possible by conventional time-integrated experimental approaches. The variation of the absorption cross section as a function of pump-probe delay reveals the temporal evolution of the system, which is described by the complete determination of density matrix elements. The experimental characterization of the ensemble averaged dynamics in terms of rather abstract density matrices now also allows—together with appropriate theoretical modeling—for the

spatio-temporal visualization of the temporally varying motion of the electron density as a function of the elapsed time.

5.4 Apparent paradoxical characteristics of ATAS

5.4.1 The uncertainty principle in pump-probe absorption spectroscopy

Since the probe pulse spectrum after absorption in the gas can be measured with essentially arbitrary precision, transient absorption spectroscopy allows recording of the frequency resolved transmitted pump spectrum of a transient process with temporal resolution provided by the attosecond XUV probe pulse. What can be perceived to be paradoxical and a violation of the Heisenberg uncertainty principle is the high frequency and temporal resolution of this measurement. Naively calculating the product $\Delta E \cdot \Delta t$ for the reported experiment, assuming an attosecond pulse duration of $\Delta t \sim 150$ as and a spectral resolution of 350 meV, yields a value of $5.2 \cdot 10^{-17}$ eVs which is a paradoxical violation of the uncertainty principle by already two orders of magnitude.

In fact, already in femtosecond absorption spectroscopy this apparent violation had arisen. W.T. Pollard and A. Mathies comment that both time and frequency resolution involved in the dynamic absorption experiment are completely independent [14]. They are not related by the Heisenberg uncertainty principle. This is correct since the measurement of one spectra for a specific delay between pump and probe pulse is not time resolved. The temporally confined interaction of the probe pulse with the target atoms creates a polarization response whose emission has the same wavevector as the probe pulse. Since the acquisition of the spectrum itself is not time resolved, the spectrum of the probe pulse and any subsequent other emission in the direction of the probe are measured together. The destructive interference between the probe pulse spectrum and the polarization response creates a spectral absorption line in the recorded spectrum. The sharpness of the detected spectral feature does only depend on the natural lifetime of the excited state (convoluted with the spectrometer resolution) and is independent of the attosecond pulse duration of the probe pulse [14].

The presented attosecond absorption experiment provides time-resolved information about the valence electron motion, since the induced polarization response which is launched in the well-confined instance of the probe pulse interacting with the atomic system, records the electron dynamics. For the general case it is important to note that the continued evolution of the initial system after the probe-pulse interaction might modulate the induced polarization response, but essential spectral characteristics of the recorded dynamic absorption spectrum, like absorption strength or position of spectral features are determined purely by the state of the system during the initial probe-pulse interaction [14]. In this general case, the pump-probe measurement is not anymore a 'true' real-time measurement which accesses intra-molecular or atomic observables at a specific time [113].

5.4.2 Spectral resolution versus quantum coherence

The presented data showing the real-time observation of valence electron motion in Kr^+ in Fig. 5.6 infers a paradox since the quantum beat is encoded on the absorption strength

of the $4p_{3/2}^{-1} \rightarrow 3d_{3/2}^{-1}$ as well as the $4p_{1/2}^{-1} \rightarrow 3d_{3/2}^{-1}$ transition. This, on first sight, seems to indicate a measurement of the coherent motion while the signal is state-resolved and emitted photons can be assigned to one specific transition. What was often perceived to be paradoxical is that spectral resolution of the two absorption lines corresponding to transitions from two initial states to one final state is independent of the observed quantum coherence. It is therefore wrong that knowledge is obtained about the transition along which an absorbed photon has probed the coherent superposition. Fig. 5.9 outlines the

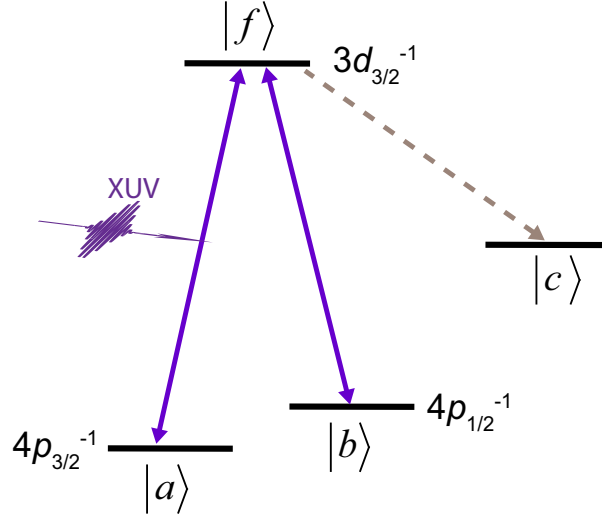


Figure 5.9: A scheme for the probing of a coherent superposition of non-degenerate quantum states $|a\rangle$ and $|b\rangle$ via two interfering quantum paths to one common final state $|f\rangle$. Corresponding states in Kr^+ are indicated.

simplified Λ scheme for the relevant levels in Kr^+ . In the present experiments the coherent superposition of the states $|a\rangle$ and $|b\rangle$ is probed by absorption of an attosecond XUV pulse. This conceptually deviates from reported measurements of a coherent superposition where the decay of the final state $|f\rangle$ to a fourth state $|c\rangle$ was observed [114].

The XUV probe pulse promotes the atom via two interfering quantum paths from two non-degenerate states $|a\rangle$ and $|b\rangle$ to one common final state $|f\rangle$. The attosecond probe pulse does initiate these excitations but does not probe both transitions. What forms the absorption lines in the spectrogram is the initiated polarization response of this excitation, namely the emission of photons corresponding to the decay of the state $|f\rangle$ to either state $|a\rangle$ or $|b\rangle$. The transition probabilities of the transitions $|a\rangle \rightarrow |f\rangle$ and $|b\rangle \rightarrow |f\rangle$ depend on the instantaneous hole density distribution at the time of probing of the superposition between states $|a\rangle$ and $|b\rangle$. Therefore, the population of the final state $|f\rangle$ is also sensitive on the quantum coherence and hence imprints signatures about the coherence onto the decay of state $|f\rangle$ to $|a\rangle$ and $|b\rangle$. This creates two absorption lines which are periodically modulated in phase as a function of pump-probe delay. However, these emitted photons do not reveal any information about the path on which the atom had been excited from

the superposition to the final state. Therefore resolving the absorption lines corresponding to the decay of the final state does not violate the ability of observing signatures of the quantum coherence since no information about the quantum path is provided.

In a gedankenexperiment a measurement could have also been performed with narrowband pulsed synchrotron or FEL light flashes. If the spectrum of the probe pulse would not support both transitions $|a\rangle \rightarrow |f\rangle$ and $|b\rangle \rightarrow |f\rangle$ at the same time, the recorded absorption spectrogram would not be sensitive to the coherent superposition since excitation is carried out only along one quantum path at a time.

5.5 Attosecond absorption spectroscopy in more complex systems: Kr^{2+}

After the observation and understanding of the quantum beat in singly charged krypton ions, the question has to be posed whether wavepacket dynamics are also launched in doubly charged ions. From a fundamental point of view, the multiplet structure of Kr^{2+} is determined by spin-orbit coupling (like in Kr^+) and in addition by hole-hole Coulomb interactions. Citing Robin Santra, 'it will take years to develop ab initio multichannel methodology for treating the ionization dynamics leading to Kr^{2+} '. Looking experimentally at double hole systems is tempting since current attosecond transient absorption technology might pioneer insight into hole-hole correlated motion.

Fig. 5.10 shows an attosecond transient absorption spectrogram which was taken at an intensity of $(3.1 \pm 0.5) \cdot 10^{14} \frac{W}{cm^2}$, where the strong NIR pulse generates Kr^{2+} besides singly charged ions. The strongest absorption line of Kr^{2+} in the spectral content of the attosecond probe pulse is observed at around 83 eV. The spectrogram was sampled in steps of 1 fs, including a delay interval ranging from 10 to 20 fs where the step size was reduced to 300 as. At first glance, the doubly charged krypton ion does not show any periodic modulation of the absorption strength. To obtain an overview of potential multiple quantum beats in krypton ions, a fast Fourier transformation (FFT) is performed for every energy lineout between 78 and 86 eV starting at -2 up to 30 fs, thus being limited on the NIR free part of the absorption spectrogram. Any non-vanishing constant offset absorbance value of a certain energy pixel column is removed before the FF transformation by subtracting the smoothened absorbance lineout. Here a smoothing approach based on the commonly used moving average technique was employed. A lowpass filter with filter coefficients equal to the reciprocal of its span covering 35 data points was utilized as a smoothing parameter. The natural logarithm of the spectral intensity as a function of energy and the frequency in electron volt is displayed in Fig. 5.11, where the graph on the left hand side indicates the position of the absorption signatures of Kr^+ and Kr^{2+} . The Nyquist frequency amounts to a frequency of 6.88 eV. The presented false color plot of the FFT clearly shows the most pronounced quantum beat at 0.664 eV corresponding to the well-understood spin-orbit wavepacket motion in Kr^+ . Also several higher frequencies are observed on the $4p_{3/2}^{-1} \rightarrow 3d_{5/2}^{-1}$ transition.

Directing the attention to the spectral range of the absorption line of the doubly charged ion, one can also observe frequencies which are isolated in terms of strength from other energy ranges. Fig. 5.12 a) shows the binned and averaged spectral intensity as a function of frequency of the Kr^{2+} extended energy range ranging from 82.3 to 85 eV, thus also covering less strong resonant transitions in doubly charged ions as analyzed by an atomic structure code (see Fig. 6.6). An energy level diagram of Kr^{2+} [108] shown in panel b), limited to the first ionic states above the ground state, visualizes the states and energy spacings. Potential quantum superpositions exceeding 0.25 eV between several ionic states (denoted as \oplus) are shown as vertical lines and placed at their expected beating frequencies in a). Frequencies of the FFT result below 0.25 eV are affected by the approach of

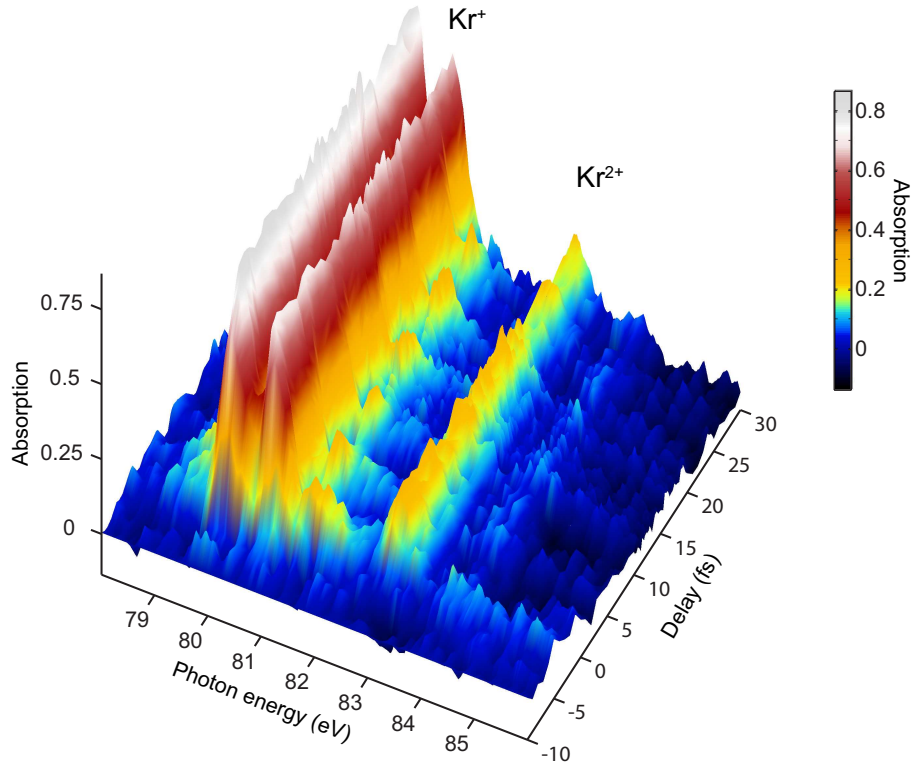


Figure 5.10: Attosecond transient absorption spectrogram taken at $3.1 \pm 0.5 \frac{\text{W}}{\text{cm}^2}$, sampled in steps of 1 fs and including a delay interval ranging from 10 to 20 fs where the step size was reduced to 300 as. Besides showing the clearly visible spin-orbit wavepacket motion in the Kr^+ ion, it inherits absorption signatures originating from the presence of the doubly charged ion, represented clearly by its strongest absorption line centered around 83 eV. Detailed transitions in the Kr^{2+} ion are shown in paragraph 6.3.1.

removing the offset of the absorbance and are therefore influenced by unphysical effects. Superpositions among the first triplet P states and the singlet D state with the triplet P states seem to explain some of the observed frequencies.

Faster quantum beats are very unlikely to be triggered since their expected wavepacket period is substantially smaller than the pulse duration of the few cycle laser pulse which would lead to an onset of ionization on several instances during the laser pulse which would in turn substantially reduce the degree of their coherence and accordingly their visibility in an attosecond transient absorption spectrogram. Fig. 5.12 provides evidence that the doubly charged krypton ion undergoes a more complex wavepacket motion which involves two holes. The fastest quantum motion which is observed is the coherent superposition of the singlet D state and the 3P_2 state at a frequency of 1.82 eV corresponding to a period of 2.27 fs. The observation of quantum beats, resulting from superpositions involving triplet

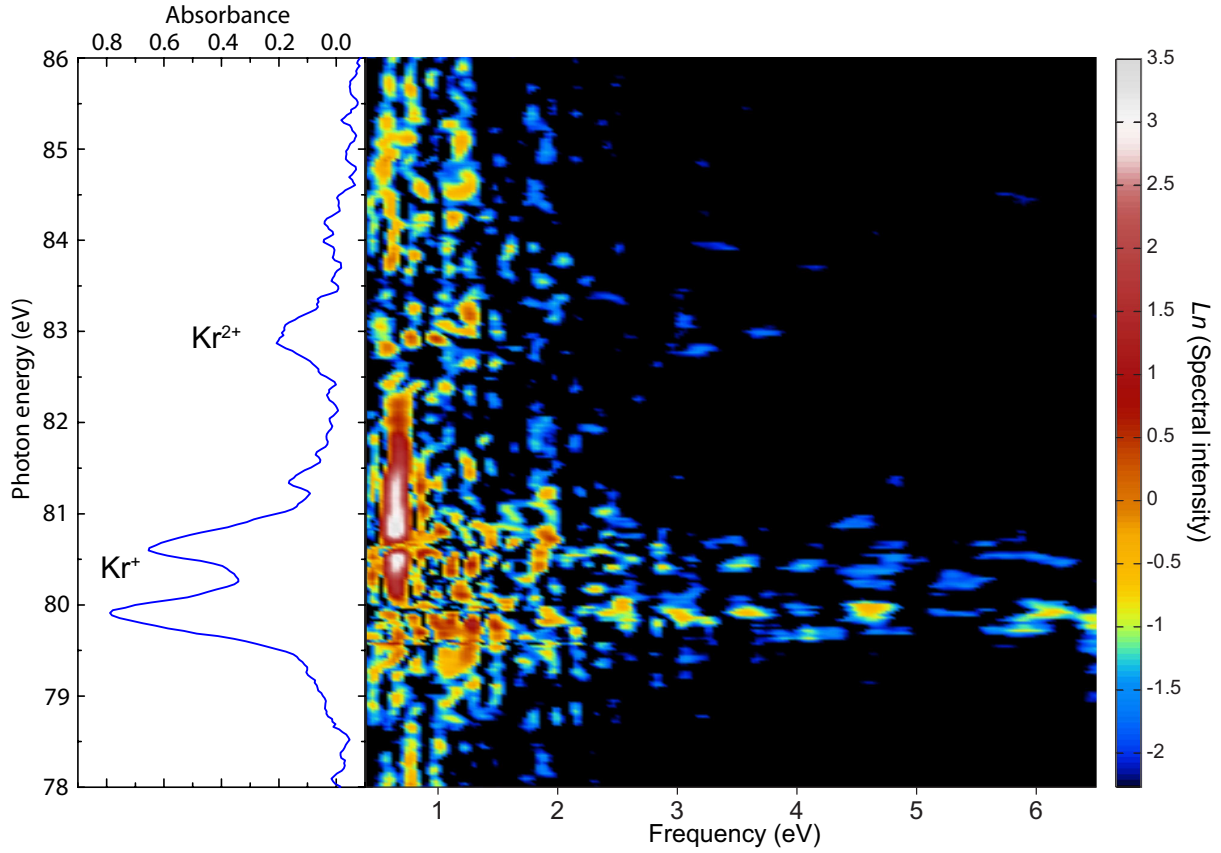


Figure 5.11: Spectral intensity of a Fast Fourier Transformation of the attosecond transient absorption spectrogram shown in Fig. 5.10, limited to the NIR field-free delay range ranging from -2 fs to 30 fs. Absorbance offset values of the resonant lines are removed before the FFT (see text for details). Graph on the left hand side shows a lineout of the absorbance curve, binned over the delay values 26 to 30 fs for easier identification of spectral ranges of interest.

P states and the singlet D state, indicates that strong-field ionization by a ~ 3.8 fs NIR laser pulse creates doubly charged ions not only in their ground state, but also in higher excited states. Applying the most naive tunneling picture, the NIR field is expected to ionize the two $4p_z$ electrons (z -axis is the quantization axis aligned with the laser polarization) [72, 115]. The corresponding two-hole wavepacket would be a superposition of the two-hole singlet D and singlet S states. Based on this perspective, one would only expect the beating frequency at 2.29 eV to appear. The current observation of beats however indicates that superpositions are arising between triplet P states, which involves their population and thus is inconsistent with the unsophisticated tunneling picture but expected from an energy point of view. Other observed frequencies in the range of absorption lines of Kr^{2+} which can not be explained by superpositions in Kr^{2+} , might be attributed on a

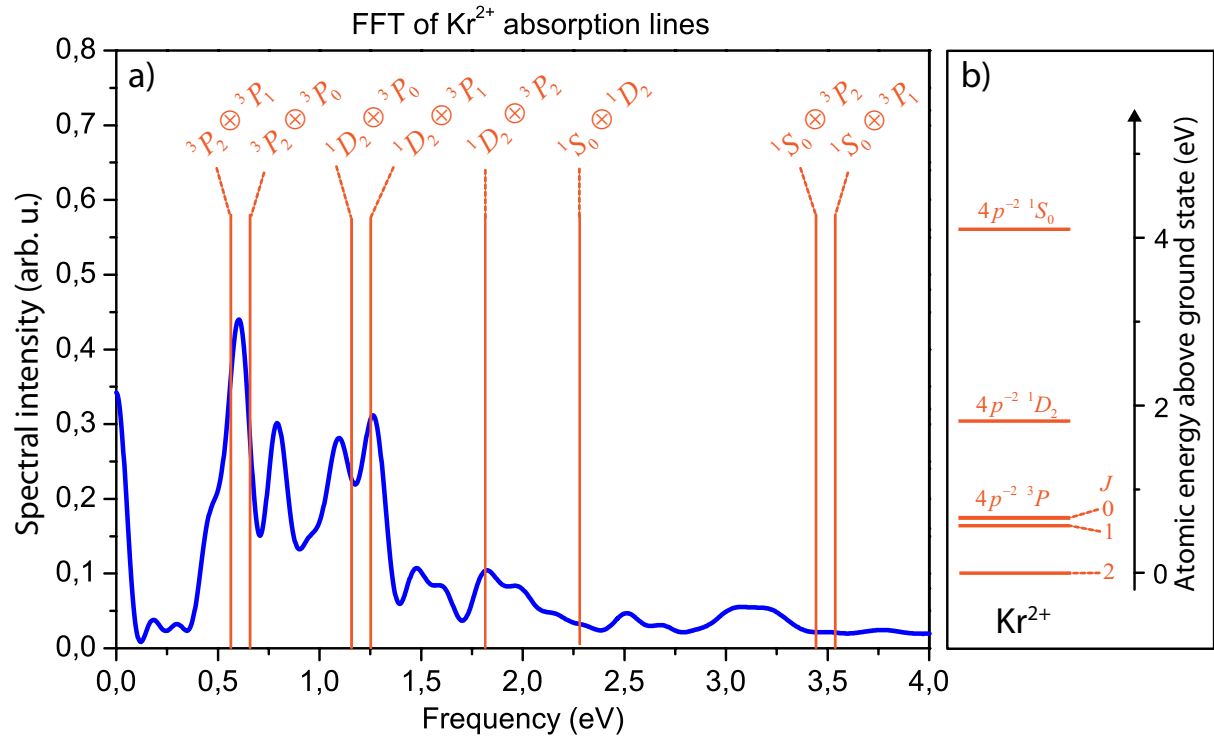


Figure 5.12: Binned and averaged lineout of the FF transformation of Fig. 5.11, covering the energy range of absorption lines of Kr^{2+} (82.3 – 85 eV) and selection-rule-allowed beating frequencies displayed as vertical lines (a), where potential quantum superpositions between two states are denoted by \oplus . An underlying energy level diagram of Kr^{2+} , limited to the first few excited states above the ground state 3P_2 [108], is shown in (b).

speculative basis to quantum superpositions in excited Kr^+ ions which might have resonant XUV transitions in the spectral range of the doubly charged ion.

Further experiments, performed with higher sampling resolution and longer scan ranges, will increase the resolution in the frequency domain and will be a prerequisite for more detailed studies on double and potentially even triple hole dynamics.

