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Ultrafast chemical dynamics of atoms and molecules studied by femtosecond time-resolved extreme ultraviolet transient absorption spectroscopy

By Ming-Fu Lin

A dissertation submitted in partial satisfaction of the requirements for the degree of Doctor of Philosophy

In

Chemistry in the Graduate Division of the University of California, Berkeley

Committee in charge: Professor Stephen R. Leone, Chair Professor Daniel M. Neumark Professor David T. Attwood Ultrafast chemical dynamics of atoms and molecules studied by femtosecond time-resolved extreme ultraviolet transient absorption spectroscopy

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Ming-Fu Lin

Abstract

Ultrafast chemical dynamics of atoms and molecules studied by femtosecond time-resolved extreme ultraviolet transient absorption spectroscopy

by Ming-Fu Lin Doctor of Philosophy in Chemistry University of California, Berkeley Professor Stephen R. Leone, Chair

Ultrafast femtosecond (10^{-15} s) dynamics of atomic xenon, vinyl bromide and carbon disulfide molecules are studied using a newly developed method of extreme ultraviolet (XUV) transient absorption spectroscopy. This research work is devoted to a deeper understanding of the fundamental electronic and nuclear dynamics using XUV light pulses from a high-order harmonic generation source. The produced XUV light pulses are utilized to selectively probe the chemical reaction coordinate with femtosecond temporal resolution. The experimental apparatus for transient absorption pump-probe spectroscopy is described in detail. The research described in this thesis contains four different gaseous atomic and molecular systems. The first system in the study is motivated by a goal to gain a better understanding of the core-excited state couplings of atomic xenon near zero delay between an intense NIR pump pulse (780 nm) and an XUV probe pulse. Secondly, the ionization and dissociation dynamics of molecular vinyl bromide (C₂H₃Br) under the influence of strong-field ionization are investigated. Finally, an ongoing research project of CS₂ and thiophene molecules is presented for future studies of spin-orbit wavepacket and ring-opening dynamics, respectively.

The NIR induced core-excited state coupling of atomic xenon is studied using femtosecond XUV transient absorption spectroscopy with photon energies between 50 eV to 72 eV. Coupling of the core-excited states $4d^{-1}(^{2}D_{5/2})6p(^{2}P_{3/2})$ (65.1 eV) and $4d^{-1}(^{2}D_{3/2})6p(^{2}P_{1/2})$ (67.0 eV) to neighboring states by the NIR field results in a threefold enhancement of XUV transmission. The induced transmission at 65.1 eV (67.0 eV) changes from $3.2 \pm 0.4\%$ (5.9 \pm 0.5%) without the coupling laser to $9 \pm 2\%$ (22 $\pm 5\%$) at the maximum of the NIR field. A NIR field induced broad XUV absorption feature ranging from 60 eV to 65 eV is explained by the splitting of the field free absorption lines into multiplets when the Rabi frequencies of the coupling transitions higher than the NIR frequency. This assignment is supported by a numerical integration of the von Neumann equation for a few level quantum system.

The dissociative ionization dynamics of vinyl bromide, C_2H_3Br , initiated by a strong laser field ionization are investigated. XUV light pulses with photon energy between 50 eV and 72 eV are utilized to detect the subsequent dynamics. Several dynamic features are observed including the neutral C_2H_3Br depletion, the formation of $C_2H_3Br^+$ ions (\tilde{X} and \tilde{A} states), the production of $C_2H_3Br^{++}$ dications, and the emergence of neutral Br (${}^2P_{3/2}$) atoms from dissociative ionization. Free Br (${}^2P_{3/2}$) atoms appear on a timescale of 330 ± 150 fs. The singly charged ionic \tilde{A} state displays a time-dependent XUV absorption energy shift of ~0.4 eV during the first 300 fs after strong-filed ionization. The signal intensity from Br atoms correlates with the signal intensity from singly charged parent ions in the \tilde{A} state as a function of NIR laser peak intensity. The experimental observations suggest that vibrationally excited C₂H₃Br⁺(\tilde{A}) ions possibly undergo ultrafast intramolecular vibrational energy redistribution concurrent with the C-Br bond dissociation within a time scale of 330 ± 150 fs. The C₂H₃Br⁺(\tilde{X}) and C₂H₃Br⁺⁺ ions are relatively stable as a consequence of deeper potential wells and a high dissociation barrier, respectively.

Two ongoing experiments of sulfur-containing molecules are presented that are aimed at future studies of a molecular spin-orbit wavepacket in CS_2^+ ions and ultrafast ring-opening dynamics of thiophene. Strong-field ionization can coherently populate two spin-orbit states in CS_2^+ ions. The spin-orbit splitting originates from the atomic sulfur (~60 meV). The small splitting offers the possibility to probe a coherent beating on a time scale of 69 fs, well beyond our temporal resolution of 25 fs. For thiophene, an ultrafast ring-opening process initiated by one-photon excitation at 193 nm is studied through multiphoton ionization at 780 nm. The parent ion population exhibits a fast decay on a time scale of 200±30 fs. This offers a reference for the future XUV transient absorption experiments using one-photon excitation at 193 nm and sulfur (2*p*) L-edge detection at 165 eV.

To my family

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Chapter 1 Introduction to Femtosecond Time-Resolved Extreme Ultraviolet Transient Absorption Spectroscopy

1.1 Development of time-resolved pump-probe experiments

Femtosecond (1 fs = 10^{-15} seconds) laser technology from chirp-pulse amplification (CPA)¹ has been widely applied to measure ultrafast electronic and nuclear dynamics in complex molecular systems.²⁻⁷ For the fastest nuclear motion, the vibrational period of a hydrogen molecule is ~8.3 fs.⁸ This corresponds to only three cycles of the optical laser field at 800 nm. For an electron, the rest mass is 1836 times lighter than that of a proton, indicating an ultrashort dynamic that occurs in the attosecond regime (e.g. 1 attosecond = 10^{-18} second).⁹⁻¹¹ These time scales underlie the elementary processes that need to be studied for a better understanding of the ultrafast photochemistry and photophysics in complex systems. Various types of techniques have been developed to investigate ultrafast relaxation and dissociation processes (i.e. internal conversion, intersystem crossing, bond breaking and charge migration) in polyatomic molecules initiated by femtosecond laser photoexcitation. Snapshots in "optical-optical" pump-probe experiments capture intermediate states and structures in chemical reactions both in the gas and liquid systems.^{2-7,12-14} The detection of excited species by a delayed optical probe can provide valuable time-resolved quantum information. Measurements may include the detection of transmitted photons, induced fluorescence, generated ions and electrons. Optical probes in the ultraviolet (UV) regime promote valence-to-valence transitions that involve wavefunctions, which are delocalized across the entire molecule. In contrast, core-shell-to-valence transitions provide a detection of specific atoms in a polyatomic molecule.¹⁵⁻¹⁷ By carefully choosing a probe wavelength in extreme ultraviolet (XUV) or X-ray regions, a selective detection in the vicinity of a specific reaction center can be achieved.¹⁸⁻²⁷ The new emerging field of studies using advanced attosecond to picosecond XUV and X-ray laser pulse sequences sheds light on future research that will greatly improve our understanding of elementary processes in complex chemical systems.

Brilliant XUV and X-ray laser pulses with pulse durations down to a few femtoseconds are now available at free electron laser facilities.²⁸⁻³² The unprecedented high peak intensity and short wavelengths (~0.12 nm to 47 nm) are applied to perform single shot imaging of biomolecules, aerosols, nanoparticles, and nanodroplets.³³⁻³⁷ Ultrafast dynamics of cyclohexadiene molecules (ring-opening and photo-isomerization) have been studied by using UV pump and X-ray probe pulse sequences.³⁸ Double core-holes of small molecules generated by strong femtosecond soft X-ray pulses have been studied.^{39,40} Real-time ultrafast charge transfer in Ruthenium-centered dye sensitized ZnO nanocrystal on TiO₂ films has been studied

for a better understanding of interfacial and intramolecular charge separation dynamics.⁴¹ In synchrotron X-ray facilities, femtosecond slicing technique^{42,43} has been applied to study spincrossover, dissociation dynamics of metal complex molecules and ferromagnetic materials with picosecond time resolution.^{18-22,26,27,44} On the other hand, the development of tabletop XUV and soft X-ray photon sources based on high harmonic generation (HHG) has led to unprecedented short pulse durations as small as 67 attoseconds that may be used to measure the coherent electron motion in charge migration processes.^{45,46} Longer driving wavelengths for HHG currently extend the tabletop XUV photon energy range to soft and even hard X-ray regimes.⁴⁷⁻⁴⁹ The broad bandwidth large tuning range, ultrashort pulse durations and small-scale tabletop size grant HHG light sources an important place in the field of time-resolved core-level pump-probe experiments.

In this thesis, a novel apparatus for femtosecond time-resolved XUV transient absorption spectroscopy is described. The setup is used to study ultrafast relaxation and dissociation dynamics in atomic xenon and small polyatomic molecules. The detailed experimental setup is presented in Chapter 2. The conditions for femtosecond XUV pulse generation up to 180 eV, optics layouts for the studies of different chemical elements (Xe, Br, Kr, Si and S atoms, see Fig. 1.1), alignment of XUV optics and beam focus characterizations, and frequency up-conversion setups for the pump laser beam are described. Finally, estimates of the temporal resolution for up-converted ultraviolet (UV) laser pulses at 263 nm and 193 nm are given as preparation for one-photon excitation experiments in the near future.



Fig. 1.1

The static and transient absorption spectra of atomic Xe $(4d^{-1})$, Kr $(3d^{-1})$, vinyl bromide (bromine $(3d^{-1}))$, silicon tetrachloride $(2p^{-1}))$ (silicon and sulfurcontaining compounds (thiophene and CS_2 at sulfur $(2p^{-1})$ edge) obtained by using tabletop XUV light sources in current studies. The positive and negative values represent the formation and depletion of transient species, respectively. For SiCl₄, thiophene and CS₂ molecules, only the static absorption spectra are shown. Two spin-orbit series in each spectrum are observed.

1.2 Laser-induced core-excited state couplings in xenon

Several studies of laser-induced core-excited state coupling using an "optical pump" and "XUV probe" have led to an advanced understanding of the manipulation of laser dressed atomic species.⁵⁰⁻⁵⁷ Core-excited states possess lifetimes of typically a few femtoseconds, i.e. they relax much faster than valence-excited electronic states (~nanoseconds).⁵⁸⁻⁶⁰ In order to compete with the relaxation rates of core-hole states, a high peak intensity NIR laser is used to couple different core-hole states. Under this condition, fast Rabi oscillations can occur. Fig. 1.2.1 shows a



schematic of the energy levels involved in the dynamic coupling experiments.

Fig. 1.2.1

A three-level system including coupling to the ionization continuum. The population of core-excited state 1 is prepared by XUV laser excitation from the ground state. The NIR laser transfers population to the core-excited state 2 and then back to state 1. Both core-excited states are coupled to the ionization continuum and their energy levels may be subject to AC stark shifts.

Core-excited state 1 is prepared by XUV excitation from the ground state. The NIR field transfers

population between core-excited states 1 and 2. Both core-excited states are subjected to multiphoton ionization to the continuum. The ionization potential may shift due to the NIR laser field. Thus, the underlying physics at high coupling fields is different from laser-dressing effects in atoms in perturbative "optical-optical" pump-probe experiments in the nanosecond regime. In this thesis, the first transient absorption spectroscopy experiment is performed on gaseous atomic xenon to study the ultrafast core-excited state coupling by NIR laser pulses. Core-excited states of $4d^{-1}6p$ electron configurations are prepared by XUV laser excitation at 65.0 eV and 67.1 eV.



Fig. 1.2.2

The alignment and orientation of quantum states m_J at total angular momentum J=3/2. The distributions of quantum states m_J on the left side represent electronic alignment. The distributions on the right side represent electronic orientation. Strong-field ionization by a linear polarized electric field can only produce alignment in the ionic states. For J=1/2, by definition no alignment can occur.

The observed broad Autler-Townes multiplet splitting in the vicinity of atomic resonances from core-excited states implies that the rotating wave approximation (RWA) breaks down for the highest laser field. This interpretation of broad light induced structures is supported by theoretical work.⁵³ The inducedtransmission at the atomic resonance may be used as a slicing technique in synchrotron-based light sources to provide femtosecond temporal resolution.

Strong laser fields can also ionize neutral xenon atoms. This ionization process produces two different atomic valence spin-orbit states (${}^{2}P_{3/2}$ and ${}^{2}P_{1/2}$). The ions can exhibit electronic alignment with respect to the populations of the sublevels (mJ) of the total angular

momentum. Exemplary mJ distributions presenting alignment and orientation are shown in Fig. 1.2.2.

A revisit of valence hole-alignment in the generated Xe^+ ions at a resonant absorption energy of 57.3 eV confirms the tunnel ionization of atomic xenon in the presence of strong laser field and the production of relatively lower hole-alignment in comparison to theoretical works.^{11,61,62} The results are presented in Chapter 3.

1.3 Dissociative ionization dynamics of vinyl bromide

Strong-field ionization of polyatomic molecules is a non-perturbative and non-resonant ionization process. The applied laser field strength (10⁸ V/cm to 10⁹ V/cm) is comparable to the Coulomb field between the electron and its binding ion-core. The produced molecular ions usually correlate to various ionization continua.⁶³⁻⁶⁶ The coherent generation of several ionic states and vibrational excitations by a strong laser field can produce electronic and vibrational wavepackets.^{11,67-71} The major differences between strong-field ionization of atoms and molecules are from the electronic cloud distributions (molecular orbitals) that are subjected to strong-field ionization. The bonding and antibonding characters of molecular.⁷²⁻⁷⁵ Electrons in conjugated molecular orbitals may respond to the applied field non-adiabatically, possibly reducing ion production.^{64,76} The lower ionization yields in molecules in comparison to atoms of the same ionization energy is called "suppressed ionization", a common phenomenon in polyatomic molecules. The energy required for multiple electron excitations in a molecule can be lower than the first valence ionization potential. This is in contrast to noble gas atoms where the ionization energy is usually lower than the threshold for double valence electron excitations.



Fig. 1.3

Molecular orbitals of neutral vinyl bromide calculated by using the Gaussian 09 program. (a) Highest occupied molecular orbital (HOMO). This orbital is a delocalized molecular orbital between two carbon atoms, and an antibonding part between a carbon and the bromine atom, and (b) second highest occupied molecular orbital (HOMO-1). This orbital dominantly localizes on the bromine atom, indicating a lone-pair electron character. Note that the orbital distributions are completely different from each other. The alignment of the applied electric field vector of the NIR laser beam (E) is also shown to illustrate that the molecular orbital orientation relative to the field can affect the strong-field ionization efficiency. Therefore, a multi-electron response to the applied laser field can lead to the formation of excited ionic states through non-adiabatic multielectron excitation.⁶³ The study of ultrafast molecular dissociative ionization of vinyl bromide subjected to strong-field ionization is presented in Chapter 4. Strong-field ionization of neutral vinyl bromide (CH₂=CHBr) from two molecular orbitals that possess different electron cloud distributions is discussed. The molecular orbitals subjected to strong-field ionization are illustrated in Fig. 1.3.