5.6 Attosecond absorption spectroscopy in more complex systems: Xe ions

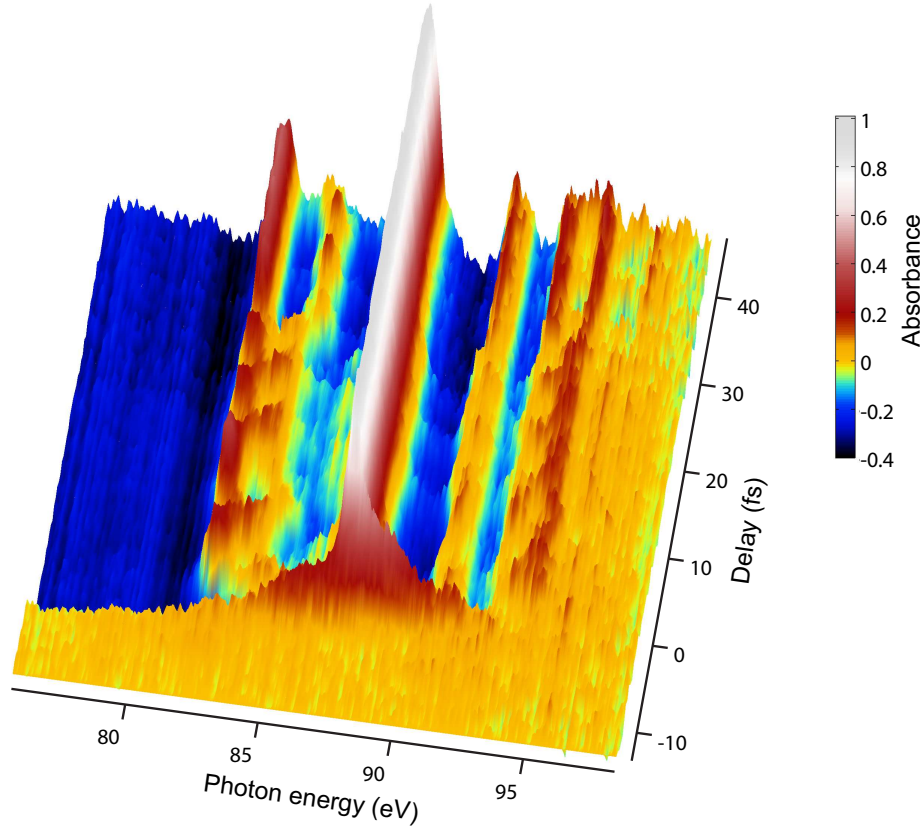


Figure 5.13: Attosecond transient absorption spectrogram obtained in xenon. Neutral atoms were strong-field ionized by sub-4 fs NIR laser pulses at $\sim 5 \cdot 10^{14} \text{W/cm}^2$. The backing pressure in the quasi static gas cell was 26 mbar. The generated ionic ensemble was probed with synchronized attosecond XUV laser pulses for different delays. Experimental details are the same as for the first proof-of-concept study carried out on krypton as described in section 4.2. The time dependent absorbance topography comprises multiple quantum beats and a spectrally broad area of negative absorbance. These additional phenomena were not observed in the first study carried out on krypton atoms.

Besides the study of coherent electron motion in singly and doubly charged *Kr* ions, also attosecond transient absorption experiments were carried out on more complex electronic systems. Here we discuss strong-field ionized xenon atoms at an NIR intensity of $\sim 5 \cdot 10^{14} \text{W/cm}^2$. In this first experiment in xenon, the NIR laser pulses were not CEP locked. But since the laser pulses are very short (sub 4 fs), they produce for most CE phases isolated attosecond probe pulses.

Fig. 5.13 shows the recorded attosecond absorption spectrogram. Since the ionization potential of xenon is lower than the one of krypton, we expect the emergence of several charge states by irradiation of the neutral xenon atoms with the strong NIR laser pulses. It is observed that one discrete absorption line at 87.8 eV dominates the spectrum. On the high, as well as on the low energy side of this major absorption line there are several absorption lines visible, from which most of them carry a conspicuous modulation of their absorption cross-section as a function of the delay. Some of the observed beatings seem to be aperiodic in time which indicates that there are several quantum beats super-imposed on some lines. Besides the increase of absorption for the resonant absorption lines at positive delays, a spectrally broad increase of transmission is observed at photon energies below 92 eV. An unexpected observation is the sudden spectral change located at a delay of 30.8 fs, after which the line at 83.6 eV disappears and a new line at 84.6 eV appears. This sudden feature is also accompanied by a change of the beating pattern encoded most resonant lines.

For positive delays (XUV follows the NIR laser pulse) the trace shows a build-up of discrete absorption structures to which we refer as resonant absorption signatures and spectrally broad absorption characteristics which are created by resonant (close to the continuum) and nonresonant (into continuum) XUV absorption. Both contributions will be explained in detail later. Since it is not clear, which charge states are created and what their cross-section $\sigma(\omega, \tau)$ is, in general the absorption for more complex systems can be expressed in the following way by assuming the correctness of the Lambert Beer's law:

$$I(\omega, \tau) = I_o(\omega) e^{-[n(\tau)\sigma(\omega, \tau) + \sum_{q=1}^r n^{(q+)}(\tau)\sigma^{(q+)}(\omega, \tau)] \cdot L} \quad (5.31)$$

where $I_o(\omega)$ is the spectral density before and $I(\omega, \tau)$ after the target. L denotes the propagation length, n and σ the number density and corresponding absorption cross-section of neutral absorbers and $n^{(q+)}(\tau)\sigma^{(q+)}(\omega, \tau)$ correspondingly for ions up to a charge state of $r+$. Furthermore, the sum of all number densities has to be constant and equals the number density n_0 of neutral atoms before the interaction with the NIR laser field for all delays τ :

$$\forall_{\tau} n_0 = n(\tau) + \sum_{q=1}^r n^{(q+)}(\tau). \quad (5.32)$$

By substituting Eq. 5.32 into Eq. 5.31, the experimentally observed absorbance $A(\omega, \tau)$ can be written as:

$$A(\omega, \tau) = \ln \left(\frac{I_o(\omega) e^{-n_0 \sigma(\omega)}}{I(\omega, \tau)} \right) = - \sum_{q=1}^r \{ n^{(q+)} [\sigma(\omega) - \sigma^{(q+)}(\omega)] \} \quad (5.33)$$

For the investigated spectral photon range of our experiments (70 - 100 eV) the absorbance of xenon and concomitant ions is not quantitatively documented in detail. However, in the spectral range of our experiments, absorption of an XUV photon leads with very high probability to the creation of the next ionic charge state if the absorbed photon energy exceeds the necessary ionization potential of the absorbing ion. For completeness, it shall

be mentioned that absorption of XUV photons can lead to photoionization via several different processes whose probability depend mainly on the photon energy of the incident radiation. Fig. 5.14 is taken from [116] and shows the sum of single- and double- photoionization yields for Xe^+ , Xe^{2+} and Xe^{3+} photoion yields in arbitrary units as a function of photon energy.

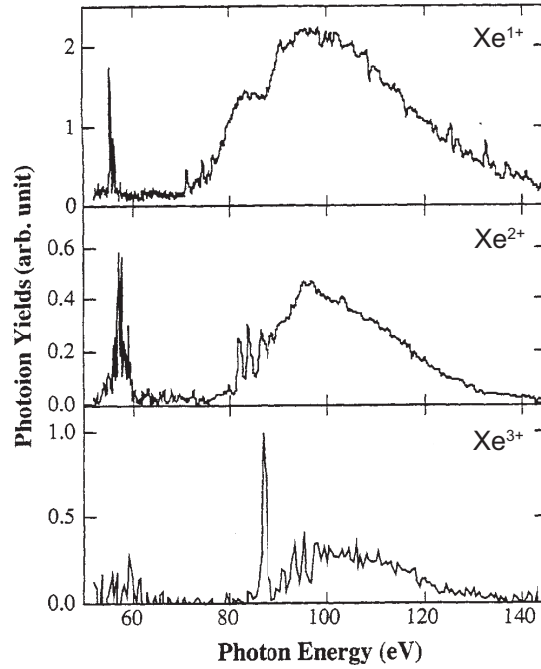


Figure 5.14: Qualitative photoion yields of the sum of single- and double- photoionized ions of Xe^+ , Xe^{2+} and Xe^{3+} upon irradiation with XUV radiation [116]. It shows that the single-photon photoionization cross-section of xenon consists of spectrally broad and discrete contributions.

The first kind of process is the excitation of the atom by absorbing the XUV photon into excited states below the ionization threshold and following resonant Auger processes can lead to subsequent ionization [117, 118]. Since the electron undergoes a transition from one bound state to another bound state for low lying excited states, this process results in sharp characteristic resonant signatures (Fig. 5.14). Absorbing XUV photons with higher energy will promote bound valence or inner shell electrons into continuum states above the ionization threshold (ϵf), where ϵ is the notation for main quantum numbers in the continuum. Since this effect is spectrally very broad, it is in literature referred to as “giant resonance” [119, 117].

In view of those processes where one XUV photon is absorbed and leads to photoioniza-

tion, the measurement of photoion yields or photoionization cross-section as a function of photon energy represents qualitatively the expected XUV photon absorption and can be therefore used as a first step towards an interpretation of the observed spectral lines of Fig. 5.13. A prerequisite for understanding and learning something about strong field ionization from the observed coherences in the ions of xenon, as clearly inferred from the attosecond transient absorption measurement, is the identification of created and observed charge states of xenon and the determination of the resonant transitions which lead to the discrete absorption lines.

5.6.1 Identifying absorption lines

For delays $\tau > 4$ fs the pump pulse has passed the medium and therefore the created charge states and ensemble averaged level populations are not anymore subject to the NIR field. Since the attosecond spectrogram does not show any effects of a fast atomic decay processes, which would be expected to show up as a gradually changing phenomenon, an atomic structure code has been used for calculating expected dipole spectra for different charge states and transitions which might reveal the charge states of ions created in the NIR laser pulse and the electronic transitions which caused the observed absorptive behavior of xenon. In the last years, several atomic structure and spectra codes were written and improved and can for instance calculate dipole spectra, photoionization cross-sections, autoionization transition probabilities or total lifetimes of atomic structure problems based on ab-initio approaches. Among several available packages that can provide information on the structure of laser excited ions, we opted for the user friendly Cowan code [120]. This opened us the door for exploiting potential new electronic systems for first attosecond transient absorption experiments and will provide very essential first-order interpretation - almost in real-time during the conduction of experiments - about created charge states of different investigated structures. The Cowan Code utilizes the superposition-of-configuration method [111] and consists of several small programs which have to be executed one after the other. First it calculates one-electron radial wave functions for each of any number of specified electron configurations which should be taken into account. Second, those wave functions are needed to determine the configuration-interaction Coulomb integrals and electric dipole and quadrupole radial integrals between pairs of interacting configurations. Finally the routine sets up energy matrices for each possible value of the total angular momentum and after diagonalization calculates energy levels and the corresponding wave functions. Based on the solution of this eigenvalue problem it determines for instance radiation spectra and several other quantities which are related to the electronic structure. Several self-developed Matlab programs reprocess the complex output of the Cowan atomic structure code calculation and finally display the desired dipole spectra for different ionic charge states.

Fig. 5.15 shows the calculated absorption cross-section for singly, doubly and triply ionized xenon in the spectral range of the utilized attosecond XUV probe pulses under the perspective of explaining the absorption lines. The shown spectra are obtained by electronic

structure calculations considering the following initial and final electron configurations:

$$\begin{aligned}
 Xe^{1+}([Kr] 4d^{10}5s^25p^5) + h\nu &\rightarrow Xe^{2+*}(4d^95s^25p^6, 4d^95s^25p^5np^1, 4d^95s^25p^5mf^1) \\
 &\quad \text{with } 6 \leq n \leq 9, 4 \leq m \leq 9 \\
 Xe^{2+}([Kr] 4d^{10}5s^25p^4) + h\nu &\rightarrow Xe^{2+*}(4d^95s^25p^5, 4d^95s^25p^4np^1, 4d^95s^25p^4mf^1) \\
 &\quad \text{with } 6 \leq n \leq 8, 4 \leq m \leq 8 \\
 Xe^{3+}([Kr] 4d^{10}5s^25p^3) + h\nu &\rightarrow Xe^{3+*}(4d^95s^25p^4, 4d^95s^25p^3np^1, 4d^95s^25p^3mf^1) \\
 &\quad \text{with } 6 \leq n \leq 8, 4 \leq m \leq 8 \\
 Xe^{4+}([Kr] 4d^{10}5s^25p^2) + h\nu &\rightarrow Xe^{4+*}(4d^95s^25p^3, 4d^95s^25p^2np^1, 4d^95s^25p^2mf^1) \\
 &\quad \text{with } 6 \leq n \leq 8, 4 \leq m \leq 8
 \end{aligned}$$

where several hundreds of levels are added up incoherently for one charge state (no coherent superpositions) and for comparison with the experimental spectra, the theoretical spectra for the different levels are individually broadened by Gaussian functions (FWHM=0.3 eV) to account for the finite experimental resolution of the detection apparatus (section 3.2). The finite individual Lorentzian linewidth of the calculated transitions can be neglected since the spectrometer resolution is on average around 30 times lower than the intrinsic linewidth which is of the order of ~ 20 meV [121]. However, for a very precise comparison with the experiment, those details have to be implemented. From the Cowan code analysis it can be inferred that the expected discrete resonant absorption lines originating from exiting 4d electrons into low-lying Rydberg states are located within the experimentally observed spectral range for the ions Xe^{2+} , Xe^{3+} and Xe^{4+} but not for Xe^+ . The discrete resonant lines of Xe^+ are located well below 75 eV and therefore it can be concluded that no observed discrete absorption signatures can be attributed to Xe^+ . For comparison with the experimental measurement, Fig. 5.15 furthermore shows on the right vertical scale the delay-wise binned lineouts of the absorption spectrogram (Fig. 5.15) for the delay range 11.8 to 28.8 fs referred to as before the 'step' feature at ~ 30.8 fs and for the range 36.8 to 46.8 fs after the 'step'. In view of the very good agreement between the ab-initio calculated resonances and observed absorption lines it can be concluded that the discrete resonant absorption lines can be attributed to Xe^{2+} and Xe^{3+} whereas no major Xe^{4+} content had been generated by the NIR pump laser. It is known that the absolute energy of resonances calculated by theoretical atomic structure and spectrum codes can be off by a few 100 meV, nevertheless the relative energy spacing between states of the Rydberg series is quite accurate.

In order to approach an interpretation which states are coherently populated by strong-field ionization and therefore create the observed quantum coherence, the attempt was made to assign transitions to the absorption lines. Fig. 5.16 a) shows the result for the doubly charged xenon ions. The $4d \rightarrow 5p$ transitions are located outside of the spectrally observed window for Xe^{2+} and all other investigated ions. This shows that the final electron configuration after absorbing an XUV photon is not located in the valence shell which is in sharp contrast to the absorption process in Kr^+ and Kr^{2+} where the electron was exited from

the $3d$ into the $4p$ valence shell and directly probed the spin-orbit wave-packet motion as described in section 5.2.1 in real time. The principle of observing quantum coherences in xenon is different and will be discussed in section 5.6.3.

Besides the overall good agreement between the calculated ionic spectra and observed

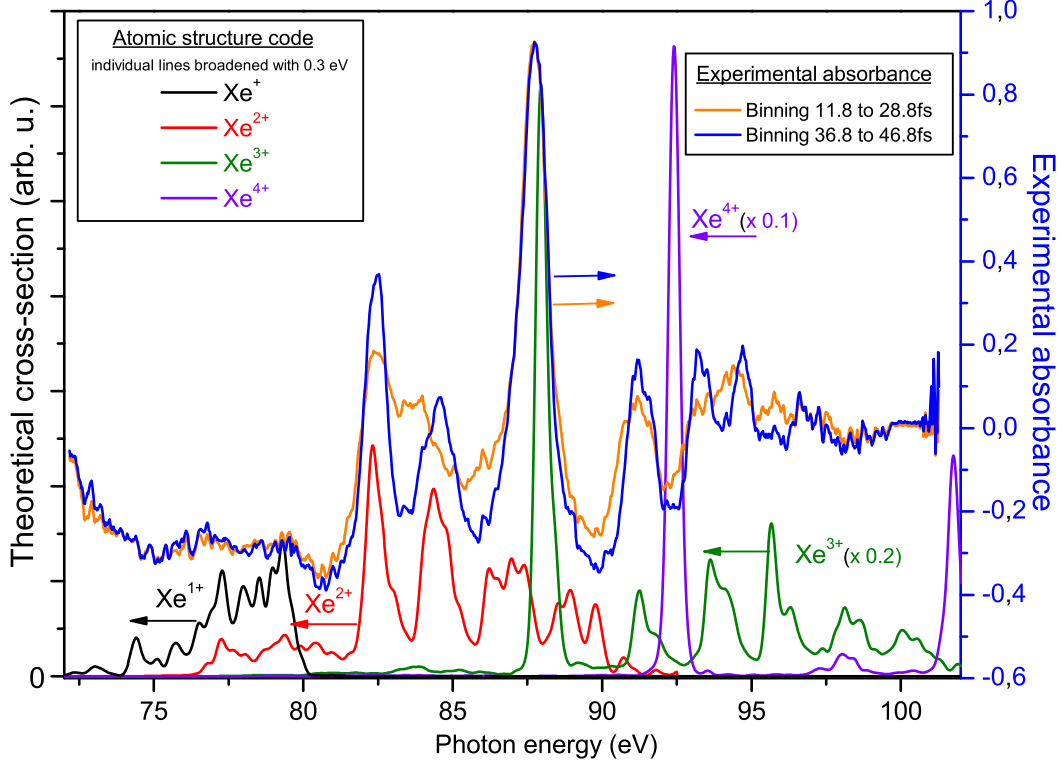


Figure 5.15: Calculated electric dipole spectra (COWAN code) for Xe^+ up to Xe^{4+} . Only transitions of relevance in the observed spectral window were taken into account: $4d \rightarrow np$, mf transitions (for details see text). The orange curve displays the averaged experimental absorbance averaged over the delay range 11.8 to 28.8 fs obtained from Fig. 5.13 (before the step-like feature) and the blue curve the averaged absorbance in the range 36.8 to 46.8 fs (after the abrupt spectral change at 30.8 fs). Values of both curves are shown on the right vertical axis. The discrete resonant absorption lines can be attributed to Xe^{2+} and Xe^{3+} .

resonant absorption lines as shown in Fig. 5.15, one can observe that at around 82 - 85 eV the calculated dipole spectrum of Xe^{2+} explains the absorption signature after the jump but not before. The experimental binned lineout from 11.8 - 28.8 fs in Fig. 5.15 (orange curve) shows substantial oscillator strength between the two absorption series of $4d \rightarrow 7p$ and $4d \rightarrow 5f$ at around 83.5 eV which can not be explained by the calculated absorption spectra for Xe^{2+} where the ion was assumed to be in the initial electron configuration $5s^2 5p^4$. Repeating the atomic structure calculation for Xe^{2+} in initially higher excited

electron configurations of $5s^1 5p^5$ and $5s^2 5p^3(^4S) 5d^1$ before the XUV photon absorption shows that the resonant absorption spectra deviate substantially from the atomic spectrum of Xe^{2+} in the $5s^2 5p^4$ ground-state containing electron configuration. The obtained dependency of the XUV photo absorption of Xe^{2+} on the initial state's electron configuration is summarized in Fig. 5.16 b). Therefore a possible explanation for the additionally observed absorbance at ~ 83.5 eV might be created by the absorption of highly excited Xe^{2+} ions, predominantly in their $5s^1 5p^5$ electron configuration. One possible finding related to the sudden feature would be that strong-field ionization of xenon atoms results first in the case of the creation of doubly charged xenon in the population of excited ions. After approximately 31 fs the observed absorbance in the range of Xe^{2+} can be mainly understood by only considering ions in the $5s^2 5p^4$ manifold which indicates that population from the excited configuration was transferred to the ground state containing electron configuration. The exact mechanism which leads to the almost abrupt jump at 30.8 fs is not yet understood and further experiments are planned aiming at recording the absorbance over substantially longer delay ranges. If it turns out that the sudden effect repeatedly appears at delays >48 fs then this will be a proof that a very rapid intra-atomic process might be responsible for the observed fast step-like jump¹.

Delay-dependent effects originating from the finite lifetime of excited Rydberg states (which is in general of the order of ns) can be neglected for the comparably very short scanned delay range of 48 fs.

For completeness it shall be mentioned that decay channels involving mainly resonant Auger processes which very likely occur after the absorption of XUV photons [117] do not have to be taken into account for interpreting the attosecond transient absorption spectrograms since all processes are happening after the absorption of the XUV probe pulse and due to their lifetime, which is substantially longer than the XUV pulse duration, are invisible for the attosecond XUV probe. If it turns out that strong-field ionization itself is able to create highly excited ions then decay schemes have to be taken into account. But as far as we can judge, our attosecond transient absorption spectra of xenon do not show absorption signatures originating from very highly excited Rydberg states. Investigating the absorbance of ions of xenon by means of an ab-initio atomic structure code has shown that the observed dominant resonant absorption signatures are originating from $4d \rightarrow np, mf$ dipole allowed Rydberg transitions in doubly and triply charged Xe ions.