The HOMO exhibits delocalized π bonding character between the two carbon atoms, and π^* antibonding character between a carbon and the bromine atom. The HOMO-1

orbital consists predominately of an isolated lone-pair electron located on the bromine atom. The difference in the electron cloud distributions may lead to difference in the ionization efficiencies as a consequence of suppressed ionization and nonadiabatic multielectron excitation. The observation of a dynamic XUV absorption energy shift imprinted on the inner-shell Br (3*d*)-to-valence orbital transition indicates that the measurement is sensitive to the details of electronic and nuclear dynamics during relaxation and dissociation processes. The appearance of atomic Br (${}^{2}P_{3/2}$) with a time constant of 330±150 fs supports a conclusion that the ionic \tilde{A} state correlates to the C-Br bond dissociation channel. This study demonstrates that time-resolved XUV transient absorption spectroscopy can be applied to explore the relaxation and dissociative ionization of a molecular ion from a viewpoint of different chemical elements contained in the molecule.

1.4 Toward femtosecond XUV studies of sulfur-containing molecules

The ultrafast XUV light source has been successfully extended to 180 eV photon energy to enable inner-shell studies of silicon and sulfur-containing chemical compounds. Fig. 1.1 shows an overview of static and transient absorption spectra using the current apparatus. The experiments for atomic xenon and molecular vinyl bromide are presented in Chapter 3 and 4. XUV photons ranging from 80 eV to 120 eV have been successfully used to record absorption spectra of Kr⁺ ions, Kr atoms, and SiCl₄ molecules in a short absorption cell. The example spectrum of SiCl₄ obtained from a tabletop XUV light source shows that ultrafast photochemistry and photophysics of silicon-containing compounds (Silcon 2*p* edge ~100 eV) can be studied by using time-resolved femtosecond XUV transient absorption spectroscopy. In Chapter 5, preliminary studies of the ultrafast dissociation and relaxation processes of molecular systems comprising sulfur atoms are presented. Atomic sulfur has an absorption resonance at ~165 eV, corresponding to the excitation of inner-shell sulfur 2*p* electrons to empty valence orbitals. The molecular systems studied here are CS₂ and thiophene. These experiments are still ongoing. Preliminary results are presented.

1.4.1 Toward the study of molecular spin-orbit wavepackets in CS_2 molecule

The first molecule of interest for studies of molecular spin-orbit wavepackets is carbon disulfide (CS₂). Atomic valence spin-orbit wavepackets have been observed in Kr⁺ ions using attosecond XUV transient absorption experiments.¹¹ The generated quantum coherence of an electronic wavepacket indicates that the studies of inter- and intramolecular charge migrations can be achieved by using ultrashort X-ray pulses with atomic site resolution. The temporal resolution at the setup presented here is 30 fs. This limits the detection of quantum beating to periods of ~30 fs and longer. Within this limits, a promising system to exhibit an electronic wavepacket is the highly symmetric carbon disulfide (CS₂) molecule. The ionic ground state (\tilde{X}) of the linear CS₂ molecule possesses two spin-orbit split states originating from the lone-pair

non-bonding electrons on the two sulfur atoms.⁷⁷⁻⁷⁹ The spin-orbit splitting is approximately ~55 meV (440 cm⁻¹), providing a possibility to detect the "molecular" spin-orbit wavepackets generated by the ionizing laser field. The expected quantum-beating period is 76 fs. The similar bond distances of the ionic \tilde{X} state and the neutral ground state may prevent the generation of a vibrational wavepacket in the stretching mode. Vibrational excitation in the bending mode may occur, which would result in an expected beating period of 100 fs. In contrast to the first ionic state, the second ionic state (\tilde{A}) of the CS₂ molecule has a longer equilibrium C-S bond distance in comparison to the neutral ground state.⁷⁹ This indicates that significant vibrational excitation may occur upon strong-field ionization to the ionic \tilde{A} state. Strong-field ionization can generate molecular ions that correlate to different ionization continua, implying the generation of ionic \tilde{X} and \tilde{A} states that can possibly be probed by time delayed XUV photons to monitor electronic and vibrational wavepackets simultaneously.

1.4.2 Ultrafast ring-opening dynamics of thiophene

Thiophene is a five-membered ring molecule with conjugated double bonds. It is an important molecular building block of polymer-based organic solar cells (OSC).^{80,81} OSC's can be easily manufactured. Advantages such as lightweight materials, flexibility, and low cost have made this type of solar cell important to the studies of light-to-electricity conversion technology. The photostability of an organic solar cell is a critical issue when compared to silicon based solar cells. In OSC, thiophene molecules are exposed to sunlight, oxygen molecules and water, which eventually causes a ring-opening process and reduces the charge propagation efficiency.^{82,83} This decreases the charge separation efficiency, and the created radical ion may also lead to complicated chemical reactions. The sunlight-induced photochemistry (ring-opening) that occurs in the vicinity of the sulfur atoms is so far poorly understood. Element-sensitive XUV spectroscopy offers new insight into the fundamental damage mechanisms in the study of ultrafast bond dissociation dynamics in a complex system.

The ring-opening process of thiophene on a metal surface has been identified as an initial key step in removing unwanted thiophene-derivatives from petroleum gasoline.⁸⁴⁻⁸⁸ "Hydrodesulfurization" (HDS) is a chemical reaction that breaks down a thiophene molecule on a metal surface into a small hydrocarbon and H₂S molecule before the next refinery process. In the experiments of thiophene, one-photon excitation leading to unimolecular ring-opening and dissociation of thiophene has been studied by using a nanosecond laser at 193 nm. Photo-fragmentation of the vibrationally hot molecule in the electronic ground state to five dissociation channels is reported.^{89,90} Hot ground state molecules are generated by ultrafast internal conversion from the initial excited state. Femtosecond photoelectron pump-probe experiments combined with theoretical work indicates an ultrafast ring-opening process in the excited state.^{91,92} For a better understanding of ultrafast relaxation and bond breaking in thiophene, a direct detection of local C-S bond scission in the excited state can provide a deeper understanding of the ring-opening process. The same pump-probe transient absorption spectroscopy technique can also be applied to study the ring-opening process of thiophene

molecular ions in different ionic states produced by a strong laser field. This can distinguish whether the bond dissociation happens on the C-C bond or C-S bond and in a concerted or stepwise process in the ground ionic state.⁹³

1.5 Summary

Chapter 6 presents summary and conclusion for the studies of ultrafast core-excited states dynamics of atomic xenon and dissociative ionization dynamics of vinyl bromide ions using tabletop femtosecond XUV light sources. The studies toward molecular spin-orbit and vibrational wavepackets in carbon disulfide (sulfur 2*p* edge at 165 eV) are also summarized, providing a deeper understanding of nuclear and electronic dynamics in ions. The time-resolved transient absorption experiments with atomic species resolution can shed new insight not only into the strong-field physics and chemistry (atomic xenon, vinyl bromide, and carbon disulfide), but also to the one-photon excitation excited-state dynamics (e.g. thiophene ring opening). The further applications to complex chemical systems (e.g. solar cell, surface science and biomolecules) can provide unprecedented time-resolved and atomic scale information that cannot be obtained by using conventional "optical-optical" pump and probe techniques. The direct probe on the "multi-reaction centers" in a photocatalysis system can help to understand the elementary mechanism of electron-hole migrations that is useful to the design of better conversion efficiency in the transition metal photocatalysis process.

Chapter 2 Experimental Setup and Data Analysis

In this chapter, detailed experimental conditions for XUV generation, methods for XUV optics alignment, and the NIR photon up-conversion (crystal-based doubling, tripling and quadrupling) scheme are described in the different sections. Sec. 2.1 described the layout of the apparatus for strong-field physics studies of atomic xenon and vinyl bromide molecules. Several modifications to the experimental setup are made for studying different molecular systems (e.g. sulfur compounds). These changes are discussed in the subsequent chapters. Sec. 2.2 describes femtosecond XUV light generation techniques for two different photon energy regions (50-72 eV, 105-180 eV), the alignment of XUV optical components, and the characterization of the generated XUV light sources. Sec. 2.3 discusses the energy resolution of the transient absorption setup based on the characteristics of the XUV beams and the two-dimensional photon detectors. For the one-photon pump-probe experiments, the optical up-conversion layout for the pump beam generation is given in Sec. 2.4. Finally, Sec. 2.5 presents the data acquisition and analysis procedure for all experimental results.

2.1 Apparatus layout

The apparatus layout for the femtosecond time-resolved XUV transient absorption spectroscopy experiments is shown in Figs. 2.1(a) to 2.1(c). Specific details related to the study of different molecular systems (e.g. Xe, Br, Kr, Si, and S atoms absorption edges) will be presented in the respective chapters. Here, the XUV generation conditions, alignment of toroidal mirror and frequency up-conversation for one-photon experiments are described.

The driving light source for the experiments is a femtosecond Red Dragon laser system from KMLabs that delivers a NIR pulse width of 25 fs and a center wavelength of 780 nm. The maximum power of the laser system is 15 W at a repetition rate of 3 kHz. In the current experiments, a NIR average power of 10 W is used. This NIR beam is split into two parts by a 50/50 beam splitter (CVI, BS1-780-50-2008-45P-UV). Half of the NIR energy is focused into a gas cell by an f/30 lens for generating the XUV beam ("probe"). The measured NIR focal spot size is 90 μ m (1/e²). The nominal length of the XUV generation gas cell is 25 mm. The gas cell is initially sealed by 3M Scotch[®] tape with a stacked thickness of 1 mm. The focused NIR beam drills holes through the tape, leading to a minimum gas load into the surrounding vacuum chambers. In all experiments, neon gas is used as the medium for the XUV generation. A nominal gas pressure of 3.33 kPa is used for the experiments. Experiments are performed in the photon energy range between 50 eV and 72 eV (see Chapter 5 for studies beyond 100 eV). Behind the XUV generation cell, a 300 nm thick aluminum filter (Lebow, 0.3Al-0-L1.0) is installed to block the NIR light that is transmitted through the harmonic generation cell. The transmitted XUV laser beam is focused by a toroidal mirror (ARW, TM-130×25×20) into a



Fig. 2.1

Apparatus layouts for the XUV transient absorption experiments. (a) The red and blue color lines represent the NIR and the XUV beams, respectively. The design shown here is used for the strong-field ionization experiments on xenon and vinyl bromide. In the position marked by the dashed box for the pump beam, the NIR photon can be up-converted to third and fourth harmonics (e.g. 263 nm and 193 nm) for one-photon excitation experiments. (b) Detailed dimensions and incident angles for the XUV optics including the imaging distance of the toroidal mirror and the spherical grating and incident angles. This layout is for the XUV energy region from 50 eV to 72 eV. (c) The detailed layout for XUV generation up to 180 eV. Note that the lens for HHG is f/20 and the grating is a flat field grating.

short target sample cell. The XUV photon flux at the target sample cell is ~10⁵ photons per pulse in the spectral region from 50 eV to 72 eV. The measured XUV beam diameter (1/e²) at the target cell position is $90 \pm 10 \ \mu$ m. A turbo

molecular pump with a pumping speed of 1000 L/s (Shimadzu, TMP1003LMC) is attached to the toroidal mirror (TM) chamber to evacuate the gas load from the XUV generation cell. During the experiments, the gas pressure in the TM chamber is $\sim 1.33 \times 10^{-2}$ Pa. The distances from the XUV generation region to the TM and from the TM to the sample cell is shown in Fig. 2.1(b) and 2.1(c).

A second turbo molecular pump with pumping speed 3000 L/s (Shimadzu, TMP3203LMC) attached to the sample chamber is used to pump the sample and purge gas loads. The base pressure without gas load remains below $\sim 1.3 \times 10^{-4}$ Pa. In the experiments, the pressure rises to ~ 0.133 Pa. After the XUV beam is transmitted through the absorption sample cell, the XUV light is dispersed by a constant line-spacing spherical grating with a center groove density of 1200 lines/mm (Newport, 52051FS02-701R). The dispersed XUV photons are detected by a chevron-mounted pair of microchannel plates (MCPs). A phosphor screen and a CCD camera (Prosilica, GC1380) are used to image electrons that emerge from the MCPs. A CCD camera is coupled to the phosphor plate. The obtained image is transferred to a computer for data analysis. The whole spectrometer chamber is equipped with a turbo molecular pump with a pumping speed of 300 L/s (Varian, V301AG). The base pressure in the spectrometer

section stays below 1.33×10^{-4} Pa during the experiments. The energy resolution of the spectrometer in the spectral region from 50 eV to 72 eV is presented in Chapters 3 and 4.

For the higher XUV photon energies up to 180 eV in the studies of sulfur-containing molecules, an f/20 lens is used for HHG in the same gas cell at the same NIR input power as for the lower photon energies. The detailed XUV optics layout is shown in Fig. 2.1(c). An optimized neon gas pressure of 0.5 kPa is obtained in order to reach the maximum XUV photon energy. After the XUV generation cell, a 200 nm thick silver filter (Lebow, 0.2Ag-0-L1.0) is installed to block the rest of the NIR light. In the spectrometer, a variable-line-space-grating with a center groove density of 1200 lines/mm (Hitachi, 001-0660) is employed to achieve the flat-field focusing on the detector plane. The voltages for MCP and phosphor screen are 2000 V and 4500 V, respectively. The MCPs voltage is ~400 V higher than during 50 eV to 72 eV experiments in order to increase the detection sensitivity. The estimated XUV photon flux from 150 eV to 180 eV is approximately two orders of magnitude lower than the total flux in the range from 50 eV to 72 eV. To achieve a better spectrometer energy resolution, an X-ray CCD camera (Princeton Instrument, PIXIS-XO-2048B) is installed. The estimated energy resolution will be discussed in Chapter 5.

The second NIR beam is focused by an f/40 lens and is used for strong-field ionization ("pump"). The measured focal spot size of the NIR beam at the target cell position is 150 ± 10 μ m. The estimated NIR peak intensities range from 1×10^{14} W/cm² to 3×10^{14} W/cm². The pump and probe beams are combined by an annular mirror placed in front of the sample cell. The angle between pump and probe beams is $\approx 1.3^{\circ}$. Argon gas is used to purge the surface of the annular mirror during the experiments. This procedure reduces the chemical deposition of molecules on the mirror surface, which changes the focusing properties of the NIR pump beam at the sample cell position.

In addition to pump schemes for strong-field ionization of polyatomic molecules, onephoton excitation schemes in the perturbative regime are prepared for future studies of ultrafast relaxation and dissociation dynamics in neutral molecules. For these experiments, the NIR photon energy is up-converted to the third (263 nm) and fourth (193 nm) harmonics using combinations of nonlinear crystals. These ultraviolet (UV) photons promote valence electrons to empty molecular orbitals at well-defined excitation energies. The detailed layout and characterization of the up-conversion schemes (as indicated in the dashed box in Fig. 2.1(a)) are presented in Sec. 2.4.

2.2 High harmonic generation based femtosecond XUV light sources

Inner-shell transitions provide an element-specific spectroscopic probe for detailed studies of polyatomic molecules. In general, the XUV light sources are optimized for highest flux in the vicinity of specific absorption edges. For the XUV photon energy from 50 eV to 72

eV, the generation process is tuned to have the best phase matching condition, which produces the highest flux in this spectral region. The tunability of the light source in this spectral region is presented in Sec. 2.2.1. For the highest XUV photon energy up to 180 eV (cut-off region), the experimental condition for high harmonic generation is different. The maximum XUV photon energy is optimized at low gas pressures in order to prevent plasma defocusing that reduces the peak intensity of the NIR pulse in the generation volume and degrades the phase matching condition for the highest XUV photon energy generation.⁹⁴ The grating compressor in the laser system is at the best compression position that is a compensation for the positive chirp introduced by the air and the optics before the XUV generation region. The spectra up to 180 eV are shown in Sec. 2.2.2. The XUV beams from these two energy regions focused by a toroidal mirror are characterized and shown in Sec. 2.2.3. Sections 2.2.4 and 2.2.5 describe useful guidelines for the alignment of the toroidal mirror and the imaging grating.