5.6.2 Explanation for spectrally broadband negative absorbance

The broad structure-less absorption <92 eV can be explained by a difference in the spectrally broadband photoabsorption cross-section feature (Fig. 5.14) between different charge states. Resulting from the finding of the analysis of the resonant absorption lines it is

¹A most recent experimental revisit of attosecond transient absorption experiments in xenon was aiming at illuminating the reversibility of the sudden feature. Even though the fidelity of the data acquisition was worse than for the data set being investigated in this chapter, strong indications exist for the reversible character of the sudden spectral change, indicating a fast atomic process to be responsible for the sudden change in the spectral behavior. More details are provided in section 5.6.4

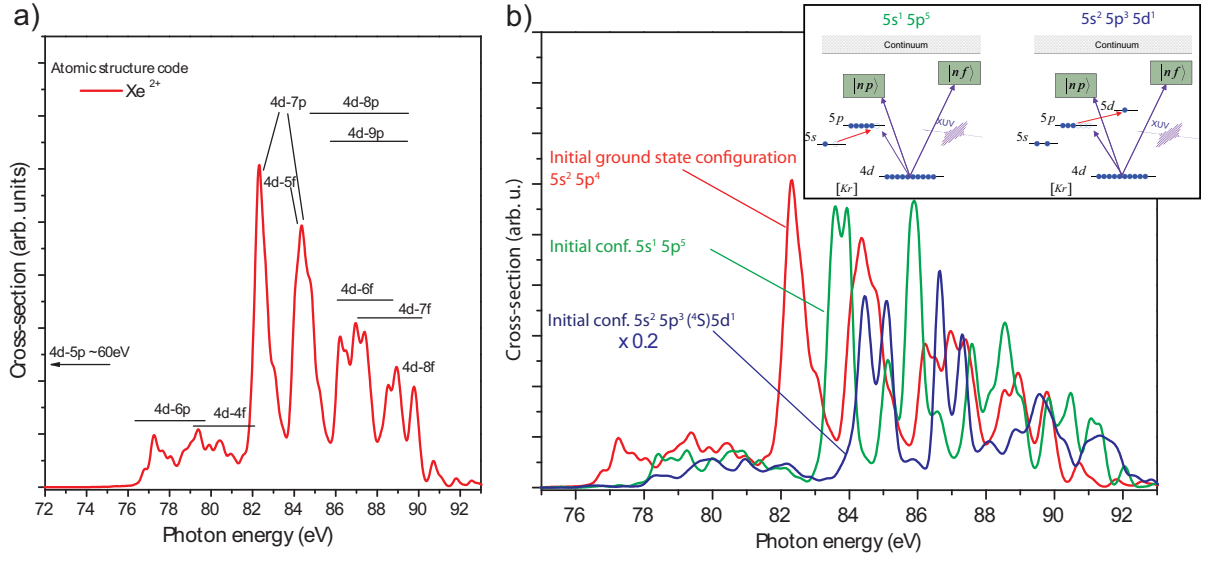


Figure 5.16: Calculated atomic dipole spectrum (COWAN atomic structure code) including assignment of absorption series to specific underlying transitions for doubly charged xenon ions **a)** and dependence of calculated atomic dipole spectra on the initial electron configuration **b)**. Shown are the absorption dipole spectra for XUV radiation originating from Xe^{2+} ions in the $5s^2 5p^4$, $5s^1 5p^5$ and $5s^2 5p^3(^4S) 5d^1$ electron configuration. Considered final states are $|np\rangle$, $|mf\rangle$ with $6 \leq n \leq 8$, $4 \leq m \leq 8$.

known that the utilized strong-field NIR laser pulse creates ions up to Xe^{3+} . Based on Eq. 5.33, a negative absorbance is expected if the photoabsorption cross-section $\sigma^{(q+)}(\omega)$ of all Xe ions for $1 \leq q \leq 3$ is smaller than the interaction cross-section of neutral xenon atoms $\sigma(\omega)$. In literature, photoionization cross-sections are qualitatively documented in [116, 121], but not with the necessary accuracy to furthermore put the observation on a quantitative ground. Therefore, our observation is a very distinct and direct finding that clearly shows without any ambiguity that in the observed spectral range the (non)resonant spectrally broad photoabsorption cross-section is higher for neutral xenon than for the corresponding ions. This is in sharp contrast to the oscillator strength of transitions from $4d$ to low-lying Rydberg orbitals which make up for the sharp absorption characteristics and whose cross-section increase with increasing charge state as shown in Fig. 5.15 or [116]. Further theoretical investigations are planned to quantitatively elucidate the effect. An explanation of the reversed scaling of oscillator strength for the broadband absorption feature as a function of charge state is based on the energetic shift of the $4d$ giant resonance ($4d \rightarrow \epsilon f$) to higher energies with increasing charge state. Reference [122] reports the ionization energy of $4d$ electrons at ≈ 67.5 eV. This shows that photons with energies exceeding 67.5 eV are absorbed in the regime of the giant resonance and the absorption probability is higher than for lower XUV photons. In the case of Xe^+ the $4d$ threshold is located at around 76 eV [117] and therefore the beginning of the low-energy wing of the

giant resonance is located at higher energy. Effectively, the structure of the giant resonance shifts to higher energies with increasing charge state. Assuming the same trend for Xe^{2+} and Xe^{3+} with respect to the behavior of neutral xenon in the investigated spectral range, explains the observed strong negative absorbance.

5.6.3 Preliminary interpretation of multiple beats and their probing

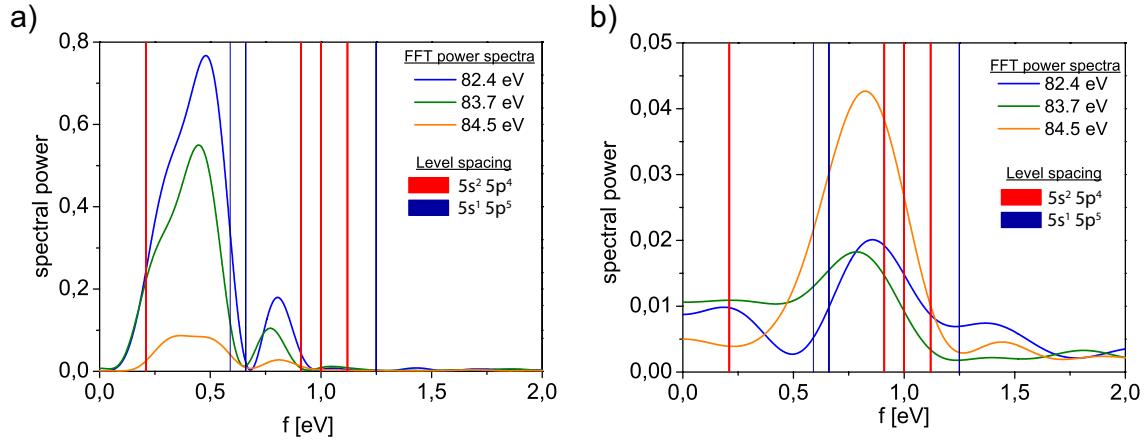


Figure 5.17: Observed beating frequencies on Xe^{2+} lines before **a)** and after **b)** the sudden jump at ~ 30.8 fs. Before FFT transformation, timetraces of individual absorption lines centered at 82.5, 83.7 and 84.5 eV were on average spectrally binned over ± 0.5 eV around their center. Straight vertical lines in both graphs show expected level spacings and therefore potential beating frequencies between ground and excited states in doubly charged xenon for electron configurations $5s^2 5p^4$ and $5s^1 5p^5$ [123].

In order to determine the observed multiple quantum beat frequencies, a Fast Fourier Transform (FFT) was performed along the delay axis on the measured xenon absorption curve for every photon energy increment of the sampled spectral range. The FFT was furthermore subdivided into a delay range of 11.8 - 28.8 fs referred to as before the jump and of 36.8 - 46.8 fs after the sudden spectral change. The obtained power spectra are shown in Fig. 5.17 for Xe^{2+} , where the spectral power was averaged over appropriately chosen spectral windows fully covering the absorption line of interest. For the absorption line centered at 82.4 eV the averaging was performed in the energy range 82.13 to 82.73 eV, for the line centered at 83.7 eV in the interval 83.10 to 84.04 eV and the absorption line placed at 84.5 eV in the spectral window of 84.18 to 84.98 eV. The representative power spectra for Xe^{3+} are shown in Fig. 5.18 where the spectral density of the line centered at 87.7 eV was obtained in the spectral window extending from 87.19 to 88.25 eV, of the line at 91.1 eV in the window 90.55 to 91.97 eV and the spectral feature placed around 93.2 eV in the interval 92.51 to 93.88 eV. Multiple beating frequencies are observed which

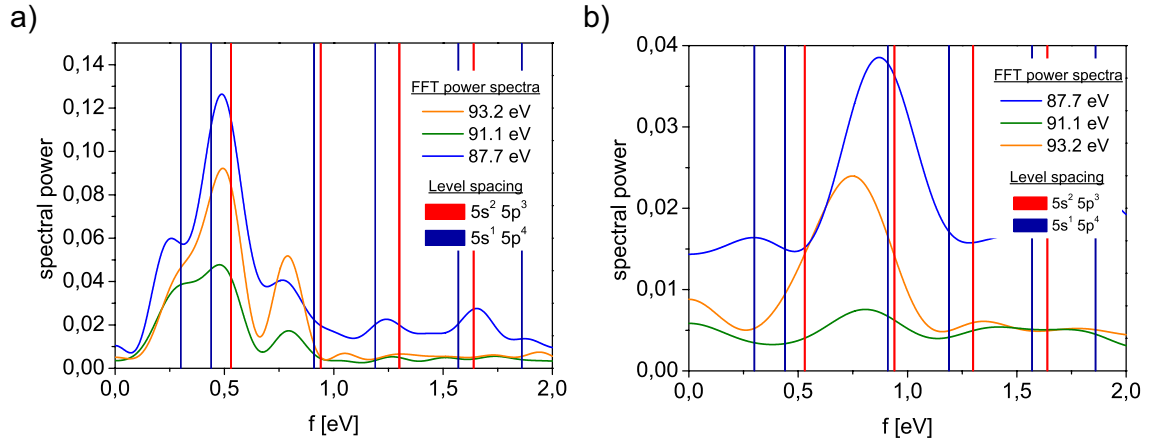


Figure 5.18: Observed beating frequencies on Xe^{3+} lines before **a)** and after **b)** the sudden jump at ~ 30.8 fs. Details see text and caption of Fig. 5.17. Straight vertical lines in both graphs show expected level spacings and therefore potential beating frequencies between ground and excited states in doubly charged xenon for electron configurations $5s^2 5p^3$ and $5s^1 5p^4$ [123].

are similar on all observed lines. A pronounced difference between the frequencies before and after the discrete feature at ~ 30.8 fs is determined. The following paragraph will provide a preliminary interpretation of some of the observed delay dependence.

In contrast to the probing scheme of the quantum beats in krypton, where the coherent

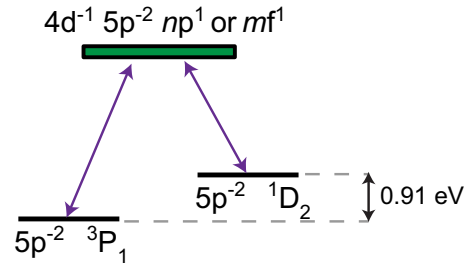


Figure 5.19: Λ -scheme of a superposition of the triplet P_1 and a singlet D_2 state in Xe^{2+} . The superposition would be visible by a XUV transition to a final $4d^{-1}5p^{-2}np^1$ or mf^1 Rydberg state. In elements lighter than xenon, where nonrelativistic selection rules are valid, transitions involving a triplet and singlet state in the Λ -scheme would be dipole forbidden.

superposition of states in the $4p$ valence shell was probed by an XUV transition between the $4p^{-1}$ and the $3d^{-1}$ manifold of states, the detection in the case of xenon is somewhat different. The multiple valence electron dynamics of Xe^{2+} are probed by promoting the ion for instance from the $5p^{-2}$ manifold of states into the $4d^{-1} 5p^{-2} 6p^1$ manifold. On

first sight, it seems to be questionable why this XUV transition should be sensitive to a coherent superposition created in the valence shell of the ion. However, if written down in the state picture, one obtains a well-known Λ -scheme (Fig. 5.19) and therefore two quantum paths are interfering. In the case of the quantum coherence in the singly charged ion of krypton, only two of the three resonant absorption lines were sensitive to the coherent superposition. In xenon however, all resonant core to Rydberg transitions which are dipole allowed and have a second quantum path with which they can interfere should carry signs of the same spin-orbit frequencies. This is supported by the obtained FFT power spectra for all three lines of Xe^{2+} and all three major Xe^{3+} lines as indicated in Fig. 5.17 and Fig. 5.18. All power spectra of absorption lines belonging to the same charge state show similar frequencies. Only their relative amplitude is subject to deviations if compared to each other.

In order to determine the coherently superimposed states in the xenon ions, selection rules have to be taken into account, too. For light elements and π (linear) polarized radiation, the selection rules are $\Delta L = 0, \pm 1$, $\Delta J = 0, \pm 1$, $\Delta M = 0, \pm 1$, $\Delta S = 0$ and $\Delta m = 0$. Spin-forbidden transitions ($\Delta S \neq 0$) are never rigorously forbidden in real atoms. They only weakly appear as the LS -coupling conditions are closely met [111]. Heavier atoms show increasing deviation from a pure LS -coupling and intercombinations (transitions with $\Delta S \neq 0$) gain in strength. Therefore it is not very accurate to make predictions based on the LS coupling scheme for transitions in xenon. The only reliable transition criteria are the J and parity selection rules: $\Delta J = 0, \pm 1$ and $\Delta L = 0, \pm 1$ which is a relaxation of the nonrelativistic dipole selection rules.

Based on the softened selection rules Fig. 5.17 shows expected level spacings and therefore potential beating frequencies between ground and excited states in doubly charged xenon for electron configurations $5s^2 5p^4$ and $5s^1 5p^5$ depicted as vertical lines [123]. Besides the agreement between the 0.21 eV quantum beat in Fig. 5.17a) which would originate from a superposition of the 3P_0 and 3P_1 states in $5s^2 5p^4$, no good agreement is observed and an explanation for the observed beating frequencies at 0.48 eV and 0.8 eV is still missing. Of course, if one would consider all substantially higher Rydberg states and potentially originating quantum beats, one would find several pairs of level superpositions which would give an explanation for the observed quantum beat at 0.48 eV or 0.8 eV. But also a vast amount of other frequencies would be potentially created, which are not observed in our experiment. A better agreement is obtained by considering the FF transform on lines which we have identified to originate from absorption of Xe^{3+} (Fig. 5.18) and comparing the frequencies to level spacings expected by linear superpositions in Xe^{3+} of $5s^2 5p^3$ and $5s^1 5p^4$. From Fig. 5.18 a) it can be preliminarily concluded that strong-field created Xe^{3+} ions are coherently populated in the $5s^2 5p^3$ and $5s^1 5p^4$ manifolds of states. Thus, the experimental observation supports the linear superpositions in $5s^2 5p^3$ of $^2D_{3/2}$ and $^2D_{5/2}$ (0.53 eV) and of $^4S_{3/2}$ and $^2D_{3/2}$ which amounts to 1.66 eV and therefore corresponding to a spin-orbit wave-packet period of 2.5 fs. Furthermore, superpositions in $5s^1 5p^4$ of $^4P_{3/2}$ and $^4P_{1/2}$ (0.3 eV), of $^2D_{3/2}$ and $^2D_{5/2}$ (0.44 eV) and of $^4P_{5/2}$ with $^4P_{1/2}$ (1.19 eV) have to be taken into account to explain other observed wave-packet frequencies which cannot be explained by solely considering states of the electron configuration $5s^2 5p^3$.

5.6.4 Conclusions and most recent experimental indications

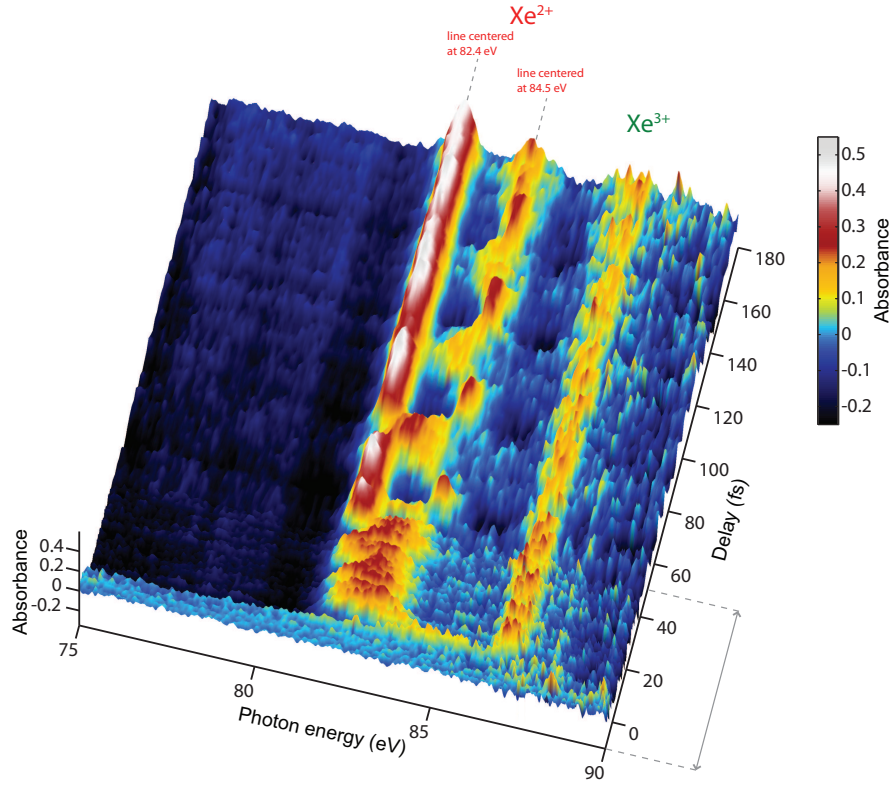


Figure 5.20: Preliminary revisit of transient absorption experiments in xenon. Extension of the delay range over 190 fs as compared to 60 fs (marked by gray arrow) for the investigation presented in Fig. 5.13, shows the reversible character of the sudden spectral feature, which had been observed in Fig. 5.13. It seems to be compatible with the onset of the periodically modulated and shifted absorption line of Xe^{2+} at 84.5 eV. Both absorption lines of Xe^{2+} at 82.4 and 84.5 eV show effects of a process that affects both lines. This points towards an intra-atomic process being responsible for the abrupt change of the spectral content which had been observed in more detail in Fig. 5.13 at a delay of 30.8 fs.

In order to conclude, it shall be emphasized that this is the current preliminary understanding of the observed quantum beats in such a complex system. However, it is not yet understood which process creates the sudden jump in the attosecond transient absorption spectrum and why this process destroys some of the observed quantum beats, but on the other hand does not affect all absorption lines. Further investigations are currently being carried out from a theoretical as well as experimental point of view. For instance, in order to address the origin of the sudden feature we are planning to revisit the experiment and expand the scanned delay range to larger delays to see, whether the currently not explain-

able feature is reversible. To provide the newest insights, we would like to mention that the most recent experimental revisit, aiming at scanning the absorbance over substantially longer delay ranges, has just been performed. Even though the measurement accuracy was worse than that for the data sets discussed in the scope of this chapter, important indications are observed. The preliminary ATAS scan measured over an extended delay range of -10 to 180 fs, obtained with a different, but quite similar laser system [124], providing in this experiment less intensity on target (Xe^{3+} is hardly observed), are presented in Fig. 5.20. The shown spectrogram is obtained by averaging over 12 scans which were scanned with a step size of 3 fs and therefore not being able of sampling fast features as shown in Fig. 5.13. The scanned range of the earlier investigation is indicated by the gray arrow. In the latest experiment the spectral content and breadth of the attosecond probe pulse were different, but the main spectral absorption lines up to 87 eV of the measurement shown in Fig. 5.13 can be still recognized, consisting of the resonant absorption lines of Xe^{2+} at 82.4 and 84.5 eV as well as the main line of Xe^{3+} . The significant and periodic modulation of the Xe^{2+} lines (period ~ 35 fs) in combination with a recognizable fading of their spectral shift, for delays exceeding the scan range of the earlier measurement, provide indications supporting the reversible character of the previously observed sudden change in the spectral content happening at 30.8 fs (Fig. 5.13) which had been the onset of the strong modulation and spectral shift of the absorption line of Xe^{2+} at 84.5 eV. However, the detailed process is not yet understood and still remains elusive, but the latest preliminary investigation provides evidence for an intra-atomic process being the origin of the complex phenomenon.

Disregarding the still open question about the origin of the observed quantum beats in the ions of xenon and the reversibility of the sudden spectral changes, multiple quantum beats in different charge states of xenon up to Xe^{3+} and concomitant excited states were configuration-resolved in real-time. The experiment holds promises to access and to shed light on hole-hole and multi-hole correlations in multi-electron atoms/ions whose theoretical ab-initio modeling is not yet within reach. First efforts have been presented focusing at the understanding of the measured coherences.

Chapter 6

Attosecond transient absorption studies II: Real-time observation of atomic ionization

6.1 Motivation

The preceding chapter focused on attosecond transient absorption measurements in which pump and probe fields were not overlapping temporally. Long-lasting quantum coherences in several atomic systems were observed, which for instance allowed the complete reconstruction of valence electron motion in Kr^+ ions.

Another very interesting regime for attosecond transient absorption spectroscopy is the delay range in which the pump and probe pulse have temporal overlap and therefore absorption happens in the presence of the strong pump field. Here, the ultimate goal would be to record atomic ionization in real time. In the presented first proof-of-concept experiments this regime of ATAS is explored in krypton.