2.2.1 XUV generation between 50 eV and 72 eV

An f/30 lens is used to focus the NIR laser beam for high harmonic generation. The usable photon energy region in the current experiment is determined by the design of the spectrometer. The position of the detector chip in the spectrometer determines the XUV spectral region for the experiments. A neon gas pressure of 3.33 kPa is used to achieve the best HHG phase matching condition. The focal position in the generation cell is optimized for maximum XUV intensity within a specific energy range and/or the exact energy of specific harmonic. Fig. 2.2.1 shows high harmonic spectra versus the variation of focal spot position in the gas cell and grating compressor position in the laser system. The energy distribution can be tuned by scanning the NIR focal position within the harmonic generation cell.⁹⁵ The tunable range is approximately 0.8 eV. Introducing a negative chirp in the driving NIR pulse can effectively broaden the XUV peaks.⁹⁶⁻⁹⁸ The degrees of freedom in tuning the XUV photon energy and width are useful to bridge the gaps between the discrete harmonic peaks. In both spectra, a 300



Fig. 2.2.1

The XUV spectra from high harmonic generation at different conditions. (a) At different focal position in the gas cell. The focal position in the gas cell is tuned by 8 mm. The shift of XUV energy of each peak is ~0.8 eV. (b) At different grating compressor position in the Red Dragon laser system. Each individual harmonic peak in the red color spectrum is broader. The black solid line in both figures represents simulated transmission curve of a 300nm thick Al filter. The XUV spectrum shows a cutoff at ~72.6 eV due to increased absorption above the aluminum L_3 -edge. Note that the harmonic intensity is plotted on a linear scale.

nm thick aluminum filter is used to block the intense NIR light that co-propagates with high harmonic light. The resulting XUV photon distributions abruptly energy decrease ~72.6 eV. at corresponding to the Al (2p) L₃edge. Fig. 2.2.1(a) shows two harmonic distributions at different NIR focal positions in the gas cell. Fig. 2.2.1(b) shows two harmonic distributions with different chirps introduced by the grating compressor in the laser system. The black solid lines in both

figures represents simulated transmission curves for a 300 nm thick aluminum filter.

2.2.2 XUV generation between 72 eV and 180 eV

An f/20 lens is installed for XUV generation between 72 eV and 180 eV used for studies of silicon- and sulfur-containing molecules. The Si (2p) and S (2p) L absorption edges are located near 100 eV and 160 eV photon energies, respectively. Fig. 2.2.2 shows the XUV photon energy distributions from 72 eV to 130 eV and from 72 eV to 180 eV, respectively. A 200 nm thick aluminum or silver filter is placed 0.9 m away from the high harmonic generation region in order to remove unwanted NIR light. In Fig. 2.2.2(a), the maximum XUV photon energy reaches 130 eV at a neon pressure of 6.7 kPa. A slight drop in the XUV intensity between 100 eV and 115 eV (red curve) is caused by a slightly damage area on the MCP detector. With an aluminum filter inserted in the XUV propagation path, a clear absorption edge at ~72.6 eV is observed (blue curve). Fig. 2.2.2(b) shows the harmonic distribution with and without aluminum metal filter (300 nm) at high and low neon gas pressures, respectively. The maximum XUV photon energy





is obtained by using a lower neon gas pressure, 0.9 kPa. At higher pressure, the total XUV flux is higher but the cutoff energy is lower due to plasma defocusing.⁹⁴ Fig. 2.2.2(c) shows a comparison of the XUV spectra at two different neon pressures. The

maximum XUV energy changes from 170 eV to 160 eV as the pressure increases from 0.6 kPa to 1.1 kPa. Note that the spectral intensity is on a logarithmic scale. The maximum XUV photon energy at 180 eV is achieved at an estimated NIR peak intensity of ~ 1.5×10^{15} W/cm². The maximum cut-off energy is highly dependent on the temporal width of the NIR pulse and the gas pressure. A slight adjustment of the grating compressor and neon

Fig. 2.2.2

The XUV spectra for different generating conditions. (a) High harmonic generation at 6.7 kPa of neon. Blue and red curves represent the XUV photon energy distribution with and without aluminum filter (300nm), respectively. The decrease in XUV intensity between 100 eV and 115 eV (red curve) is caused by slightly damage of the MCP detector. The green solid line represents simulated transmission curve of a 300 nm thick aluminum filter. (b) High harmonic generation at high neon pressure with 300 nm Al filter (blue), and low neon pressure without metal filters (red). The maximum XUV photon energy reaches 180 eV. (c) The harmonic spectrum with silver filter (200 nm thick) at low (0.6 kPa, red) and high (1.1 kPa, blue) neon pressures. The cutoff energy for low pressure is higher but overall flux is lower. Note that the high harmonic generation intensity distributions are on logarithmic scales and the scales are relative to each other.

gas pressure significantly changes the maximum XUV photon energy. Note that apparent spectral contributions between 72 eV and 80 eV in Fig. 2.2.2. (c) are due to second order diffraction of the grating. i.e. they correspond to the photon energies between 144 eV and 160 eV. According to the grating equation (in Eq. 2.2.5 in Section 2.2.5), the second order diffraction implicitly provides a higher energy resolution, which can

be employed in future studies. Preliminary results that demonstrate this effect are presented in Chapter 5 for the sulfur-containing molecules (e.g. CS_2 and thiophene).

2.2.3 Characterization of the XUV laser beams



Knife-edge measurements of XUV focal spot size in the horizontal plane in two photon energy regions (a) 50 eV to 72eV, and (b) 110 eV to 180 eV in the horizontal plane. The measured beam diameters $(1/e^2)$ for 50 eV to 72 eV and 110 eV to 180 eV are $90\pm10 \,\mu\text{m}$ and $170\pm20 \,\mu\text{m}$, respectively.



Figs. 2.2.3(c) and (d)

High harmonic spectra in two different XUV energy regions. The numbers in the figures represent the harmonic orders. (c) 31^{st} to 45^{th} order with aluminum filter (300 nm) at a neon gas pressure of 3.33 kPa. A vertical profile (grey) and a Gaussian fit (red) are shown on the right. The averaged full divergence $(1/e^2)$ is 8.1 mrad. (d) 79^{th} to 109^{th} order with silver filter (200 nm) at a neon gas pressure of 0.6 kPa. The intensity distribution of the harmonic spectrum from 69^{th} to 109^{th} orders follows the transmission curve of the silver filter. The sharp intensity drop between the 77^{th} and 79^{th} harmonics is caused by a damaged area on the MCP detector. At the right side of the spectrum, XUV photons from 2^{nd} order diffraction off the grating can be seen. The vertical profile of the harmonic spectrum cannot be fitted with a Gaussian Function. The estimated full divergence of XUV photons from 110 eV to 180 eV is ~ 2 mrad. This is a factor of four smaller than the full divergence in the photon energy range from 50 eV to 72 eV.