Utilizing the same experimental apparatus and pulse parameter as introduced before, this regime can be explored for the first time. Fig. 6.1 shows a fine scan, averaged over 17 consecutive scans, with a delay resolution of 200 as in krypton at the experimentally highest possible intensity of $(6.8 \pm 1.1) \cdot 10^{14} \frac{W}{cm^2}$. As it will be analyzed in detail in section 6.3.1, the NIR pump laser pulse produces krypton charge states up to Kr^{3+} . Due to the spectral broadness of the attosecond XUV probe pulse, all generated charge states, including neutral atoms, possess absorption lines in the measured spectrogram. While the absorption of the ions is building up with increasing delay (Fig. 6.1), the population of the neutral atoms is reduced which leads to a negative absorbance in the range of 91-93 eV. Fig. 6.2 displays a lineout of the spectrogram shown in the previous figure, averaged over ± 90 meV around the peak of the main absorption line which forms due to the creation of

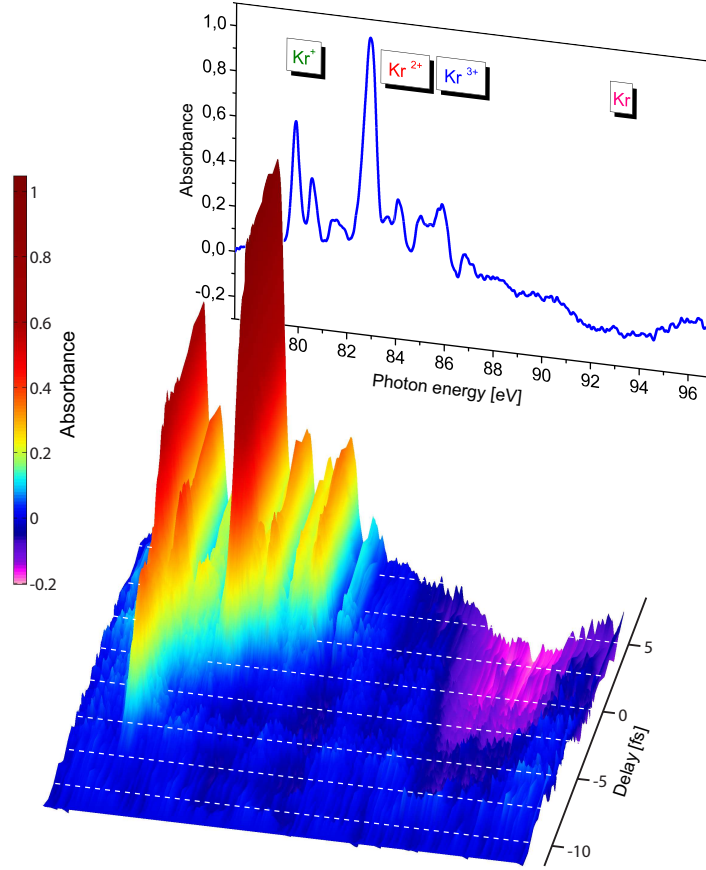


Figure 6.1: High resolution XUV transient absorption spectrogram of krypton ions with emphasis on the ion population build up. The delay is varied in steps of 200 as. As analyzed in detail in Fig. 6.6, the XUV pulse tracks the formation of charge states up to $Kr^{(3+)}$ as indicated in the spectrum in the background which was taken at $\tau = 8.5$ fs. The reduction of the neutral krypton population in the atomic sample in favor of charged states, manifests itself as a decrease of the absorption strength in the range 91-93 eV, where neutral krypton atoms absorb resonantly.

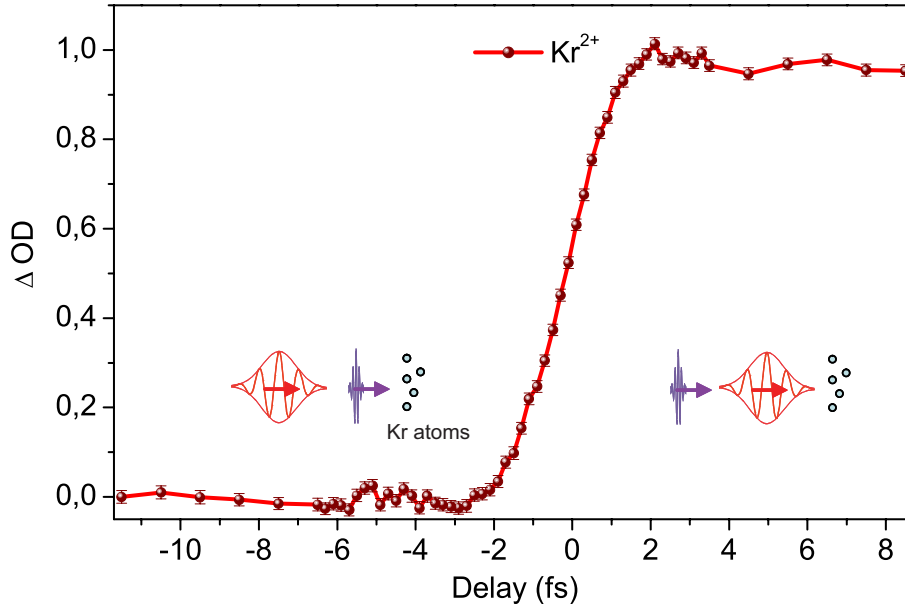


Figure 6.2: Change of optical density of the strongest absorption line (corresponding to Kr^{2+}) contained in the spectrogram shown in Fig. 6.1, averaged in an interval of ± 80 meV around its peak. The two schematic insets illustrate the delay convention used throughout the next sections.

doubly charged Krypton ions [125]. The error bars represent the standard error based on 17 consecutive ATAS scans. For negative delays (XUV first) no absorption due to Kr^{2+} ions is observed whereas the change of the optical density grows for increasing delays and finally results in a quasi-static optical density. The two insets in Fig. 6.2 visualize the utilized delay convention.

However, the question has to be posed to which extent the strength of the transient absorption of specific spectral lines corresponds to the underlying formation of absorbers, which is, as it will be discussed in the next chapter, a non-trivial relation in the presence of a strong laser pulse. Addressing this issue is a necessary milestone for the linkage between the formation of ion population and the observed absorbance.

Besides getting real-time access to ionization dynamics for several charge states, ATAS might also grant insight into strong field laser coupling between different excited states on an attosecond time scale provided that excited states can be spectroscopically resolved. All mentioned potential merits, experimentally motivated by Fig. 6.1, are extremely interesting for acquiring new insight into for example sub-cycle ionization mechanisms which are still discussed controversially.

6.2 Towards a theoretical description of ATAS under strong field influence

6.2.1 Inapplicability of the reduced density matrix description

In chapter 5.1 the theoretical framework for attosecond transient absorption experiments was derived for the delay configuration, with no temporal overlap between the pump and probe pulse. In this case, the XUV absorption process is not influenced by the presence of the strong ionizing NIR field.

In the presence of the strong pump field however, the state of the electronic structure $|\Psi_{pu}(t)\rangle$ is still subject to changes driven by the pump field. However, this state can still be expanded in eigenstates $|\varphi_i\rangle$ with eigenenergies E_i but the expansion coefficients $\alpha_i(t)$ are now time-dependent. Substituting

$$|\Psi_{pu}(t)\rangle = \sum_i \alpha_i(t) e^{-i(E_i - E_0)t} |\varphi_i\rangle \quad (6.1)$$

into Eq. 5.7 and setting for convenience $x = 0$, yields

$$P^{(1)}(t) = in \sum_{i,i'} \int_{-\infty}^t E_{pr}(t') \langle \varphi_i | \hat{\mathcal{Z}} \hat{\mathcal{U}}_{pu}(t, t') \hat{\mathcal{Z}} | \varphi_{i'} \rangle \alpha_i^*(t) \alpha_{i'}(t') e^{i(E_i - E_0)t} e^{-i(E_{i'} - E_0)t'} dt' + c.c. \quad (6.2)$$

The time t' denotes the instance of absorption and t the time at which the polarization response is evaluated. In the previous description, where the pump field was absent at the time of probing, both expansion coefficients $\alpha_i^*(t)$ and $\alpha_{i'}(t')$ had been time independent which allowed the relation of $\alpha_i^* \alpha_{i'}$ to the reduced ionic density matrix $\tilde{\rho}_{ii'}$. The time dependent expansion coefficients can not be related to the reduced density matrix $\tilde{\rho}_{ii'}$ without any assumptions since they depend on two different time variables t and t' . Only for $t = t'$ the previous density matrix can be employed. This would be a good approximation if the decay of the XUV excited states is faster than the characteristic timescale of changes of $\alpha_i(t')$. However in the general case and in consideration of the underlying $Kr^+ 3d$ hole lifetime of 7.5 fs, the polarization response of the XUV excited states lasts substantially longer than the expected sub-cycle dynamics during the pump pulse.

Depending on the atomic structure and the utilized intensities, the depletion of excited states, Stark shift and Auger decay might influence the polarization response. Including a complete set of final states where $\mathcal{H}_0|f\rangle = E_f|f\rangle$, Eq. 6.2 goes over into

$$P^{(1)}(t) = in \sum_{i,i'} \sum_{f,f'} \int_{-\infty}^t E_{pr}(t') \langle \varphi_i | \hat{\mathcal{Z}} | f \rangle \langle f | \hat{\mathcal{U}}_{pu}(t, t') | f' \rangle \langle f' | \hat{\mathcal{Z}} | \varphi_{i'} \rangle \alpha_i^*(t) \alpha_{i'}(t') \cdot e^{i(E_i - E_0)t} e^{-i(E_{i'} - E_0)t'} dt' + c.c. \quad (6.3)$$

Assuming that the NIR field does not mix different final states $\langle f | \hat{\mathcal{U}}_{pu}(t, t') | f' \rangle = 0$ for $f \neq f'$, the polarization response can be expressed as

$$P^{(1)}(t) = \sum_{i,i'} \sum_f \int_{-\infty}^t E_{pr}(t') \langle \varphi_i | \hat{\mathcal{Z}} | f \rangle \langle f | \hat{\mathcal{U}}_{pu}(t, t') | f \rangle \langle f | \hat{\mathcal{Z}} | \varphi_{i'} \rangle \alpha_i^*(t) \alpha_{i'}(t') \cdot e^{i(E_i - E_0)t} e^{-i(E_{i'} - E_0)t'} dt' + c.c. \quad (6.4)$$

Introducing the depletion of probe-excited states by the NIR laser pulse, the Stark effect and Auger decay phenomenologically, the propagator term $\hat{\mathcal{U}}_{pu}(t, t')$ can be approximated as

$$\langle f | \hat{\mathcal{U}}_{pu}(t, t') | f \rangle = \exp \left(-\frac{1}{2} \int_{t'}^t [\Gamma_f(t'') + i \cdot E_f(t'')] dt'' - \frac{1}{2} \Gamma_f^{(Au)}(t - t') \right)$$

where Γ_f is the ionization rate originating from final state $|f\rangle$, $\Gamma_f^{(Au)}$ the Auger decay rate of the final state and E_f the energy of the final state in the presence of the strong pump field. Thus, Eq. 6.4 yields

$$P^{(1)}(t) = \sum_{i,i'} \sum_f \int_{-\infty}^t E_{pr}(t') \langle \varphi_i | \hat{\mathcal{Z}} | f \rangle \langle f | \hat{\mathcal{Z}} | \varphi_{i'} \rangle \alpha_i^*(t) \alpha_{i'}(t') e^{i(E_i - E_0)t} e^{-i(E_{i'} - E_0)t'} \cdot \exp \left(-\frac{1}{2} \int_{t'}^t \Gamma_f(t'') + i \cdot E_f(t'') dt'' - \frac{1}{2} \Gamma_f^{(Au)}(t - t') \right) dt' + c.c. \quad (6.5)$$

Since the wave functions in Eq. 6.5 describe the bound and free electrons of the atomic system in the presence of a strong laser field, a numerical solution of the time-dependent Schrödinger equation is currently not within reach for multi-electron systems, especially since it is necessary to consider two unbound electrons to describe the absorption of singly charged krypton ions. The NIR field ionizes a valence shell electron of the neutral atom and the second electron is needed to describe the XUV excitation of the ion upon the interaction with the probe pulse.

In view of the unique experimental tool of attosecond transient absorption spectroscopy, which offers the exploration of atomic ionization on an attosecond time scale, the very essential question arises if the experimentally observed absorbance $A(\omega, \tau)$ can be directly related to the population of the generated ions via a constant absorption cross-section $\sigma(\omega)$ as dictated by the Lambert Beer's law in the short-pulse approximation (see chapter 5.1.2) during the presence of a strong laser field. The next paragraph will describe a first approach of answering this fundamental question.

6.2.2 Atomic excitation cross-section in the presence of a strong laser field

According to Beer's law, the absorbance $A(\omega, \tau)$ is proportional to the population and the absorption cross-section. The field-free absorption cross-section of a given transition can be calculated straight forward, whereas the determination of the absorption cross-section

in the presence of a strong field remains as a challenge for multi-electron systems. Interpretation of the absorption build-up recorded under strong-field influence might lead to a misinterpretation of the ion population as a function of the delay if the XUV excitation cross-section is modified by the presence of a strong NIR-field. In order to elucidate a potential effect of strong-field influences on the absorption cross-section, the time-dependent Schrödinger equation (TDSE) for a one electron system in one dimension had been solved numerically without the need of approximations as they would have been necessary for solving Eq. 6.5. However, before introducing the conditions and discussing the results of this TDSE simulation, a very important question has to be addressed. Fig. 6.1 shows the formation of absorption lines as a function of the delay between pump and probe pulse. In order to track the ion population within the NIR field, a quantity has to be defined which is proportional to the number density of absorbers. It is known that the ionization of XUV excited states by the NIR field truncates the decay of the excited state and results in a shorter lifetime which in turn leads to a spectral broadening and weakening of the absorption line [126]. Tracing the height of the peak of the absorption line as a function of the delay is therefore not a good measure for the population since it is not invariant to the apparent lifetime of the excited state.

Based on Eq. 5.19, 5.20 and 5.24 we can write

$$\begin{aligned} \frac{\tilde{I}_{pr}(L, \omega)}{\tilde{I}_{pr}(0, \omega)} &= \exp \left(-\frac{4\pi\omega L}{c} \operatorname{Im} [\chi^{(1)}(\omega)] \right) \\ &= \exp \left(-\frac{4\pi\omega L n_0}{c} \operatorname{Im} \left[\sum_{i,i'} \tilde{\rho}_{ii'} \sum_f \frac{\mu_{fi'} \mu_{if}}{E_f - E_{i'} - i\Gamma_f/2 - \omega} \right] \right), \end{aligned}$$

where n_0 is the number density of all atoms in the probing volume. Integrating both sides over ω after taking the natural logarithm on both sides and moving the ω -pre-factor to the left hand side gives

$$\begin{aligned} \int_{-\infty}^{\infty} \ln \left[\frac{\tilde{I}_{pr}(L, \omega)}{\tilde{I}_{pr}(0, \omega)} \right] \frac{1}{\omega} d\omega &= \int_{-\infty}^{\infty} -\frac{4\pi L n_0}{c} \operatorname{Im} \left[\sum_{i,i'} \tilde{\rho}_{ii'} \sum_f \mu_{fi'} \mu_{if} \frac{E_f - E_{i'} - \omega + i\frac{\Gamma_f}{2}}{(E_f - E_{i'} - \omega)^2 + (\frac{\Gamma_f}{2})^2} \right] d\omega \\ &= -\frac{4\pi^2 L n_0}{c} \sum_{i,i'} \tilde{\rho}_{ii'} \sum_f \mu_{fi'} \mu_{if} \int_{-\infty}^{\infty} \frac{\frac{\Gamma_f}{2\pi}}{(E_f - E_{i'} - \omega)^2 + (\frac{\Gamma_f}{2})^2} d\omega \\ &= -\frac{4\pi^2 L n_0}{c} \sum_{i,i'} \tilde{\rho}_{ii'} \sum_f \mu_{fi'} \mu_{if}. \end{aligned} \tag{6.6}$$

This shows that the expression on the left hand side is a lifetime invariant quantity which is proportional to the number density of ionic absorbers. The left hand side of Eq. 6.6 can be transformed by introducing the absorption cross-section according to Beer's law where

n denotes the number density of ionic absorbers:

$$\int_{-\infty}^{\infty} \ln \left[\frac{\tilde{I}_{pr}(L, \omega)}{\tilde{I}_{pr}(0, \omega)} \right] \frac{1}{\omega} d\omega = -nL \int_{-\infty}^{\infty} \frac{1}{\omega} \cdot \sigma(\omega) d\omega.$$

Finally, another lifetime-invariant quantity is

$$\int_{-\infty}^{\infty} \frac{1}{\omega} \cdot \sigma(\omega) d\omega = \frac{4\pi^2 n_0}{c n} \sum_{i, i'} \tilde{\rho}_{ii'} \sum_f \mu_{fi'} \mu_{if}, \quad (6.7)$$

which is independent on the number density of absorbers since n_0 in combination with the diagonal matrix elements of the reduced density matrix $\tilde{\rho}_{ii'}$ provides the amount of ionization. For absorption signatures being spectrally well-confined within the energy interval $2\Delta\omega$ as compared to the central photon energy ω_0 , saying that the photon energy does only merely change within the absorption profile, the invariant quantities can be approximately expressed as the area under the absorption profile divided by the central photon energy ω_0 of the absorption pattern:

$$\int_{-\infty}^{\infty} \ln \left[\frac{\tilde{I}_{pr}(L, \omega)}{\tilde{I}_{pr}(0, \omega)} \right] \frac{1}{\omega} d\omega = - \int_{-\infty}^{\infty} A(\omega) \frac{1}{\omega} d\omega \stackrel{\omega_0 \gg \Delta\omega}{\approx} - \frac{1}{\omega_0} \int_{\omega_0 - \Delta\omega}^{\omega_0 + \Delta\omega} A(\omega) d\omega$$

or the area enclosed by the absorption cross-section (Eq. 6.7) and divided by the central energy ω_0 respectively.

Care has to be taken when applying Eq. 6.7 at delays where both pump and probe pulses overlap. Currently carried out TDSE simulations (not shown here) performed by V. Yakovlev seem to indicate that the area enclosed by the absorbance $A(\omega)$ is insensitive to the depletion of XUV excited states by the strong NIR laser field acting on the atomic system after the XUV pulse has passed the atom and therefore proof that the area underneath the absorbance is a relatively good measure to follow ionization build-up during the presence of a strong ionizing laser pulse if the following conditions are fulfilled:

- Line broadening and weakening only occurs due to the depletion of XUV excited states
- The line shape of the absorbing transition can be also described by a Lorentzian function during the laser pulse.

For connecting the area of the absorption profile to ion population it has to be emphasized that this is only possible as long as the cross-section $\sigma(\omega, \tau)$ does not undergo changes that result in absorption lines which cannot be anymore described with Lorentzian line shapes. In this context, a recent experimental report about time-resolved autoionization and corresponding XUV absorption lines in argon in the presence of a strong NIR laser

field has shown that the absorption lines can also undergo significant structural changes in the presence of a strong laser field [126]. Furthermore, the dipole matrix elements μ_{fi} , μ_{if} might become delay dependent due to the presence of the strong pump field which will distort and polarize the wave function. Under this perspective we will display and analyze in the next paragraphs transient build-up absorption results in quantities related to the area of the absorption profile, even though it is noted that this is probably not the ultimate way of relating transient absorption to atomic population, but at least the most meaningful approach given the current situation of understanding and limited theoretical capabilities.

In order to elucidate the effect of strong-field influences on the absorption cross-section

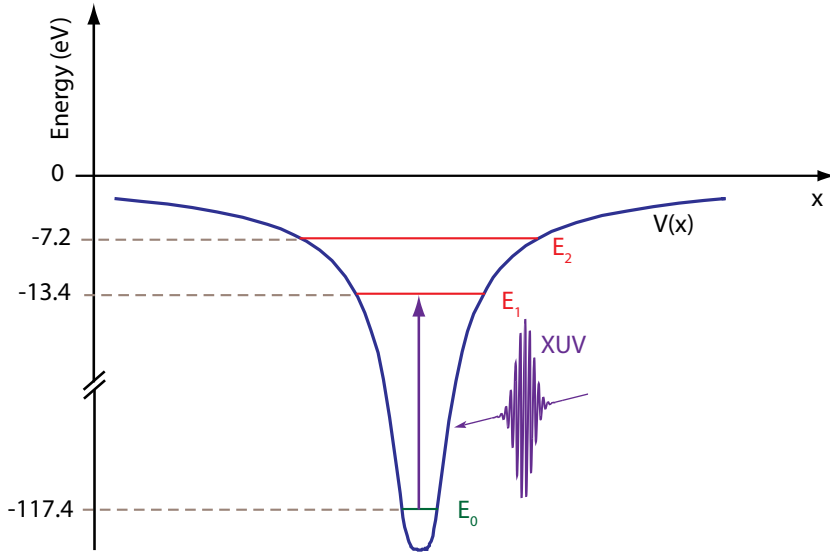


Figure 6.3: Soft-core potential for a 1D one electron TDSE calculation. The ionization potential of the atom in the ground state amounts to 117.4 eV, ensuring the absence of NIR driven high harmonic generation. The XUV probe pulse, centered at 104 eV, resonantly promotes the atomic system from its ground state E_0 into the first excited state E_1 .

$\sigma(\omega, \tau)$, a TDSE simulation for a one electron system in one dimension had been performed by Vladislav Yakovlev for temporally overlapping pump and probe pulses without the need of introducing a reduced density matrix based on venturesome assumptions.

The properties of the pulses and the electronic potential have been chosen such that the 3.5 fs NIR laser pulse at intensities in the order of $10^{14} \frac{\text{W}}{\text{cm}^2}$ is not strong enough to affect the population of the ground state E_0 of the atom. In order to ensure this, the soft-core potential $V(x)$ was adjusted such that the artificial atom has an ionization potential of 117.4 eV as sketched in Fig. 6.3. A weak XUV probe pulse centered at 104 eV with ~ 8.8 eV FWHM bandwidth and a duration of 270 as resonantly excites the atom from the ground state to the first excited state E_1 . In this configuration, the absorption characteristic imprinted on the spectral content of the XUV probe pulse can be numerically investigated for different delay steps of the XUV pulse inside the NIR field. The binding potential of the first excited

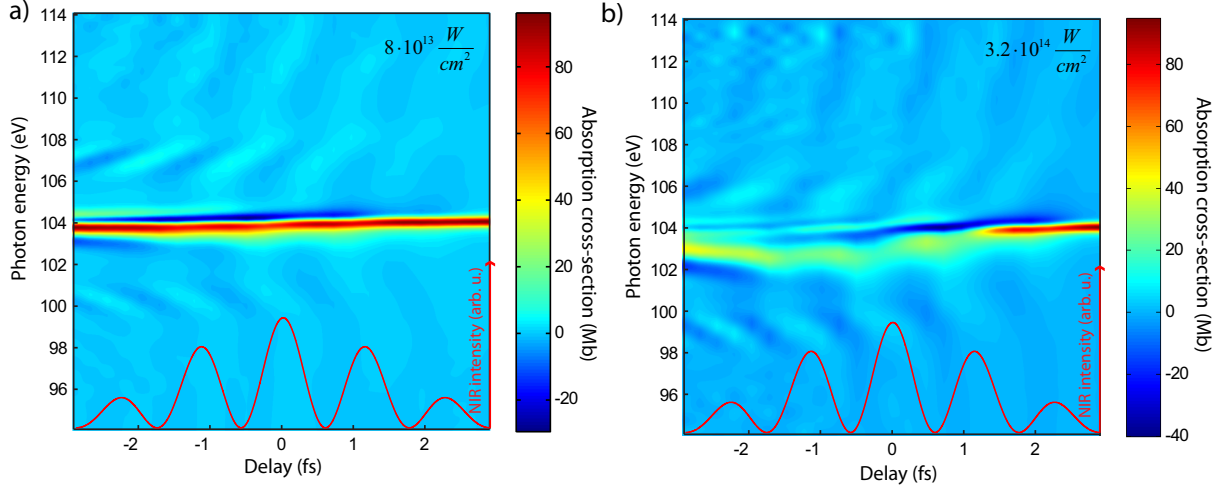


Figure 6.4: Absorption cross-section $\sigma(\omega, \tau)$ as a function of the pump-probe delay investigated by a one electron 1D TDSE simulation as described in the text. It investigates for a very simplified atomic system the influence of a strong NIR field onto the absorption of an XUV pulse where the potential is chosen such that the strong NIR field can not affect the population of the ground state (see Fig. 6.3). Simulation results are shown for a NIR intensity of $8 \cdot 10^{13} \frac{W}{cm^2}$ (a) and $3.2 \cdot 10^{14} \frac{W}{cm^2}$ (b). The natural lifetime broadening is assumed to be 88 meV. The presented plots show the absorption cross-section after convolution with an experimentally feasible Gaussian spectrometer response function of 0.35 eV resolution. For positive delays, the NIR pulse comes before the XUV probe pulse. Insets on the bottom show the corresponding evolution of the NIR pulse intensity.

state E_1 is close to the ionization potential of neutral krypton of 14.00 eV [127]. Hence, the simulation evaluates the XUV absorption during the presence of a strong NIR laser field in a neutral krypton-like model system. Due to the huge ionization potential of the ground state, the population of the atom can not be influenced by the presence of the NIR laser pulse, inferring that there is no NIR initiated ionization and also no high harmonic generation taking place. Numerically solving the time-dependent Schrödinger equation provides the polarization response and division by the spectrum of the XUV probe pulse yields the linear susceptibility which is directly related to the absorption cross-section $\sigma(\omega, \tau)$ of the $E_0 \rightarrow E_1$ transition. Fig. 6.4 shows the absorption cross-section as a function of the pump-probe delay for a NIR intensity of $8 \cdot 10^{13} \frac{W}{cm^2}$ (Fig. 6.4 a) and $3.2 \cdot 10^{14} \frac{W}{cm^2}$ (Fig. 6.4 b). The natural lifetime broadening is chosen to be 88 meV, thus mimicking the Auger lifetime of a 3d vacancy in krypton [112]. The presented plots show the absorption cross-section after convolution with an experimentally feasible Gaussian spectrometer response function of 0.35 eV resolution. For positive delays, the NIR pulse reaches the atom before the XUV probe pulse. For large positive delays the absorption cross-section displays a Lorentzian line shape whereas for smaller delay values the original line splits into two parts and develops negative values. In both intensity cases, the lines are Stark-shifted to lower resonance

frequencies. The origin of the negative absorption during the interaction between pump and probe pulse is still not understood and has to be confirmed by an analytical model on which we are currently working on. Calculating the value $\zeta(\tau) = \int_{-\infty}^{\infty} \frac{\sigma(\omega, \tau)}{\omega} d\omega$ (Eq. 6.7) as a function of delay which was proven to be invariant to broadening of absorption lines due to NIR depletion of excited states (Eq. 6.7), carries the influence of the NIR light field onto the absorption behavior of the atom. Fig. 6.5 displays $\zeta(\tau)$ for different delays and four different NIR intensities as indicated in the figure legend. The interesting result is that $\zeta(\tau)$ is modulated in the presence of the pump field under the perspective that the population of the ground state can not be affected directly by the NIR light pulse. With

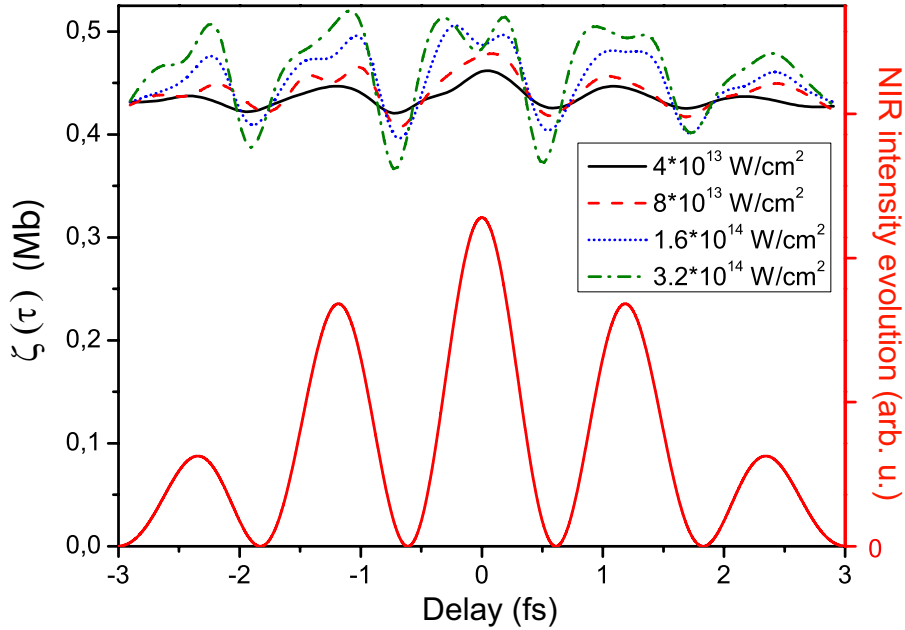


Figure 6.5: Partially based on Fig. 6.4, the quantity $\zeta(\tau) = \int_{-\infty}^{\infty} \frac{\sigma(\omega, \tau)}{\omega} d\omega$ is shown on the left vertical axis for four different NIR intensities as given in the legend. Displayed on the right hand axis is the square of the E-field of the NIR laser pulse. The modulation of the XUV excitation probability related to the intensity crests increases with increasing peak intensity. The exact temporal evolution is not yet understood.

increasing NIR intensity, the modulation of the XUV excitation probability of the atom rises and hence would lead to an interpretation of the formation of absorption lines based on a pump intensity-independent XUV absorption cross-section to misleading ionization dynamics. Further investigations have to be performed to characterize the amount of modulation on the absorption cross-section triggered by the presence of a strong pump field for experiment specific systems to investigate the severeness of this effect which currently keeps us from connecting populations with the strength of absorption for overlapping pump and probe pulses. Since this is a topic of current ongoing research we will display and analyze in the next paragraphs transient build-up absorption results in quantities related to the area

of the absorption profile, even though it is stated that this is probably not the ultimate way of relating transient absorption to atomic population, but at least the most meaningful approach given the current level of understanding and simulation capabilities, which infer an error of less than 17% for an NIR intensity of $3.2 \cdot 10^{14} \frac{\text{W}}{\text{cm}^2}$ for neutral krypton atoms (Fig. 6.5).

6.3 Ionization build-up dynamics in krypton

6.3.1 Identifying absorption lines obtained in krypton

Evaluating the COWAN atomic structure code [111] for Kr^+ ($4p^{-1}$), Kr^{2+} ($4p^{-2}$) and Kr^{3+} ($4p^{-3}$) and calculating the statistically weighted oscillator strength gf of dipole allowed XUV $3d \rightarrow 4p$ transitions, provides a very good understanding of the static absorption signatures obtained in krypton for the highest possible intensity of $(6.8 \pm 1.1) \cdot 10^{14} \frac{\text{W}}{\text{cm}^2}$ as presented in Fig. 6.1 and 6.6. For every charge state ($i = 1, 2, 3$) the atomic structure code gives all dipole allowed oscillator strengths $gf_n^{(i+)}$ and corresponding transition energies $\omega_n^{(i+)}$. The expected cross-section $\sigma(\omega)^{(i+)}$ can be calculated:

$$\begin{aligned} \sigma(\omega)^{(i+)} &\propto G(\omega) \circledast \sum_n gf_n^{(i+)} L_n(\omega) \\ &\propto \sqrt{\frac{4 \ln 2}{\pi \Delta^2}} e^{-\frac{4 \ln 2 (\omega - \omega_0)^2}{\Delta^2}} \circledast \sum_n gf_n^{(i+)} \frac{1/(2\pi)\Gamma_n}{\left(\omega - \omega_n^{(i+)} + \omega_{off}^{(i+)}\right)^2 + (\Gamma_n/2)^2}, \end{aligned} \quad (6.8)$$

where the convolution (displayed as \circledast) of the sum of Lorentzian line shape functions with the normalized Gauss function $G(\omega)$ accounts for the finite spectrometer resolution. The spectrometer resolution Γ had been 0.31 eV and we assume a charge state and j independent decay width Γ_n of the $3d^{-1}$ hole of 88 meV [112]. The parameter $\omega_{off}^{(i+)}$ allows for an overall shift of the absorption pattern along the energy axis which was used to improve the agreement between experiment and the theoretically obtained cross-section. The obtained ab-initio absorption cross-section of Kr charge states are shown together with a binned lineout of the experimental data in Fig. 6.6. The presented experimental absorbance spectrum corresponds to the delay of $\tau \approx 8.5$ fs of Fig. 6.1. The error bars indicate the standard error of the mean values acquired from 17 spectra recorded at the same delay. Comparing it to the ab-initio cross-section of the three charge states, shows a very good agreement. Hence the XUV probe pulse shows the formation of charge states up to Kr^{3+} . The absolute position of absorption lines belonging to a charge state were shifted slightly as a whole to increase the agreement with the experiment. This is justified since atomic structure codes are known to be less accurate in determining absolute energy values than relative ones and second, the calibration of the XUV spectrometer can not be guaranteed to be better than ~ 1 eV. Therefore the following absolute energy shifts are implemented: $\omega_{off}^{(1+)} = 0.65$ eV; $\omega_{off}^{(2+)} = 1.3$ eV and $\omega_{off}^{(3+)} = 1.35$ eV. The assignment of absorption lines to the charge state of krypton, from which they are originating upon

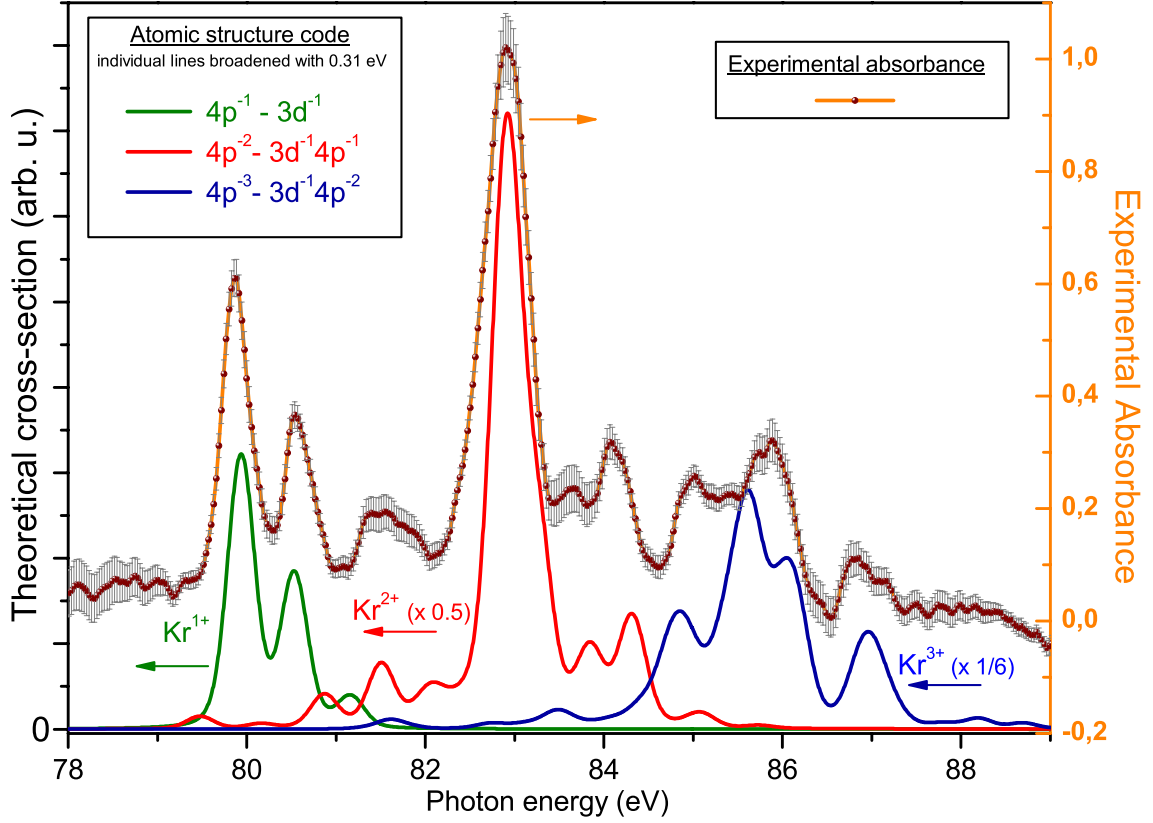


Figure 6.6: Plotted as red dots and connected with an orange line are the experimental transient absorption data points at a delay of $\tau \sim 8.5$ fs of Fig. 6.1. Error bars represent standard errors of the mean values acquired from 17 spectra recorded at the same delay. Shown on the left vertical axis are the calculated absorption cross-sections for XUV radiation of Kr^+ , Kr^{2+} and Kr^{3+} (see text for details). This demonstrates that strong-field ionization with ~ 3.8 fs laser pulses at $(6.8 \pm 1.1) \cdot 10^{14} \frac{W}{cm^2}$ leads up to triple ionized krypton ions.

XUV absorption, is very essential for defining certain spectral windows which might grant insight into atomic ionization dynamics. In sharp contrast to the measurements obtained in xenon (section 5.6), krypton does not inherit any detectable delay-introduced non-resonant absorption signatures.

The resonant absorption of the neutral krypton atoms in the range of 91-93 eV (Fig. 6.1) arises from XUV excitation of krypton to states $3d_{5/2}^{-1}5p$, $3d_{3/2}^{-1}5p$ and $3d_{3/2}^{-1}6p$ [128].

6.3.2 Observed absorption build-up dynamics in krypton

In order to trace the strength of absorption lines connected to different charge states as a function of NIR intensity, the absorption lines were spectrally integrated and the mean

value of the absorption is converted into absorbance or change of optical density $\Delta OD(\tau)$ ¹:

$$\Delta OD(\tau) = \ln \left[\frac{1}{f - s + 1} \sum_{i=f}^s \frac{I_0(\omega_i)}{I_{trans}(\omega_i, \tau)} \right] \quad (6.9)$$

where the discrete absorption values $\frac{I_0(\omega_i)}{I_{trans}(\omega_i, \tau)}$ are summed in the spectral range from ω_s to ω_f . The indices i, s and f denote the number of the finite spectrometer pixel. According to the preceding section, $\Delta OD(\tau)$ is our preliminary approach in analyzing the formation of absorption strength which will be - given the current degree of understanding - in a reasonable agreement with the underlying ion population as a function of delay.

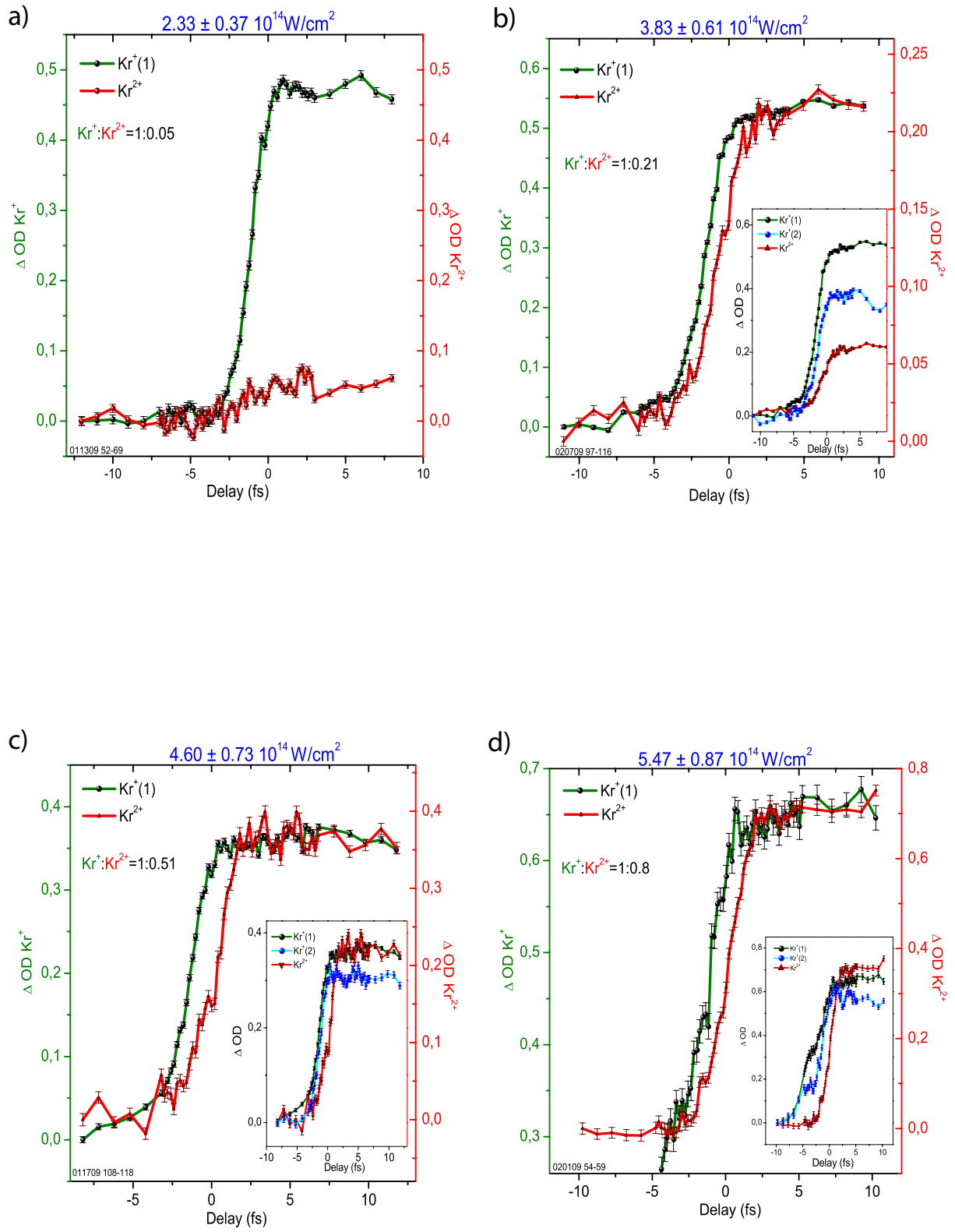
As shown in Fig. 6.6 every charge state manifests itself in several discrete absorption lines. In order to achieve better signal to noise ratios and more reliable curves showing the formation of the change in optical density ($\Delta OD(\tau)$), spectral binning over all absorption lines related to one charge state is performed for Kr^{2+} (82.3 - 83.5 eV) and Kr^{3+} (85.5 - 86.1 eV). The only exception is made for two of the absorption lines of krypton. $Kr^+(1)$ denotes the transition $4p_{3/2}^{-1} \rightarrow 3d_{5/2}^{-1}$ (79.5 - 80.2 eV) and $Kr^+(2)$ the line $4p_{1/2}^{-1} \rightarrow 3d_{3/2}^{-1}$ (82.3 - 83.5 eV) (see Fig. 5.5 for energy-level diagram of Kr^+). The sub-division between the two main lines of Kr^+ is necessary since they form differently for high intensities. As known from previous chapters, the weakest line of Kr^+ , corresponding to the transition $4p_{3/2}^{-1} \rightarrow 3d_{3/2}^{-1}$ inherits a substantial amount of oscillations which are originating from the launched spin orbit wavepacket motion. Therefore this line is not being investigated by the build up dynamics since this might be essentially influenced by the spin orbit quantum beat.

In this category of ATAS measurements, especially the build-up slope of the absorption lines was sampled with a temporal resolution of (200 ± 30) as. Several representative data sets are shown in Fig. 6.7 a) to f) for increasing intensities. At low intensities only Kr^+ is generated, whereas at high intensities charge states up to Kr^{3+} are detected. The depicted error bars show the experimental standard errors for every sampled delay point based on several absorption spectra (between 10 to 20 spectra depending on the data set) measured at the same delay. The CE-phase was locked throughout every data set. Whereas every main panel a) to f) shows selected absorption transitions scaled such that stationary ΔOD values after the build-up match each other, the inset in the individual graphs show the formation of the absorption lines on a common vertical ΔOD scale. Care has to be taken not to connect the ratios of the absorption lines directly to fractional ionization. As shown in Fig. 6.6 the higher the charge state of the ion, the higher the absorption cross-section. In order to provide real fractional ionization ratios after the pump pulse is over for every scan, the cross-section for every ionic state has been taken into account and the approximate number density of absorber has been determined at the largest delay which is expected to be NIR field-free. Those ratios are shown in every main graph a) to f) as

¹Deviating from the convention most commonly used in the literature, the optical density is defined via the natural logarithm to obtain direct linkage between the absorption strength and the population, its cross-section and the length of the gas cell.

$Kr^+ : Kr^{2+} (: Kr^{3+})$. For the two highest intensities exceeding $6 \cdot 10^{14} \frac{\text{W}}{\text{cm}^2}$ one can observe that the lines of Kr^+ drop again after a certain delay point. This saturation phenomenon indicates that the number of neutral absorbers is completely ionized and population of Kr^+ is instead transferred to higher ionic species.