The measured XUV focal spot sizes and divergences are presented in this section. The XUV focal spot size is an important parameter that determines the pump-probe contract (signal-to-noise ratio) energy resolution and the of the spectrometer setup. In the studies of atoms or molecules subjected to strong-field ionization, the diameter $(1/e^2)$ of the XUV beam should be much smaller than the NIR beam. Strong-field ionization is a multiphoton process. The effective NIR beam diameter of the ionization column is

approximately equal to ω_0/\sqrt{N} , where ω_0 and N represent the beam radius $(1/e^2)$ of NIR focus in the interaction volume and the number of NIR photons needed for the ionization process, respectively. However, for one-photon excitation at 193 nm or 263 nm the diameter of the pump beam should be about the same size as the XUV probe beam diameter in order

to increase the contrast ratio and to reduce multiphoton processes. Figs. 2.2.3(a) and 2.2.3 (b) shows knife-edge scans of the XUV foci for the spectral region from 50 eV to 72 eV and from 110 eV to 180 eV, respectively, both in the horizontal plane. The

XUV focus diameters are $90\pm10 \ \mu m$ for the 50 eV to 72 eV range and $170\pm20 \ \mu m$ for 110 eV to 180 eV range. The divergences of the XUV laser beams is derived by measuring the vertical extent of the horizontally integrated spectra on the position sensitive detector as illustrated in

Figs. 2.2.3(c) and 2.2.3(d). The full divergences for the spectral regions from 50 eV to 72 eV and from 110 eV to 180 eV are 8.1 mrad and 2.0 mrad, respectively. This indicates that the generated XUV light sources from the gas cell possess a high spatial coherence. This advantage of a tabletop XUV light sources has been employed in coherent diffractive imaging experiments.^{99,100}

2.2.4 Alignment and characterization of a toroidal mirror

The alignment of the toroidal mirror (TM) is a key step to focus the XUV beam properly into the interaction volume. Slight misalignment of the toroidal mirror can easily ruin the focal spot size. This eventually jeopardizes the signal to noise ratio due to a bad spatial overlap between the pump and probe beams. Unfortunately, there is no standard guideline that can be followed from textbooks or the literature. A procedure for toroidal mirror alignment is presented in this section. The designed grazing incident angle of the toroidal mirror used in this study is 5°, providing good reflectivity (> 40%) in the spectral range from 50 eV to 300 eV. The designed parameters of the TM are listed in Table 2.2.4. It includes the designed values for the radii of curvatures in the horizontal (R_1) and vertical (R_2) planes, all dimensions are given in millimeters. The table also shows the measured curvatures that lie within the projected uncertainty of the manufacturing process.

Fable 2.2. 4

ARW Company	Dimensions (L×H×W)	R ₁ Horizontal	R ₂ Vertical	Coating	Surface Roughness
	$130 \times 25 \times 20$	10041.7	76.3	Bare gold	< 10 Å
Error in machining	±0.1~0.15	±1 %	±1 %	NA	NA
Measurement	NA	0.2 %	0.3 %	NA	NA

Several important factors need to be considered to achieve good XUV beam focusing. First, a bigger mirror surface is preferred. The focusing properties of an XUV beam depend strongly on the surface quality. The machining process of the mirror generates a better surface



Fig. 2.2.4(a)

Schematic drawing of distances from the XUV generation region to the center of TM (L₁) and from the center of TM to the target cell position (L₂). The design is in one-to-one imaging (i.e. $L_1 = L_2$).

figure toward the mirror center (flatness, digs and scratches on surface) than the outer portion of the surface. Secondly, in the design of the setup, a one-to-one imaging geometry including the TM is preferred, i.e. the distance between the HHG source and the center of the TM is equal to the distance between the center of the TM and the interaction volume as shown in Fig. 2.2.4 (a) ($L_1=L_2$). Strong focusing of the XUV beam by using a TM usually introduces higher order aberrations. Finally, using a

moderate grazing angle (\geq 5°) for a TM system is recommended. If the grazing angle is too small (e.g. 2°), significant uncertainties in the surface figure and radii are introduced in the machining process. This means that the radii in the horizontal and vertical planes of a TM can be off by 10 % or more. The XUV beam will never be focused down to a proper size in this case.

Characterizing the performance of a TM after receiving it from the optical company is a very important procedure. This mirror can be characterized by employing an attenuated NIR beam from the femtosecond laser system or a HeNe alignment laser. The test geometry should simulate the alignment of the XUV generation conditions. As shown in Fig. 2.2.4(a), the method is to measure the actual focus distance (L_2) between the center of the TM and the focal plane in the target cell. Incorporating with the set distance (L_1) between the NIR focus for the XUV generation and the center of TM, the actual radii of a toroidal mirror can be calculated according to the TM equations shown in Eqs. 2.2.4 (a) and 2.2.4 (b).

Toroidal Mirror Equations:

$$\frac{1}{L_1} + \frac{1}{L_2^H} = \frac{2}{R_1 \cos \alpha} \quad (2.2.4 \text{ a})$$
$$\frac{1}{L_1} + \frac{1}{L_2^V} = \frac{2 \cos \alpha}{R_2} \quad (2.2.4 \text{ b})$$

Here, L_1 represents the distance from the XUV generation region to the center of the TM. The distances L_2^H and L_2^V denote the distances from the center of TM to the foci in the horizontal and vertical planes at the target cell position, respectively. R_1 and R_2 represent the radii of curvatures of the TM in the horizontal and vertical planes, respectively. The parameter α represents the incidence angle. Here, the grazing angle is 5° therefore α is 85°. From the values



Figs. 2.2.4(b) and (c)

Misalignments of the toroidal mirror in the horizontal (b) and vertical (c) planes. In (b) an non-circular oval beam profile along the laser propagation direction is observed. At one particular position (e.g. sample cell), the beam profile may be circular but the diameter is larger than in the focus. This misalignment represents a wrong incident angle. Here, the TM is in the same plane of incoming and outgoing NIR beams (vertically aligned). (c) A "tilted" TM alignment that gives a tilted oval focal spot near the focus position. This can be fixed by rotating the TM around its surface normal (from left figure to right figure in (c)). of L_1 , L_2 and α , the radii of curvatures for the TM can be calculated. The measured values of R_1 and R_2 should be within 1 % of the design parameters as expected from the machining errors. Note that these equations can also apply to spherical gratings or spherical mirrors, for which R_1 is equal to R_2 .

For better characterization, a near-field focal spot from the TM should be measured instead of a far-field spot size at several meters away from the mirror. The alignment of the TM can proceed in the designed apparatus. Once the XUV source (L₁) and XUV image (L₂) distances are set approximately to the design distances and angle, several factors should be inspected and measured. First, the illuminated area of the NIR beam on the TM surface should be centered. This can be a guide for the alignment from time to time. This also insures that the XUV beam is reflected by a better surface quality (surface figure) on the mirror. Secondly, a webcam or a laser beam profiler is placed near the TM focal position. Note that the NIR beam should be attenuated properly to avoid damage on the beam profiler. The spot size before and after the focus should be measured. An optical rail along the laser propagation direction is set to achieve this measurement.

Usually, a "non-circular" tilted oval spot is observed during the first round of alignment. The shape of the spot changes along the laser propagation direction. The misalignments can be in the horizontal and vertical planes for a toroidal mirror. In case of a horizontally misaligned in the incident angle (or grazing angle), the horizontal and vertical foci are not at same distance $(L_2^H \neq L_2^V)$. Tuning the rotation angle of the TM in the horizontal plane can optimize the focus to achieve $L_2^H = L_2^V$. Fig. 2.2.4(b) shows a schematic drawing of horizontal misalignment in the incident angle for a TM that gives astigmatism along the propagation direction. The horizontal and vertical focal spots are not located at the same distance from the TM. The resulting focal spot size at the target cell is larger than the principally achievable focus diameter.



Fig. 2.2.4(d)

A simple schematic drawing of optimized alignment for a toroidal mirror. The focal spot at the target cell position is a minimum. This implies that $L_2^{H} = L_2^{V}$. The spot size before and after the target cell position should be circular. Note that the U curve is intentional shifted vertically. The minimum sizes in the H and V planes are the same.



Figs. 2.2.4(e) and (f)

The focal spots of a attenuated NIR beam (e) at the position of the high harmonic generation cell, and (f) at the target cell postion measured by using a webcam laser beam profiler. The spot size in the target cell position is slightly smaller in accordance to the design of the TM for 1:0.84 imaging.

In addition, a tiltednon-circular beam profile along the NIR laser progagation may be observed (Fig. 2.2.4(c)). This indicates that the whole TM does not sit in a plane parallel to the plane defined by the incoming and outgoing NIR beams, as shown in Fig. 2.2.4(c). The TM should be rotated in the vertical plane around the TM surface normal untill the beam profile near the focal position is either a horizontally or vertically aligned oval profiles. Once this is achieved, an optimization of the horizontal rotation angle for the TM can reach the correct incident angle. This eventually should lead to circular profiles before and after the focal position as described in the next section.