For low intensities the formation dynamics of $Kr^+(1)$ and $Kr^+(2)$ are similar (b,c) but starting at around $5.5 \cdot 10^{14} \frac{\text{W}}{\text{cm}^2}$ both lines develop a pedestal which is more pronounced on the $Kr^+(1)$ line. The origin of this pedestal is still unclear. Attempts to explain it as a result of pre-ionization of the neutral atoms by a pre-pulse have failed for the given intensities since the pre-pulse would be too weak to launch ionization of the target at such a pronounced level. Therefore the $Kr^+(1)$ line in the main panel of Fig. 6.7 d)-f) was scaled such that the second ionization slope after the pre-structure is scaled to match Kr^{2+} and Kr^{3+} , respectively.



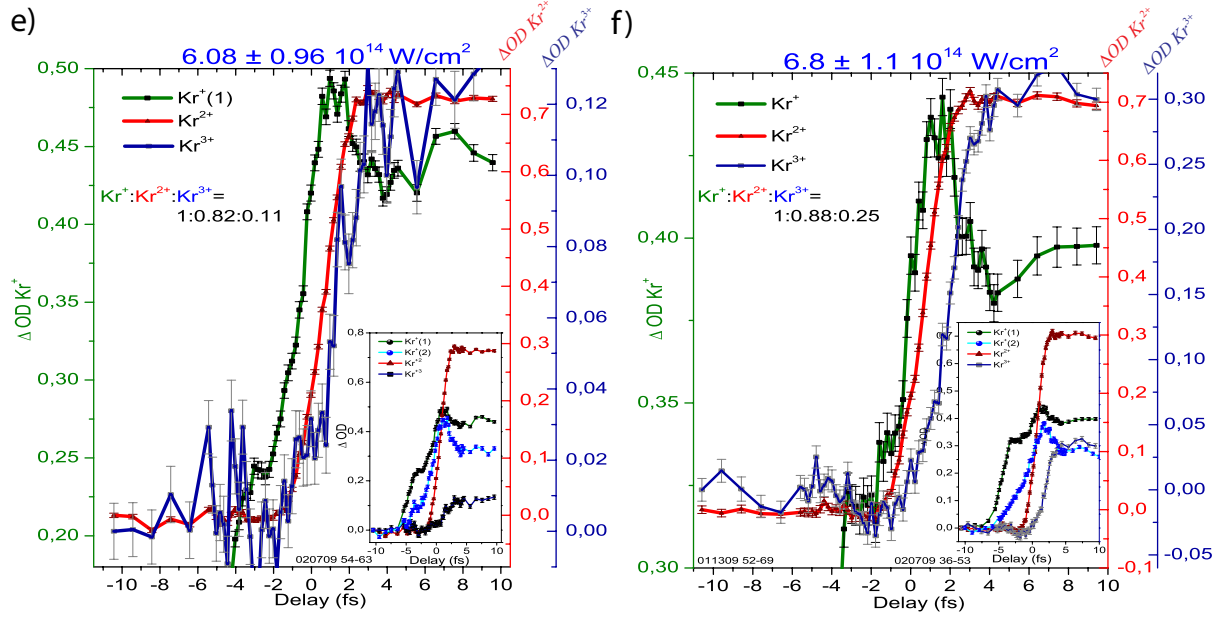


Figure 6.7: Change in optical density ΔOD (defined according to Eq. 6.9) of absorption lines as a function of pump-probe delay where zero corresponds to the delay at which the main absorption line of Kr^+ reaches 90 %. Graphs (a)-(f) show the build-up dynamics for some selected data sets at low intensity (a) up to the experimentally highest possible intensity (f). Intensities are written in the title of each graph. Depicted in the main panel are the absorption lines scaled such that they appear to be normalized to the maximum absorbance after the pulse, whereas they are shown for comparison on a common vertical axis in the sub-panel in most of the presented diagrams. Observed delays between the absorption lines of different charge states are further analyzed by Eq. 6.10. Results are presented in Fig. 6.9. Every graph furthermore contains information about ratios which describe their underlying fractional ionization number densities after the NIR pump pulse as denoted by $Kr^+ : Kr^{2+} (: Kr^{3+})$.

While comparing the rise of the absorption strength of the charge states with each other, it becomes obvious that there is a time retarded rise of absorption lines from higher charge states as compared to absorption lines of lower charged ions. To calculate the observed delay between different charge states more precisely, the formation of the strength of the absorption line $\Delta OD(\tau)$ have been fitted by an error-function:

$$\Delta OD(\tau) = a + b \int_{-\infty}^{\tau} e^{t_r^2(\tau' - \tau_0)^2} d\tau', \quad (6.10)$$

where the parameters a , b , t_r and τ_0 are fit values. This fit function assumes that the number density of generated ions is proportional to the area under the envelope of the NIR pump pulse up to the delay τ where the target is probed by the XUV pulse. The

delay where the fit function reaches 50% of its maximum value is denoted as τ_0 . Under the perspective that this assumption arises from an intuitive guess that has little to do with the real ionization processes and dynamics, the fit function merges the shape of the observed absorption dynamics very well and allows therefore a precise quantification of delay between the formation of different absorption lines. Fig. 6.8 shows this in a representative way for the data set depicted in Fig. 6.7b). The rise or formation time of any absorption line can be defined as the time it takes the line to progress from its 10% to 90% level of maximum ΔOD . It is still physically unclear why the error-function based fit curve fits the formation of the absorption quite well. Determining the rise times for several different data sets taken at different days and different intensities results in an average rise time of (3.13 ± 0.21) fs ² for the formation of the absorption strength of Kr^+ and of (3.34 ± 0.24) fs for Kr^{2+} . The rise time of the absorption line of Kr^{3+} amounts to (2.85 ± 0.10) fs which is shorter than the formation times of the singly and doubly charged ions, hence providing important information about ionization dynamics and their modeling based on these observations which have not been accessed before. This result furthermore clearly proves confinement of the ionization window of the sub-4 fs NIR laser pulse to less than 3.4 fs. Persisting, intensity dependent trends of the rise time for the same charge state were not observed.

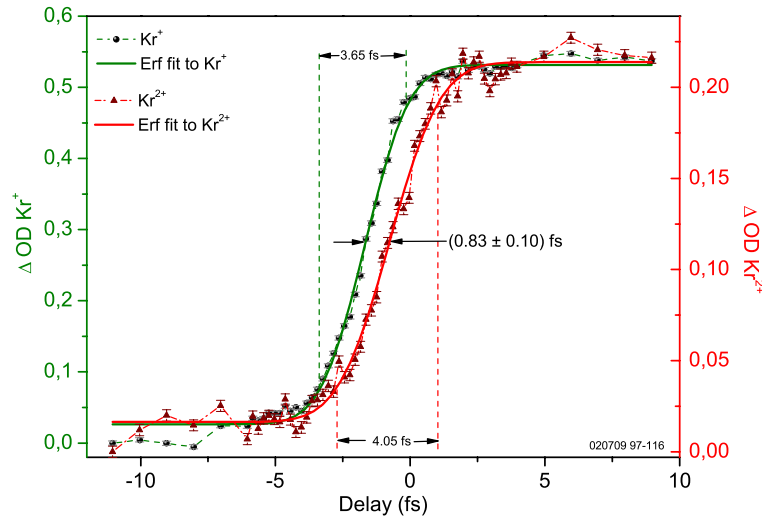


Figure 6.8: Data set shown in Fig. 6.7b) fitted by an error function as defined in Eq. 6.10. The rise times for the two charge states and the delay between the absorption lines of Kr^+ and Kr^{2+} for this representative data set are indicated.

²The rise times for Kr^+ were calculated by averaging the obtained values of the $4p_{3/2}^{-1} \rightarrow 3d_{5/2}^{-1}$ and the $4p_{1/2}^{-1} \rightarrow 3d_{3/2}^{-1}$ transition for every data set. To avoid misinterpretations, for high NIR intensities only the $4p_{1/2}^{-1} \rightarrow 3d_{3/2}^{-1}$ transition was evaluated since the $4p_{3/2}^{-1} \rightarrow 3d_{5/2}^{-1}$ line contains a pronounced pedestal.

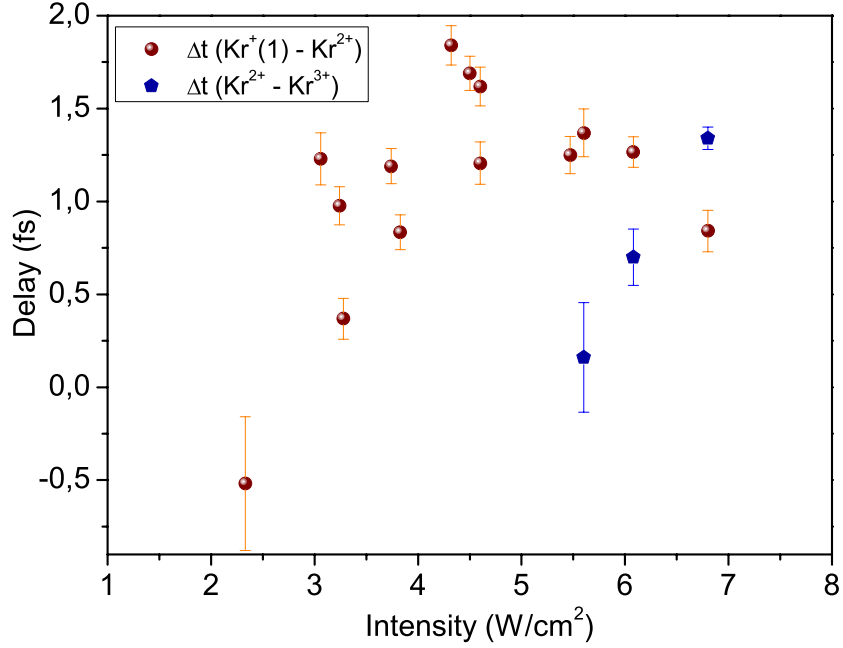


Figure 6.9: Extracted from several data sets and shown as a function of intensity are the measured delays between the formation of the absorption lines of different charge states. $\Delta t(Kr^+(1) - Kr^{2+})$ shows the delay between Kr^{2+} and the transition $4p_{3/2}^{-1} \rightarrow 3d_{5/2}^{-1}$ of Kr^+ and $\Delta t(Kr^{2+} - Kr^{3+})$ the retardation of Kr^{3+} with respect to Kr^{2+} . Positive delays indicate that the absorption of higher charge states are formed later than the lower charge states to which they are referenced. On average, the delays correspond to one-half the laser period $T_L/2 \approx 1.25$ fs. At intensities where the charge state is only marginally created, the delays seem to vanish whereas for higher intensities they are located at around 1.25 fs, equal to half a laser period (consult text for details).

By comparing different τ'_0 s for diverse charge states within one data set, the delay between the appearance of the absorption lines of different charge states can be quantitatively investigated. Repeating this analysis for the best 15 data sets which exhibit a high degree of fidelity, taken under different intensities gives a more reliable estimate for the observed delays. Corresponding delays between $Kr^+(1)$ and Kr^{2+} , marked as $\Delta t(Kr^+(1) - Kr^{2+})$, and between Kr^{2+} and Kr^{3+} labeled as $\Delta t(Kr^{2+} - Kr^{3+})$ were determined for all sets. Fig. 6.9 displays the obtained distribution of observed delays as a function of intensity. Positive delays indicate that the absorption of the higher charge state is delayed with respect to the lower charge state's appearance. The average delay of all evaluated data sets between the absorption lines of $Kr^+(1)$ to Kr^{2+} amounts to (1.08 ± 0.16) fs. For the mean delay of $\Delta t(Kr^+(2) - Kr^{2+})$ (1.19 ± 0.20) fs are extracted. This value is similar to the mean delay of Kr^{2+} if referenced to $Kr^+(1)$ and shows that the different strength of the pedestal (which is less pronounced for the second line of Kr^+) does not substantially affect the extracted delays. This well-resolved delay is close to one-half of the laser period ($T_L/2 \approx 1.25$ fs)

which is in good agreement with predictions based on the Keldysh theory (see chapter 1) [47]. For the delay between the doubly and triply ionized charge state, similar values are found. As it can be seen from Fig. 6.9, both delays seem to increase with rising intensity. At intensities where the charged states are only slightly visible, vanishing delays are observed. For higher intensities, the delays seem to average around one-half of the laser period. Ongoing theoretical investigations are being performed in order to shed light on this dependency as well as the on the shorter rise times for Kr^{3+} since it holds promise to elucidate atomic ionization on a sub-cycle time-scale and to model it based on these first ever real-time observations. This time-resolved formation of different charge states marks the first time in the history of science that the sequential (delayed) character of ionization was observed in a direct pump-probe experiment. However care has to be taken by associating the formation of absorption lines in the presence of a strong laser pulse precisely with the real evolution of the number density of absorbers. To which extend small corrections between the resonant ΔOD traces and the underlying population have to be employed is still not yet clear and remains as a subject of current research.

6.3.3 Absence of ionization half-cycle step-like structures

The ADK theory for ionization predicts an ionization rate yielding its highest values predominantly at the intensity crests of the ionizing laser field as introduced in chapter 1. Therefore one expects that the ion yield during a laser pulse strongly increases at intensity crests and thus the ion density as a function of time is expected to exhibit a step-like structure of half the laser period. Those consequences of the tunnel ionization regime have been observed by Uiberacker et al. [43]. In their experiments the attosecond XUV pulse excited and ionized neon atoms and created Ne^+ and Ne^{2+} ions. Some of the Ne^+ ions were promoted into satellite states (shake-up states) which only decay on a picosecond timescale. The intensity of a NIR laser pulse of a duration of 5.5 fs at 750 nm was adjusted such that it does not produce any Ne^{2+} ions directly. However in the presence of the XUV pulse the prepared shake-up states of Ne^+ could be easily further ionized by the NIR laser pulse. The observed ionization yield of Ne^{2+} increased by steps approximately spaced by half the laser period as a function of delay between the XUV and NIR laser pulse [43] (Fig.4 herein).

The presented proof-of-concept experiments on attosecond transient absorption spectroscopy do not show any reliable signs of sub-cycle ionization steps, neither for low, nor for high intensities as shown in Fig. 6.7. Since the gas pressure and interaction volume is larger than for streaking experiments, two maybe essential effects have to be taken into account. Upon propagation of the ionizing few-cycle NIR laser pulse through the krypton gas target, the laser pulse might undergo some plasma defocussing, as a combined effect of diffraction and ionization [129], and a distortion of the temporal structure of the E-field. This potential source of averaging originates mainly from the very strong intensities of the NIR laser pulse and from the quite dense gas target which is filled with krypton gas at 80 mbar. Both parameters are definitely substantially smaller for streaking-type experiments and therefore remain uncritical for attosecond streaking measurements. Se-

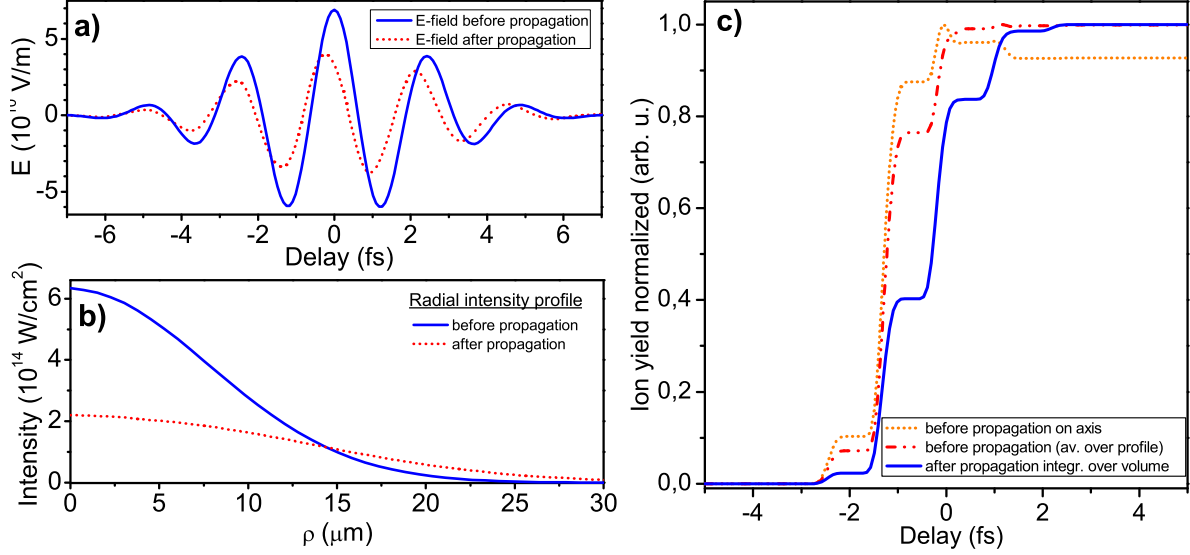


Figure 6.10: Propagation of the NIR pump pulse (duration: 3.8 fs, central wavelength: 750 nm, peak intensity: $6.4 \cdot 10^{14} \frac{\text{W}}{\text{cm}^2}$) described in the time domain before and after propagation (a) through the 1 mm long gas target at 80 mbar krypton and the corresponding radial plasma defocussing effect (b). Panel (c) displays the normalized temporal formation of the ion yield for the pulses displayed in a). Blue curve inherits all propagation and volume averaging effects. These effects can not explain the absence of ionization steps.

cond, since the quasi static gas cell has an extension of 1 mm along the beam axis, the complete radial and axial interaction volume between pump and probe pulse has to be considered. In order to estimate the importance and consequences of those propagation and volume averaging effects, a numerical simulation has been implemented which propagates the NIR laser pulse of 3.8 fs pulse duration and 750 nm central wavelength through the gas target (80 mbar) (courtesy of V. Yakovlev). Ionization is described in an ADK rate-like approach. All simulation parameters were chosen such reflect experimental conditions. The propagation length had been 1 mm and a FWHM intensity beam waist of $18.4 \mu\text{m}$ (before propagation) had been taken into account. Fig. 6.10 shows the simulation results for a Gaussian beam profile whose peak intensity is $6.4 \cdot 10^{14} \frac{\text{W}}{\text{cm}^2}$ which corresponds to the intensity of the scan shown in Fig. 6.7 f). In panel a) the 3.8 fs long electric field is shown at the beginning of the propagation distance (blue) and after the 1 mm of propagation (red). Upon propagation the peak electric field reduces because of a plasma defocussing shown in detail in b). Upon propagation the beam diameter expands substantially and the intensity drops by almost two thirds. Another effect of the propagation is the distortion of

the E-field cycles shown in a) which is also accompanied by a shift of the CE-phase. Fig. 6.10 c) shows the expected normalized single charged ion yield as a function of delay for the on-axis E-field strength before propagation (orange dotted curve), which can be compared to the formation expected before propagation but by averaging over the radial intensity distribution (red dash-dotted line). For the chosen ionization rates (which are not necessary in quantitative agreement with the experiment) the averaged formation curve before propagation shows less saturation behavior than the on axis distribution since the intensity drops laterally to lower values for a Gaussian beam profile as shown in b). The blue curve in c) displays the obtained overall ionization curve which integrates all propagation and volume averaging effects. The steps appear to be less sharp but still very pronounced. Thus, propagation and volume averaging effects assuming tunnel ionization according to ADK theory can not explain the absence of ionization steps.

In order to conclude it shall be mentioned that it can not be excluded that any sort of thermal drift in the detection apparatus or strong-field induced effect, which is not included in the modeling, has led to a smearing of the ionization steps as they are being proposed by Keldysh-like ionization processes. Furthermore, it is up to now not clear to which precise extent the strength of the absorption lines encode the ion population during the presence of a strong laser field. It is conceivable that the presence of the strong laser field alters the polarization response in such a way that it softens and smooths out expected ionization sub-cycle dynamics at maybe unfavorable experimental parameters.

6.4 Conclusion and next steps towards tracing ion populations in real-time

This chapter reports the first real-time observation of sequential ionization of atoms which was performed in a proof-of-concept experiment where attosecond transient absorption spectroscopy was performed in krypton in the presence of the strong pump laser. The sub-4 fs NIR laser pulse confines the ionization window to less than 3.4 fs, in which krypton is ionized. According to its spectral bandwidth, the attosecond XUV probe pulse can record the formation of ions simultaneously and state-resolved for more than one charge state at the same time. Therefore, absorption signatures of all generated charge states, including the neutral lines, open in principal the door to exploit sub-cycle ionization dynamics in all launched ions within the same attosecond transient absorption experiment. ATAS at high NIR intensities shows the time-resolved saturation of ionization within the ionizing NIR laser pulse. Both the real-time resolved delayed ionization of different charge states as well as the direct observation of saturation of singly-charged ions within the strong NIR laser pulse have not been experimentally established or reported before.

It has been shown theoretically in section 6.2.2 and by experimental observations contradicting expectations based on a ADK model that accessing ion populations in the presence of an ionizing strong laser field is not straight forward and remains as a topic of current ongoing research. Furthermore it was shown that the absence of ionization steps as ex-

pected by ADK theory can not be explained by propagation and volume averaging effects. However as it was investigated by the simplified 1D one electron TDSE simulation, that the presence of the strong laser field in principal can modulate the XUV excitation cross-section on a sub-cycle time scale which might lead to a smearing of expected absorption steps due to an additional modulation which might be phase shifted with respect to the NIR laser. Careful theoretical simulations will have to elucidate the influence of the strong laser field on the XUV absorbance for experimentally relevant systems.

One of the latest thoughts about following the Kr^+ ion population during their creation, has led to a surprising result which will influence the next steps towards tracing ion populations during strong-field interaction. So far, it has been assumed that the dominant channel of XUV absorption in Kr^+ ions in the performed experiments had been the excitation of $3d$ electrons into the vacancy in the $4p$ valence shell as indicated in Fig. 6.11 a). For decent NIR intensity this is probably correct, but it can not be excluded that neutral Kr atoms are excited by resonant multi-photon absorption of NIR laser photons into their first or second excited state which can be described with the electron configuration $4s^2 4p^5 5s^1$. Those excited states are located ~ 10 eV above the ground state [108]. This excitation would require 5 to 7 photons of the 3.8 fs NIR laser pulse. Fig. 6.11 b) visualizes the spectator excitation of neutral Kr atoms in which the XUV pulse would still promote a $3d$ to $4p$ dipole transition, but in the presence of the excited electron in the $5s$ shell. At first glance, those absorption lines would be expected to be substantially shifted with respect to those originating from a probing of the Kr^+ ions and would lead - if at all - to absorption lines in a different spectral range. It came as a surprise that an atomic structure calculation with which the absorption lines and their cross-section were calculated for both scenarios as shown in Fig. 6.11 a) and b), gives a similar XUV absorption pattern as indicated in Fig. 6.11 c). The red curve displays the three absorption lines of Kr^+ , namely the transition $4p^{-1} \rightarrow 3d^{-1}$ between the two manifolds and as comparison in blue the expected absorption profile for the spectator absorption of excited krypton described as $4p^{-1}5s^1 \rightarrow 3d^{-1}5s^1$. All spectral lines were assumed to have the same lifetime which dictates an intrinsic linewidth of 88 meV [112]. Furthermore, the Lorentzian line shapes were convolved with the spectrometer response function yielding our standard experimental spectral resolution of 350 meV. The term 'effective cross-section' is used to describe the cross-section profile which is convolved by the spectrometer response function. Despite a slight energetic displacement (which can be due to the atomic structure code calculation itself) of both effective cross-section curves, their similarity is striking. In the performed experiments, contributions to the absorption, originating from spectator absorption would not have been discernible from the absorption generated by krypton ions. Another unexpected effect is that due to the finite spectrometer resolution the effective cross-section of the XUV absorbance of the spectator exceeds the one of the ion by almost a factor of two, rendering the population of the spectator to be very influential onto the overall sub-cycle time-resolved experimental absorbance. Further theoretical investigations for experimental conditions will elucidate the probability of exciting neutral krypton atoms.

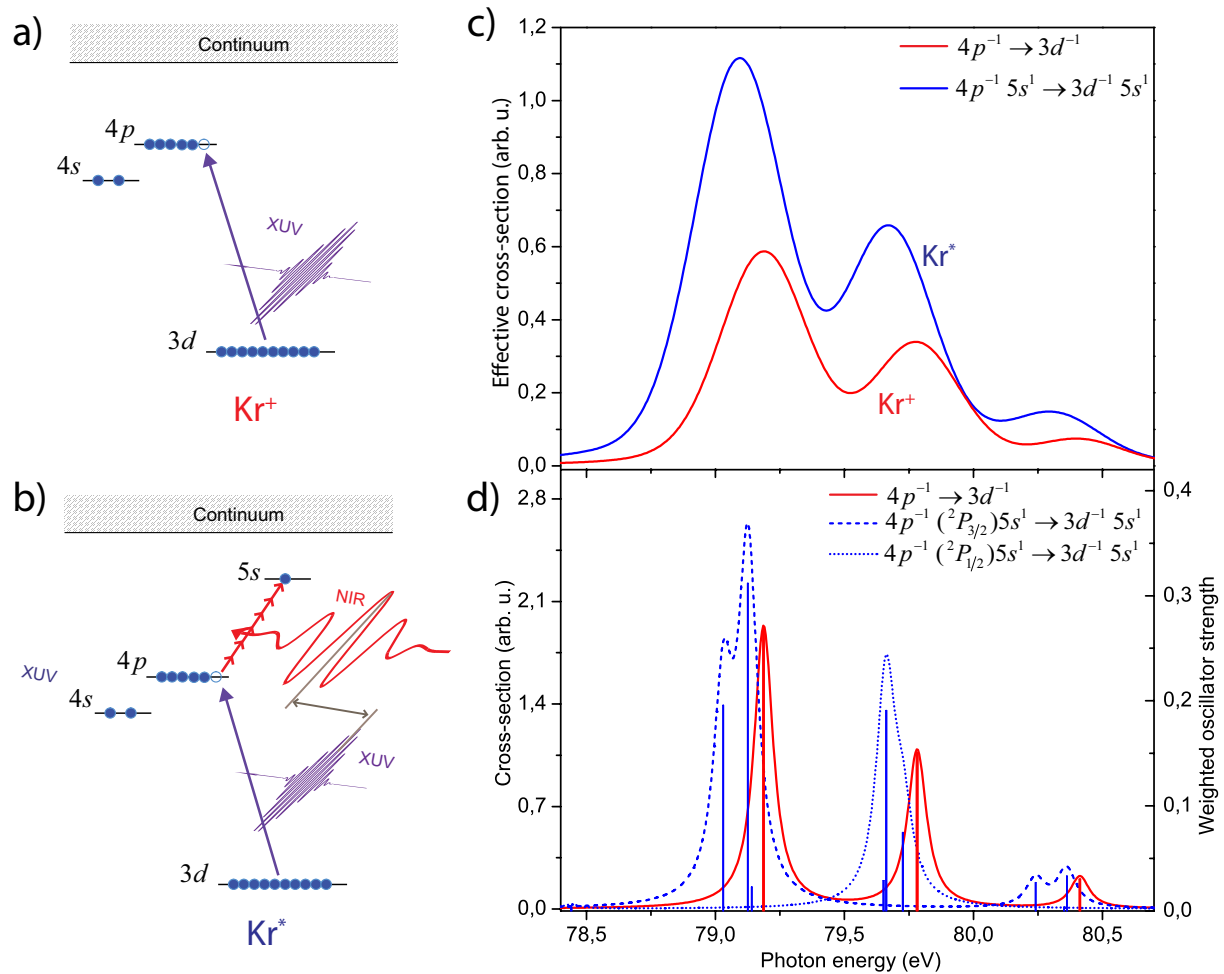


Figure 6.11: (a) Demonstrative sketch of XUV $3d$ to $4p$ excitation in side an krypton ion as it has been monitored in experiments described in detail before. Shown in panel (b) is a similar XUV absorption process ('spectator scenario') which can take place in an excited neutral Kr atom that had been excited by a multi-photon process triggered by the NIR laser field. Both absorption channels lead to similar effective cross-section profiles (shown in (c)) as investigated by the COWAN atomic structure code [111] and convoluted for the currently experimentally relevant resolution of 350 meV. Strikingly, the effective absorption cross-section of the spectator scenario is intriguingly similar to the one describing XUV absorption of the ion but is almost twice as high as the absorbance originating from the ion. A substantially higher spectral resolution would allow the identification of the different contributions to the observed and delay-resolved formation of absorption lines. For a hypothetic spectral resolution of 10 meV graph (d) presents the absorption profiles for the same transitions shown in graph c) for the ion (red curve) and for the spectator arrangement, whose contribution is split into the one originating from the first excited state of krypton ($4p^{-1}(^2P_{3/2})5s^1$) (dashed blue line) and from the second ($4p^{-1}(^2P_{1/2})5s^1$) (dotted blue line) which are both around 10 eV above the ground state of Kr and spaced by ~ 0.1172 eV [108].

Contributions of this spectator channel could have also led to a softening of ionization steps and might also be the key towards understanding the early rise of the strongest absorption line of Kr^+ ($4p_{3/2}^{-1} \rightarrow 3d_{5/2}^{-1}$) as shown in Fig. 6.7 d) to f) for the highest experimental intensities.

In order to strengthen the state-resolving power of ATAS experiments even further, implementation of an ultra-high resolution XUV spectrometer at around 80 eV would provide further knowledge on the origin of absorption signatures as shown in Fig. 6.11 d). Here the two absorption profiles of Fig. 6.11 c) for the krypton ion and the NIR excited neutral atom are shown again, but this time with a spectral resolution of 10 meV, allowing to resolve intrinsic linewidths. At such an extraordinary resolution, it would be possible to differentiate between the main contribution of the ion and the excited neutral atom which however behaves spectroscopically almost like the ion. For more insight, the absorbance originating from the spectator channel is displayed also state-resolved. The dashed line displays the absorbance originating from the first excited state of krypton 9.915 eV above the ground state and noted as $4p^{-1}(^2P_{3/2})5s^1 \rightarrow 3d^{-1}5s^1$ and the dotted line the cross-section originating from the second excited state of krypton at 10.032 eV and denoted as transition $4p^{-1}(^2P_{1/2})5s^1 \rightarrow 3d^{-1}5s^1$ [108]. The discrete vertical lines indicate the oscillator strength of the center of a transition weighted by their statistical weight and referenced onto the vertical axis on the right hand side of the graph.

Besides this opening new experimental perspective for next experiments, a fundamental question of quantum mechanics has to be addressed too, which remains as a challenge for theorists. During strong-field interaction, the wavefunction is being distorted such that the Hilbert space, based on the eigenvalues of the unperturbed Hamiltonian, does not provide a complete basis for the polarized wave-function. Hence, a projection of the wave-function onto the basis vectors is meaningless to gain access to the population of a specific state of the atom during strong-field influence. A quantity or approach has to be worked out which quantifies the amount of generated ions during the interaction of the atom with a strong laser field - or is it not possible to speak about ion populations evolving as a function of time during a strong laser field?

I am convinced that future advances in both experimental and theoretical perspective will guide this exciting and still poorly understood field of monitoring sub-cycle ionization dynamics on an attosecond time scale to new and almost unexplored details of time-resolved atomic ionization.

Chapter 7

Conclusions and Outlook: ATAS & sub-cycle waveform synthesis

7.1 Conclusions

The thesis has presented an extension of the tool box of attosecond science to include transient absorption spectroscopy, establishing a novel technique for the exploration of the microcosm, namely attosecond transient absorption spectroscopy (ATAS). By employing quasimonocycle NIR laser pulses (1.5 optical cycles in duration) as well as isolated XUV pulses (< 150 as), we have been able to demonstrate real-time access of ionization dynamics in atoms as well as valence shell electron dynamics in the generated ions.

In the range of temporal overlap between the attosecond pulse and the strong field, the formation of absorption lines corresponding to singly, doubly and triply charged krypton ions as a function of delay were measured. The presence of the strong laser field during the XUV excitation of the core hole influences the XUV absorption cross-section and renders the extraction of the formed ion population based on the observed strength of the absorption line generally challenging. We presented a first approach of relating the observed absorption strength to the underlying population. Here, I have shown the first real-time observation of the delayed formation of different charge states during the quasimonocycle NIR laser pulse, which amounts to a relative delay of approximately half a laser period. For higher intensities, the population of the neutral atoms is depleted and this results in the saturation of singly charged ions which has been resolved for the first time as a function of delay.

Important for the presented approach is not only the duration of the isolated attosecond probe pulse, but also the confinement of the quasimonocycle driving pulse, which limits the temporal window of ionization to less than ~ 3.2 fs. It launches a long-lasting coherent superposition of spin-orbit wavepacket motion ($T^{(SO)} = 6.312 \pm 0.029$ fs) in the valence shell of Kr^+ with a high degree of coherence. The unfolding coherent motion of

the valence electron density is traced by the attosecond XUV pulse, which for the first time is placed at the role of the probe. Precise modeling provided by our collaborators enabled the complete reconstruction of the evolving valence electron motion as a function of pump-probe delay, including its degree of coherence (amounting to 0.63 ± 0.17). Time-integrated spectroscopy does not grant any access to the coherence of electron motion, let alone as a function of time.

Beyond these proof-of-concept experiments, ATAS initiated and traced atomic electron dynamics in more complex systems. We also observed faster quantum beats in Kr^{2+} , the fastest one yielding a wavepacket period as short as 2.3 fs, which is indicative of ionization deviating from the simplest tunneling considerations and showing the potential of the quasimonocycle laser pulse to initiate even faster quantum beats at a sufficiently high coherence (for detection).

Multitudinous quantum beats imprinted on different charge states of xenon, up to Xe^{3+} and concomitant excited states, as a result of intricate multi-electron dynamics, have been configuration-resolved traced. This promises accession to hole-hole and multi-hole correlations in atoms and molecules, making attosecond transient absorption spectroscopy ideal for guiding and testing currently available theoretical models.

7.2 Development of ultrawide-band light wave synthesis

To explore further capabilities of the technique beyond those provided with our quasimonocycle pulses, sub-optical-cycle sculpted light pulses in the single-cycle regime will allow the precise and rigorous control of electron motion. On the basis of a newly developed approach, originally proposed in [130], we are currently developing a three-channel, 1.5-octave spanning field synthesizer which enables us to sculpt the waveform of intense, isolated sub-optical cycle pulses. The spectrally broad laser pulses, originating from the hollow-core neon filled fiber, are divided into three spectral channels, spanning the individual spectral bands of 350 to 500 nm, 500 to 700 nm and 700 to 1100 nm, respectively. Chirped mirrors, specifically designed for every light channel, compress the pulses of the three individual channels close to their Fourier limit. Installed high precision delay stages in combination with pairs of glass wedges in all channels allow the precise control of the relative delay between the pulses on an attosecond time scale and the individual carrier envelope phase of the superimposed pulses. Additional adjustment of the pulse energy of every individual channel by irises provides altogether several adjustment parameters for specifically tailoring waveforms on demand. Since the crafted light pulses provide a pulse energy of approximately 300 μJ (per pulse) they are powerful enough to ionize atoms and to efficiently generate high-order harmonic XUV photons, thereby enabling their direct application to nonlinear experiments.

The isolated waveforms are subsequently characterized using the attosecond streak camera

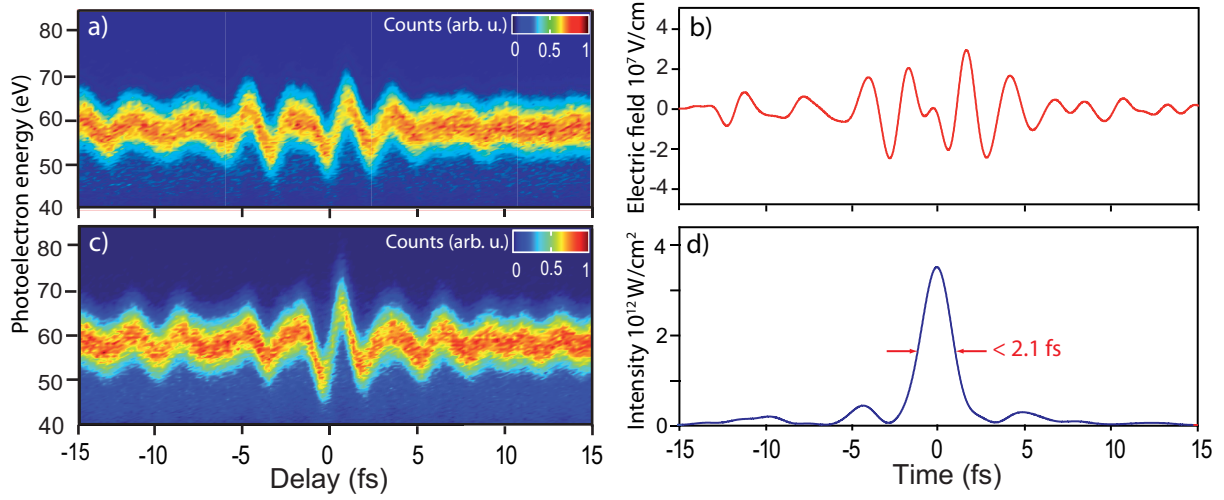


Figure 7.1: Measured streaking spectrogram of a synthesized laser waveform **a)** and its electric field **b)** demonstrating sub-cycle sculpting of the waveform. Panel **c)** presents a measured streaking trace of a sub-optical cycle pulse centered at 710 nm central wavelength. Its intensity envelope and pulse duration are shown in **d)**.

technique which had been introduced in section 2.4. Fig. 7.1 a) and c) show two measured exemplary attosecond streaking spectrograms of synthesized pulses. The spectrograms displayed in Fig. 7.1 allow the retrieval of the vector potential of the composed waveform. The electric field of the scan shown in panel a) is displayed in panel b). It comprises a pulse that demonstrates complex sub-cycle sculpting of the waveform, which is particularly interesting for steering electron dynamics. Further generated waveforms, together with their subsequent analysis and comparison to expected waveforms predicted by the knowledge of the control parameters of the synthesizer, are reported in [124]. Fig. 7.1 c) shows a different aspect of light-waveform synthesis, which even further demonstrates the power of this new technology. It presents the shortest isolated infrared waveforms up to date. Their intensity envelope, displayed in Fig. 7.1 d), yields a full width at half maximum (FWHM) of less than 2.1 fs, which manifests a sub-optical-cycle pulse encompassing only 0.88 field cycles within its intensity FWHM at a carrier wavelength of ~ 710 nm. A detailed description of the technology, its characterization and application to first experiments, is given in [124]. In consideration of the newly developed sub-optical-cycle light waveform synthesis, which will play an important part in upcoming experiments anticipated for the next years, several future prospects of this new tool, in combination with ATAS, will be outlined in the next section.

7.3 Combination of ATAS, streaking and sub-optical-cycle light waveform synthesis

Given the most recent implementation of waveform synthesis, which will be one of the most important tools for the next activities, it is no longer sufficient to describe the electric field of applied pulses only in terms of two parameters: a pulse duration and the carrier envelope offset frequency. The sub-optical-cycle shaping of the electric field of near-infrared pulses necessarily requires a measurement of the waveform. Indeed, precise characterization of the specifically tailored waveform is essential for interpreting and modeling experiments based on sub-cycle light synthesis. In order to meet these needs, a dual target module had been designed (section 3.4) which enables a combination of attosecond streaking and attosecond transient absorption spectroscopy. Following the complete characterization of the waveform in a first gas nozzle, a different target, designed for attosecond transient absorption measurements, substitutes the earlier one within seconds and makes the pre-characterized waveforms immediately available for atomic, molecular or solid state experiments.

Sub-optical-cycle pulses, as demonstrated in Fig. 7.1 c), can confine ionization to merely one optical half-cycle which will allow, probed by attosecond XUV pulses, for the real-time study of ion formation on the sub-optical cycle scale and will therefore shed light on ionization mechanisms and their relative timing within an ultrashort laser pulse.

The temporal confinement of the formation of the ionic ensemble within a fraction of the laser period is expected to increase the degree of coherence of the superposition of quantum states in ionic systems and will therefore increase the discernibility of even faster quantum beats.

The remarkable shortness of the waveform synthesized laser pulses will not only provide new insights, but also the ability of precisely controlling the waveform itself, as shown in Fig. 7.1 a),b). With sub-cycle precision [124], they will provide, in combination with ATAS, the first coherent control of electron motion in atoms. For example, a 2.1 fs laser pulse (Fig. 7.1 c) is expected to increase the degree of coherence of the observed quantum beat in Kr^+ as compared to the results presented in section 5.3, and yet more complex waveforms will establish control of the coherent motion for the first time.

Apart from these future experiments, which are the next decisive steps towards controlling electron motion on an atomic time scale, the potential of the presented attosecond absorption technique will serve different fields of science. Due to the unique features of attosecond transient absorption spectroscopy, being the gentle probing owing to the absence of strong fields and the capability to address condensed matter, this approach is ideal for future real-time observation of a wide range of electronic and concomitant processes in molecules and solids.

This potential will become fully exploitable once the extension of phase-controlled visible/ near-infrared continua to ultraviolet/ vacuum ultraviolet supercontinua spanning several electronvolts will produce half-cycle VIS/NIR pulses and near-1-fs to sub-fs UV/VUV

pulses. For instance, intense half-cycle pulses will be able to confine multiple ionization of atoms to within a fraction of their central half cycle and allow damage-free exposure of dielectrics to unprecedented field strengths. Using them as a pump, attosecond transient absorption spectroscopy will be able to look into numerous phenomena of fundamental importance, such as ultrastrong electron correlations in atoms and optical-field-control of the band structure of dielectrics (e.g. the metalization of dielectric nanofilms [131]) or the still controversial and poorly understood phenomenon of optical breakdown of solids [132]. Furthermore, this experimental technique might allow the study of previously unresolved exciton formation, hot electron relaxation and dephasing phenomena in wide-gap semiconductors. In molecules, it is conceivable that broadband UV pulses will initiate electronic wavepacket dynamics while time-delayed attosecond XUV pulses will probe the unfolding electron motion and potential concomitant structural dynamics via ATAS. This might reveal new insight into basic processes like non-Born-Oppenheimer dynamics [133] or electron transfer in large biological molecules [134].

Appendix A

Additional data sets and details

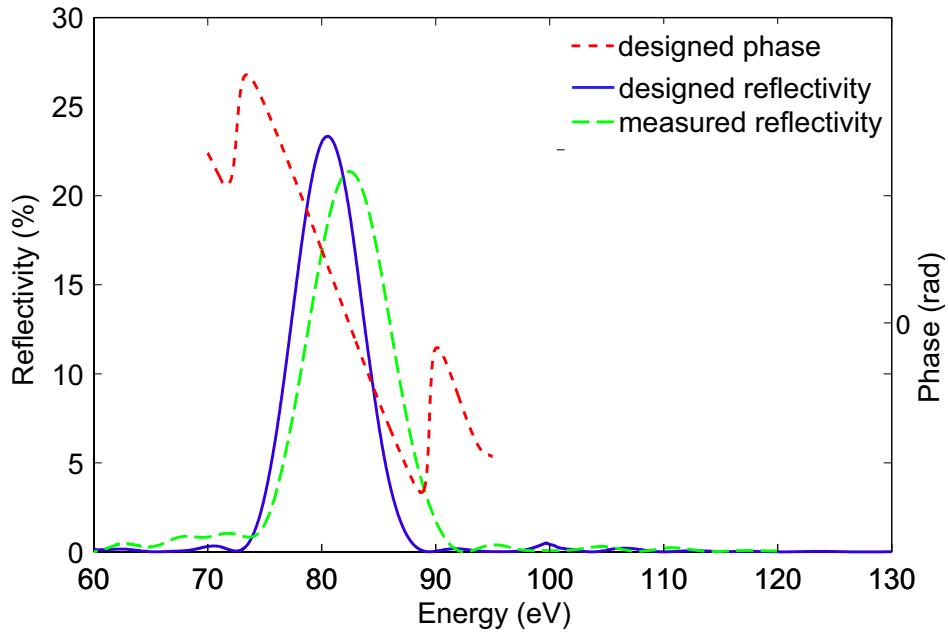


Figure A.1: XUV optic, optimized for high reflectivity and precise characterization of the NIR streaking field in an attosecond streaking experiment. Simulated and measured reflectivity curve and spectral phase of XUV optic at an angle of incidence of 5° . Mirror offers a smaller reflection bandwidth as it would have been possible, which leads to a longer pulse duration of the XUV pulse, but on the other side enhances the reflectivity. Furthermore a more narrow reflectivity curve reduces the width of the photoelectron momentum distribution in a streaking experiment and thus results in a higher fidelity for characterizing the NIR streaking field. Courtesy of M. Hofstetter.