After several iterations of the TM alignment, the profile of the NIR beam should be exactly circular in the laser progagation direction before and after the target cell as shown in Fig. 2.2.4(d). At this angle, the focal spot size is minimal, and $L_2^{H} = L_2^{V}$. The beam diameter $(1/e^2)$ at the focal position is compared to the focal spot size of the NIR beam in the high harmonic generation cell. If the design of a TM is one-to-one imaging geometry, the obtained values should be the same. Figs. 2.2.4(e) and 2.2.4(f) show the

measured, optimized foci of the attenuated NIR beam at the position of the high harmonic generation cell and at the target cell position, respectively. The NIR spot size at the target cell position is slighly smaller due to the TM design that corresponds to a 1:0.84 imaging geometry.

Finally, an unattenutated NIR beam is focused at the XUV generation cell position in atmosphere. There should be a little filamentation because of the high peak intensities. The propagated NIR beam would be focused again by the aligned TM into the target cell position. If the alignment is properly set, filamentation will be observed at the target cell position. Darkening the room light helps to see the filamentation. Once these procedures are completed, the distances of L_1 and L_2 can be measured, and R_1 and R_2 can be calculated based on Eq. 2.2.4.

Our measurements lead to values of L_1 and L_2 of 942 mm and 814 mm, respectively. The calculated R_1 and R_2 are 10020.0 mm and 76.1 mm, respectively. The differences of the measured R_1 and R_2 compared to the designed parameters R_1 (10041.7 mm) and R_2 (76.3 mm) are 0.2% to 0.3 %, better than expected from machining errors (see Table 2.2.4). According to these numbers, the toroidal mirror is properly aligned. The characterization of the XUV beam at the focus position under vacuum conditions has been presented in the previous Sec. 2.2.3. The measured XUV beam diameter at the target cell position is 90±10 μ m. This value is similar to the NIR focus spot of 90 μ m in the high harmonic generation cell.

2.2.5 Selection and alignment of a XUV grating

When choosing a grating for the spectrometer, the blaze angle θ is an important factor that should be considered.^{101,102} The blaze angle is the angle between the grating normal and the facet normal as shown in Fig. 2.2.5. The angle is designed to have the maximum diffraction efficiency for a certain wavelength region. For the XUV or X-ray wavelength, the blazed angle θ is typically small (2° to 3°). Maximum diffraction efficiency is achieved when the incidence angle is equal to the reflection angle relative to the grating facet normal on the small groove. This corresponds to $\alpha - \theta = \beta + \theta$, where α and β are the incident and 1st order diffraction angles relative to grating normal. The grating equation is,^{101,102}

$$m\lambda = d \left[sin\alpha - sin\beta \right] \tag{2.2.5}$$

where m and d are the diffraction order and groove period, respectively. The angles α and β are both positive but measured on opposite sides relative to the grating normal (Fig. 2.2.5). In current case, the first order case (m=1) is considered. From the blaze condition ($\alpha = \beta + 2\theta$), groove period (d), designed incident angle (α) and interested XUV wavelength region (λ), the blaze angle θ can be calculated. This number can help to select a better XUV and X-ray grating for the experiments.

Two kinds of gratings are used in the experiments described herein. Both are concave spherical imaging gratings. The first one is a constant line spacing grating with a groove density of 1200 lines/mm and a blaze angle θ of 2° (Newport, 52051FS02-701R); the second one is a

variable line spacing grating with a center groove density of 1200 lines/mm and a blaze angle θ of 3° (Hitachi, 001-0660). The first grating is designed for any incidence angle but the second grating is designed for a 87° incidence angle. Note that the first grating has a dispersive focal plane on a Rowland circle,^{101,102} not on a flat plane. Therefore, the energy resolution on a plane detector varies for different wavelengths. For a small XUV energy region, the resolution differences are small. The second grating has a dispersive focal plane on a flat plane. This grating has higher average energy resolution. Here, some basic concepts are given for the installation of a grating.^{101,102} (1) A grating usually has an arrow mark on the edge. The point of arrow should point to the incoming beam as shown in Fig. 2.2.5. The arrow also indicates the groove shape on the grating surface. A common mistake is to align the grating arrow to the outgoing dispersion direction. This will cause a reflectivity loss due to the less illuminated area on the grating surface (i.e. shadowing of the grooves by their neighbors). (2) The illuminated area on the grating should be uniformly spread on the surface and cover as many grooves as possible. The resolving power of a grating is proportional to the number of grooves being illuminated grooves from a XUV or X-ray beam on the grating surface. (3) The zero-order reflection and the 1st order diffraction of NIR light from the grating can be used to align the whole grating plane. The vertical height of these two beams should be the same. This insures that the dispersion plane is parallel to the incident beam.



Fig.2.2.5

Side (upper) and top (lower) view of a grating blazed at anlge θ including incoming and diffracted beams. The arrow mark on the side of grating points toward the incident beam. The illumination of the XUV beam should be uniformly spread across the surface (yellow area). The facet and grating normals are perpendicular to the groove and main grating surfaces, respectively. α , β and θ are the incident, the 1st order diffraction and blaze angle, respectively. The blue and the purple arrows indicate that diffraction is under blaze the condition and at zero order.

2.3 Estimate of the XUV spectrometer energy resolution

The XUV spectrometer energy resolution is determined by several important factors. These include the grating resolving power $E/\Delta E$ (E: absolute energy, ΔE : Energy resolution), the detector pixel size and the spot size of XUV beam in the sample cell. The combined effects of these parameters define the overall spectrometer energy resolution. The nominal resolving power (R) of a grating is proportional to the number of illuminated grooves on the grating surface. A resolving power of 3000 has been demonstrated for the variable line spacing grating

(Hitachi) has been measured at 60 eV in a setup where the diameter of the XUV HHG source is equal to the X-ray CCD detector pixel size and the source is imaged into the gas cell with a 1:1 magnification.¹⁰³ By employing the grating equation (Eq. 2.2.5), the spatial separation in the detector plane between two adjacent XUV photon energies separated by a desired energy resolution (R) can be calculated. Fig. 2.3 shows this spatial separation for different R's as a function of the XUV photon energies. By comparing the pixel size of the CCD detector and the image size of the XUV beam spot to the curves in Fig. 2.3, the overall energy resolution of the system can be estimated. The pixel size of the X-ray CCD and the effective spot size on the MCPs detector are marked by the dashed horizontal lines in Fig. 2.3. The pore size of a microchannel plate is 32 μ m. However, the spot size on the phosphor screen is ~200 μ m, due to space charge effects that spread the electron cloud during its travels between the back of the microchannel plate stack and the phosphor screen. This degrades the final instrumental energy resolution. At 70 eV XUV photon energy, the resolution limits for the X-ray CCD and MCP detector are approximately ~0.02 eV and ~0.3 eV, respectively. These values are very close to the experimental results from our measurements (MCPs) and the literature (X-ray CCD).^{103,104} For an XUV photon energy at 160 eV, the MCP detector can only achieve ~1.0 eV energy resolution. This indicates that a change of detector to X-ray CCD is necessary to obtain a better resolution. The resolution limit for the X-ray CCD detector in Fig. 2.3 is ~0.07 eV.



Fig. 2.3

Spatial separation of two adjacent XUV photon energies based on desired energy resolution (R) versus the XUV photon energy. The pixel sizes of MCP and X-ray CCD are labeled on the vertical axis. For the energy resolution of 0.1 eV at a photon energy of 160 eV, MCPs detector should be replaced with X-ray CCD. In this case, the XUV focal spot size at the target cell position should be considered.