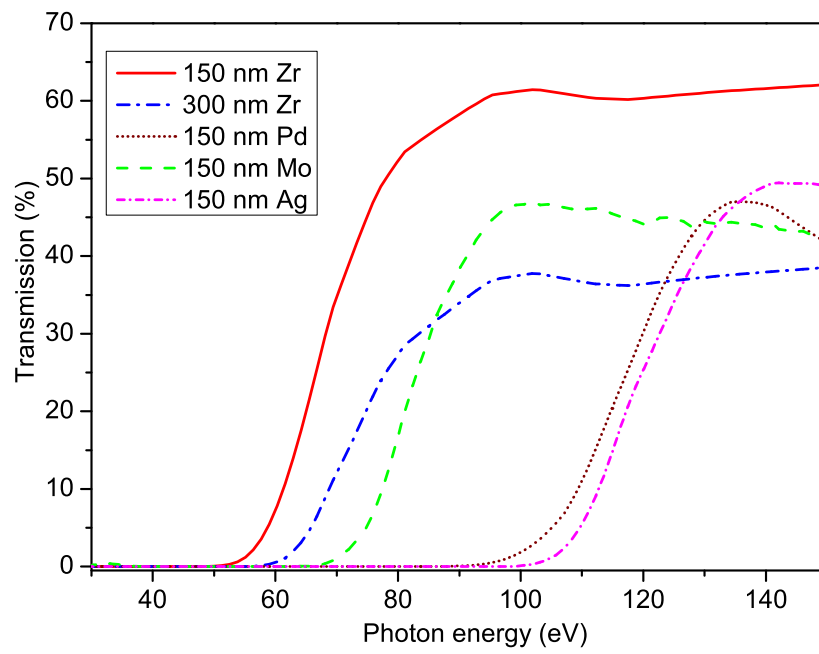


Figure A.2: Transmission curves of thin metal foils used for spectral filtering the cut-off photons of high-order harmonic generation [135]. Material and thickness is specified in the legend of the graph.

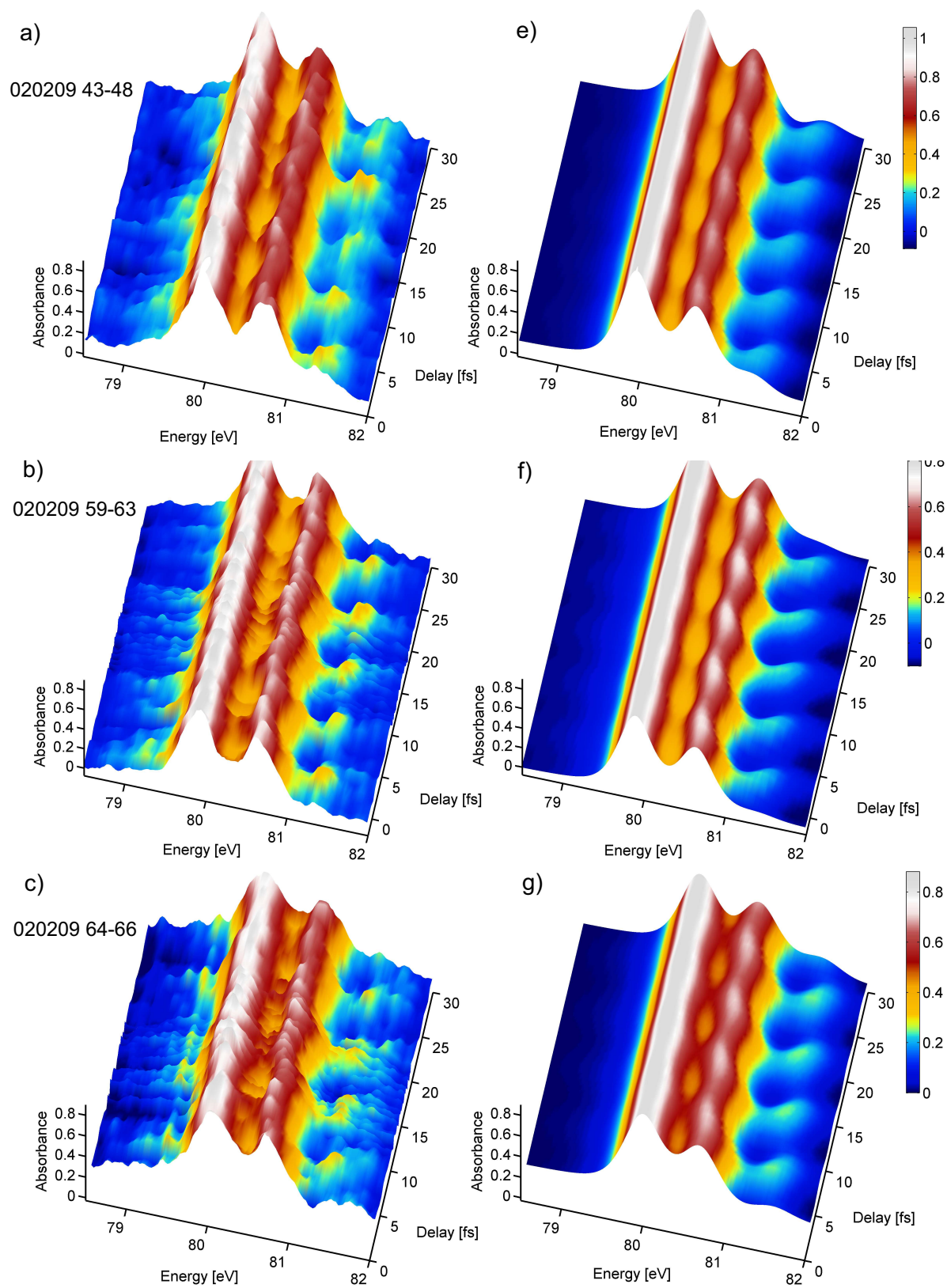


Figure A.3: Continued on next page

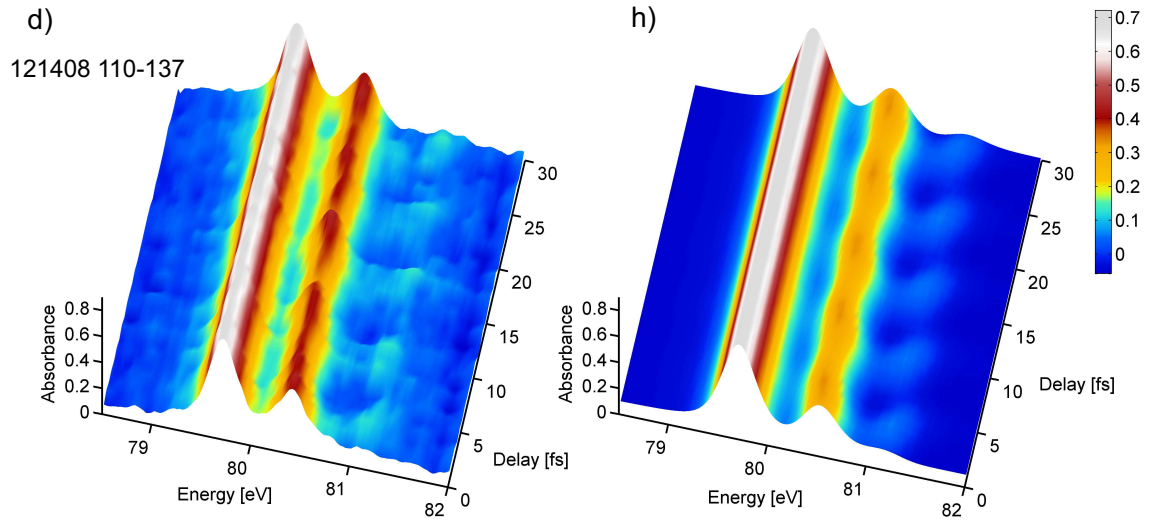


Figure A.4: **a)-d)**: Further attosecond transient absorption measurements shown for $\tau > 0$ and corresponding fit curves **e)-g)** to their right. Extracted density matrix elements are listed in Table: 5.1 & 5.2.

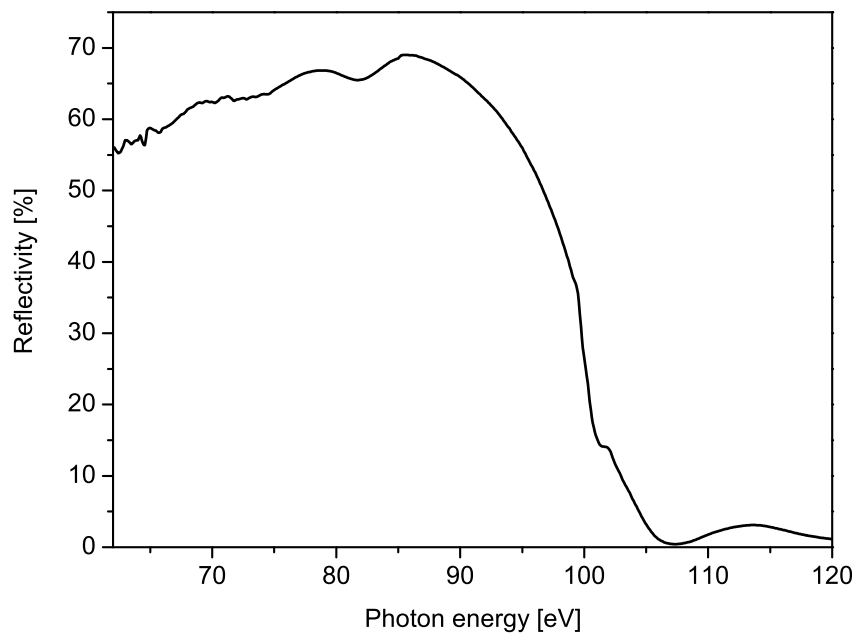


Figure A.5: Simulated reflectivity curve of broadband molybdenum-silicon XUV imaging mirror for p-polarized light at an angle of incidence of 67° . This mirror is used to image the XUV beam onto the slit of the XUV spectrometer as shown in Fig. 4.1 c). Courtesy of M. Hofstetter.

Appendix B

Storage of raw data and analysis programs

The raw data used for obtaining the results is stored on the Data Archive Computer (DAC) at the Max Planck Institute for Quantum Optics, Division for Attosecond Physics. Here, all utilized source files, MATLAB, Origin and Mathematica routines are listed according to the displayed figures in the thesis. All original data sets and analysis routines which have been utilized to generate figures that have been published in journals before, are archived in the corresponding DAC folder of this particular publication.

Figure 2.2

Data	DAC\raw data\amplifier spectrum.dat
	DAC\raw data\spectrum after HCF.dat

Figure 2.6

Data	<i>See description of Fig. 2.7 a)</i>
Routine	<i>See description of Fig. 2.7 a)</i>

Figure 2.7

Data	DAC\raw data\Converted matrix 300410_scan21.spec
Routine	Attogram Pro (by Justin Gagnon) [96]. Traces depicted in panel a) and b) are plotted using Matlab routine DAC\Matlab\plot_meas_reconstr_300410_scan21.m which calls output generated by Attogram Pro. The retrieved properties of the XUV pulse shown in panel c) and d) have also been produced by Attogram Pro and were plotted using the Origin file DAC\Origin\streaking_300410_scan21.opj

Figure 3.1

Panel e)	
Data	DAC\raw data\Matrix2.dat
Routine	DAC\Matlab\XUVprofile.m

Figure 3.2

Data	DAC\raw data\int6_2.dat
Routine	DAC\Matlab\beamprofile_int6_2_v2.m

Figures 4.1, 5.4, 5.6

Data & routine	See archiving for publication Goulielmakis_Nature_2010 on the MPQ archive server of the Division for Attosecond Physics.
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Figure 5.7

Data panel a)	Same as in Fig. 5.6 b)
Routine	Obtained by plotting the output of the least-square fit routine as described in the archiving for publication Goulielmakis_Nature_2010.

Tables 5.1 and 5.2 as well as Figs. A.3 and A.4

Data	Data extracted from DAC\raw data\.. 020209_49_56.zip scanfile: -30to10.txt 020209_43_48.zip scanfile: -30to10.txt 020209_59_63.zip scanfile: -30to10_hrsec.txt 020209_64_66.zip scanfile: -30to10_hrsec.txt 121408_110_137.zip scanfile: -30to10.txt
Routines loading	for DAC\Matlab\.. stackfile_averaging_020209_49_56_32_Kr_fitcomparison_v5.m stackfile_averaging_020209_43_48_32_Kr_beating_analyzer_2_3D.m stackfile_averaging_020209_59_63_32_Kr_beating_analyzer_thesis.m stackfile_averaging_020209_64_66_32_Kr_beating_analyzer.m stackfile_averaging_141208_110_137_32_Kr_beating_analyzer.m

Routine for re-construction	DAC\Matlab\test_qbmodelfitcurve11.m which calls qbmodelfitcurve11.m
Routine for error propagation	DAC\Mathematica\errorprop_coherence.nb provides error bars for the degree of coherence, pure state coherence and alignment based on the error bars calculated by test_qbmodelfitcurve11.m.

Figure 5.8

Data & routine	See archiving for publication Goulielmakis_Nature_2010 on the MPQ archive server of the Division for Attosecond Physics. Hole density motion in Panel d) was created using the same routine as in panel c) but with a degree of coherence of 0.12.
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Figure 5.10

Data	DAC\rawdata\020209_59_63.zip scanfile: -30to10_hrsec.txt
Routine	DAC\Matlab\stackfile_averaging_020209_59_63_32_Kr_beating_analyzer_thesis.m

Figures 5.11 and 5.12.

Data	DAC\rawdata\020209_59_63.zip scanfile: -30to10_hrsec.txt
Routine	Run first DAC\Matlab\.. stackfile_averaging_020209_59_63_32_Kr_beating_analyzer_thesis.m and then DAC\Matlab\beat_frequency_scanner_020209_59_63_v22_thesis.m. The FFT binned lineout (82.3 to 85 eV) shown in Fig. 5.12 is saved in DAC\Origin\KrIII beating 020209_59_63_for_thesis.opj

Figure 5.13

Annotation	The data set has been combined based on two successive scans.
Data	DAC\raw data\.. 020509_16_47.zip scanfile: -50to-10.txt 020509_53_70.zip scanfile: -30to10.txt Scanfile of the combined file: -50to10_combined.txt
Routine	Execute DAC\Matlab\Combining_Xe_beating_files_part_I.m first and afterwards run DAC\Matlab\Combining_Xe_beating_files_part_II_v2.m

Figure 5.15

Routine	Described in main text and in [120]. Results are provided in DAC\Origin\comp theoretical vs exp cross section xe.v1.ogg.
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Figure 5.16

Data	Simulation obtained by COWAN atomic structure code [120]. Results are imported into DAC\Origin\Res.cowan_XeIII_ground-state.ogg and in Res.cowan_XeIII_excited.ogg
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Figures 5.17 and 5.18

Routine	Execute DAC\Matlab\Combining_Xe_beating_files_part_I.m first and afterwards execute DAC\Matlab\Combining_Xe_beating_files_part_II_v2.m. Then analyze the absorption spectrogram utilizing DAC\Matlab\beat_frequency_scanner_Xe.020509_combined_v24.m and adjust parameters within the code accordingly. Results are provided in DAC\Origin\.. Xe III FFT b.v1.ogg, Xe III FFT a.v1.ogg, Xe IV FFT a.ogg and Xe IV FFT b.ogg
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Figure 5.20

Data	DAC\raw data\171210_9_20.zip scanfile: -180to10.txt
Routine	DAC\Matlab\stackfile_averaging_KrTA_171210_9_20_38_thesis.m

Figures 6.1 and 6.2

Data	DAC\raw data\020709_36_53.zip scanfile: -10to10highres.txt
Routine	DAC\Matlab\stackfile_averaging_020709_36_53_34_3D_thesis.m For producing formation curve of the absorption strength of Fig. 6.2, parameters in the routine software have to be adjusted correspondingly.

Figure 6.4

Data	Obtained by 1D TDSE simulation performed by Vladislav Yakovlev. Results are documented and stored in DAC\raw data\02.8e+13.zip and in 04.32e+13.zip for the two investigated intensities.
Routine	Plotted and analyzed with DAC\Matlab\OneDsim_analyzer_028e13_v7.m and OneDsim_analyzer_0432e13_v7.m.

Figure 6.5

Data	Obtained by 1D TDSE simulation performed by Vladislav Yakovlev. Results are documented and stored in DAC\raw data\.. 01.4e+13.zip 02.8e+13.zip 03.16e+13.zip 04.32e+13.zip
Routine	Plotted and analyzed with DAC\Matlab\.. OneDsim_analyzer_014e13_v7.m OneDsim_analyzer_028e13_v7.m OneDsim_analyzer_0316e13_v7.m OneDsim_analyzer_0432e13_v7.m Results are plotted in DAC\Origin\1D TDSE integrated crosssection.ogg.

Figure 6.6

Routine	Described in main text and in [120]. Results are provided in DAC\Origin\absorptionlines of Kr.ogg.
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Figure 6.7

Data	DAC\raw data\.. 011309_52_69.zip scanfile: -10to10highres.txt 020709_97_116.zip scanfile: -10to10highres.txt 011109_108_118.zip scanfile: -10to10highres.txt 020109_54_59.zip scanfile: -10to10highres.txt 020709_54_63.zip scanfile: -10to10highres.txt 020709_36_53.zip scanfile: -10to10highres.txt
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Routine	DAC\Matlab\stackfile_averaging_38.m analyzes individual scan files as listed above. File paths and parameters have to be adjusted correspondingly. Results are saved in DAC\Origin\Intensity KrII-KrIII comparison_v3.opj.
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Figure 6.8

Routine	DAC\Matlab\stackfile_averaging_rise_time_37.m is a modified version of stackfile_averaging_38.m that includes the determination of the rise time.
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Figure 6.9

Data	DAC\raw data\.. 012209_133_145.zip scanfile: -10to10_composite.txt 012209_147_167.zip scanfile: -10to10_composite.txt 012209_186_202.zip scanfile: -10to10_composite.txt 011309_110_131.zip scanfile: -10to10highres.txt 012209_163_178.zip scanfile: -10to10_composite.txt 020709_78_86.zip scanfile: -10to10highres.txt 021309_3_10.zip scanfile: -10to10highres.txt 012209_56_78.zip scanfile: -10to10_composite.txt 011309_52_69.zip scanfile: -10to10highres.txt 020709_97_116.zip scanfile: -10to10highres.txt 011109_108_118.zip scanfile: -10to10highres.txt 020109_54_59.zip scanfile: -10to10highres.txt 020709_54_63.zip scanfile: -10to10highres.txt 020709_36_53.zip scanfile: -10to10highres.txt
Routine	Fit of error function in Origin or utilizing DAC\Matlab\stackfile_averaging_rise_time_37.m for every data set and absorption line. Final Origin file: DAC\Origin\krypton delay.ogg.

Figure 6.10

Data	Obtained by simulation performed by Vladislav Yakovlev as described in the text.
Routine	DAC\raw data\propagation simulation 9.80.zip Results are plotted in DAC\Origin\ionization volume averaging_v3.ogg.

Figure 6.11

Data	Simulation obtained by COWAN atomic structure code [120]. Results are imported into DAC\Origin\krypton_spectator_a.ogg and into krypton_spectator_b.ogg.
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Figure 7.1

Data	Panel a): DAC\raw data\Converted_matrix_110810_scan19.asc Panel c): DAC\raw data\Converted_matrix_110810_scan6.asc
Routine	DAC\Matlab\wfs_streaking_analyzer_v21.m The routine requires several linked .exe files and text files which are all included in the folder DAC\Matlab.

Figure A.1

Data	DAC\Origin\WFS XUV optic.ogg
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Figures A.3 and A.4

Data/Routine	<i>See information for tables 5.1 and 5.2</i>
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Figure A.5

Data	DAC\Origin\Reflectivity 67° mirror for 2nd campaign.opj
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Gamma Beta Phi Society For outstanding academic ranking	2007 Austin, TX, U.S.A.
Silver medal of Jugend Forscht/Germany Wind channel prototype <i>Mistral Deux</i> for in situ measurement of the effectiveness of wind energy converters by using perpendicular air flows.	2003 Ludwigshafen, Germany
Winner of Jugend Forscht/Bavaria Field: Technology	2003 München, Germany
Awarded Gold and Silver medal for inventions at IENA IENA (exhibition for innovations and inventions). Awards for innovative probe and experimental setup.	2003 Nürnberg, Germany
Schott Glass Award For pre-eminent secondary school thesis in Physics. Awarded by German Universities of Augsburg, Bayreuth, Erlangen-Nürnberg, München (LMU/TU), Regensburg and Würzburg.	2002 Ebern, Germany

Grants & Scholarships**RISE DAAD support**

2009

Germany - U.S.A.

Financial support for a North American internship candidate granted by DAAD's RISE program (Research Internships in Science and Engineering)

IMPRS-APS

2007-2010

Germany

Scholarship in the framework of the International Max Planck Research School on Advanced Photon Sciences

C. Paul Boner fellowship

2006-2007

Paul Boner Graduate Scholarship in Physics

U.S.A.

DAAD

2006-2007

German Academic Exchange Service

Germany

Publications

8 peer-reviewed publications in scientific journals. 5 oral conference contributions at international meetings.