The diameter of the XUV source in the gas cell also has to be considered in the dertermination of the resolution. In the current case, the XUV spot size at the imaging source (target cell position) of the grating is on the order of ~170 μ m (see Fig. 2.2.3(b)). According to Fig. 2.3, the final resolution limit for this spot size is ~0.7 eV at a photon energy of 160 eV. Minimizing the XUV source spot size and its image in the sample cell can improve the energy resolution, provided that the image is larger than or comparable to the detector pixel size. A small hole in the target cell can also serve as a slit to improve the spectral energy resolution at the expense of a reduced transmitted XUV flux. The measured instrumental energy resolution for each setup is discussed in the repsective chapters.

2.4 Generation of third and fourth harmonics

In addition to strong-field ionization in the non-perturbative regime, electron excitation to neutral excited states by one-photon transitions using the third (263 nm, TH) and fourth (193 nm, FH) harmonics of the 780 nm fundamental are used for the studies of molecular systems. These excitation processes promote an electron from one molecular orbital to another or to a set of electronic configurations with well-defined excitation energies. In polyatomic molecules, these excited states can be (π, π^*) , (π, σ^*) , (n, π^*) and (n, σ^*) , where (a, b) refers to configurations that are characterized by excitation of an electron from orbital a to orbital b. *n* refers to a nonbonding orbital. By properly selecting an excitation wavelength, transitions to different electronic states can be chosen. The photochemistry and photophysics through the non-radiative decay (e.g. internal conversion, intersystem crossing and dissociation) is monitored by a timedelayed incoming XUV light pulse that detects specific chemical elements and reaction centers. In this section, a detailed layout for the third and fourth harmonic generation is shown. Next, the conversion efficiency is tabulated for comparisons of different generation schemes. Finally, an estimation of the pulse widths is presented.

2.4.1 Collinear and non-collinear THG upconversion configurations

Pulse energies of ~10 μ J to 20 μ J for third and fourth harmonics are required for the experiments. The estimated fraction of excited molecules in the pump-probe interaction volume is then ~ 20 % for perfect spatial overlap between the pump (UV) and probe (XUV) beams. In order to generate high fluxes of the excitation light source, crystal-based optical components are used for the photon energy up-conversion. However, in this generation scheme the temporal pulse stretching is substantial. Short pulse of UV and VUV lights can be produced by harmonic generation in a gas cell or by four-wave mixing. However, the generation efficiency is usually only ~ 0.01 % to 0.1 % and the setup requires more instrumentation and financial resources.^{105,106} Here, a crystal-based method that has an efficiency of a few percent (4 % to 8%) for third harmonic generation (THG) and ~0.7 % for fourth harmonic generation (FHG) is employed.



Fig. 2.4.1(a)

A schematic of the THG and FHG setups. M193, M263 and M780 denote dielectric mirrors for 193 nm, 263 nm, and 780 nm lights, respectively. The entire third harmonic generation setup is only 15 cm long. This is a very compact design for 263 nm generation.

Fig. 2.4.1(a) shows a schematic of a collinear scheme for THG and FHG. Fig. 2.4.1(b) shows the actual size of THG generation setup. In this layout, the alignment is simple. Before entering the UV generation system, the NIR beam is telescoped down to one fourth of the original beam size by using a combination of a positive (+40 cm) and a negative (-10 cm) lens. The beam diameter $(1/e^2)$ after this


Fig. 2.4.1(b)

Third harmonic generation setup. Phase matching is optimized through a combination of rotational and kinematic mounts. The time plate is used to compensate the group velocity delay between the 393 nm and 780 nm beams that is induced by the first crystal, time plate and air between the optical components.

telescope is ~ 3 mm. In the up-conversion system, the first crystal is a type-I β -Barium Borate crystal (BBO, BaB_2O_4) with a 0.5 mm thickness at a cut angle of 29.2° (Eksma Optics, Type-I p/n BBO-1003H). The generation efficiency of 393 nm from 780 nm is 24.7 %. A 1.0 mm thick α -BBO cut at a angle of 60° with P-coating on both sides (United Crystal) is used as a time-plate to compensate the traveling delay between 393 nm and 780 nm laser beams in air and optics. The 390 nm and 780 nm beams are mixed in a 0.3 mm thick type-II β -BBO cut at a angle of 57.2°. This scheme produces 57 μ J of 263 nm light for a NIR input pulse energy of 1.5 mJ, i.e. the overall TH conversion efficiency is 3.8 %.

A 263 nm mirror is placed after the $2^{nd}\beta$ -BBO to reflect the third harmonic and to transmit 780 nm. A dispersion compensation prism pair made of calcium fluoride (CaF₂) compresses the 263 nm pulse. The compressed third harmonic is mixed with the NIR beam in a type-I β -BBO (0.15 mm thick cut at a angle of 71°) to generate the fourth harmonic (193 nm). The distance in the prism pair is optimized to have the best fourth harmonic generation efficiency. The optimized distance of the prism pair is 260 mm. The travel delay between the 263 nm and the NIR beams is carefully tuned by using a translation stage installed on the NIR laser beam path. In addition, the mixing angle between the 263 nm and the NIR beam is optimized.



Fig. 2.4.1(c)

Non-collinear path for THG and FHG. The type-I β -BBO has a higher generation efficiency for the third harmonic than the type-II β -BBO. Half-wave plates (HWP's) rotate the NIR polarization to a vertical direction. The NIR beam mixes with vertical polarized 393 nm at the 2nd BBO. This generates horizontal polarized third harmonic. Similarly, the NIR laser polarization is rotated again by a 2nd HWP to the horizontal direction. The NIR beam overlaps with the third harmonic at the 3rd BBO. The vertical polarized fourth harmonic is generated. All the travel delays are adjusted by using translation stages. Note that M193, M263, M393 and M780 represent dielectric mirrors for the reflection of the light beams. The symbols \leftrightarrow and \bigcirc indicate polarizations in the figure plane and perpendicular to it, respectively.

The output at 193 nm is $7 \mu J$ per pulse from a NIR pulse energy of 1.48 mJ, corresponding to a conversion efficiency of 0.47%.

In the collinear THG setup, the generation efficiency for 263 nm light using a type-II crystal is lower than for a type-I crystal. For the experiments at 263 nm excitations, the TH intensity is sufficient. But the intensity of the fourth harmonic (193 nm) at the interaction region is only sufficient to excite a few percent of the molecules, taking into account the absorption by air and optics. Since the generation efficiency of 193 nm is limited by the intensity at 263 nm, the type-II crystal is replaced with a type-I crystal to improve the third harmonic intensity. A non-collinear geometry for 263 nm light generation is shown in Figs. 2.4.1(c) and 2.4.1(d). Due to the relative polarizations of the up-conversion laser beams, half wave plates (HWP's) are installed in the 780 nm beam path to rotate the polarization into the correction alignment for the mixing schemes. For a type-I crystal, the mixing components should have the same polarizations. In contrast, perpendicular relative polarizations are used in a type-II crystal in the collinear setup.



Fig. 2.4.1(d)

Non-collinear setup for the THG system. Note that this figure only shows the optics after doubling of 780 nm to the generation of 263 nm. The red and blue colors represent the 780 nm and 393 nm laser beams, respectively.

A third-order harmonic pulse energy of 128 μ J is generated at a NIR pulse energy of 1.5 mJ in the non-collinear THG setup. The generation efficiency is more than twice as high as for the 0.3 mm thick type-II β -BBO in the collinear setup. For the generation of the fourth harmonic, the relative angle between the NIR and the third harmonic are optimized in order to obtain the maximum conversion efficiency. Careful adjustment of the grating compressor in the laser system is also important to improve the conversion efficiency. The conversion efficiency of the fourth harmonic improves to 0.69 % in comparison to the 0.47 % of the collinear THG setup. The results of collinear and non-collinear setups in the frequency up-conversion system will be presented in Sec. 2.4.2.



Fig. 2.4.1(e)

The second (393 nm), third (263 nm) and fourth (193nm) harmonic spectra. The FWHM values for 393 nm and 263 nm are $4.0\pm(0.2)$ nm and $1.3\pm(0.1)$ nm, respectively. Due to the limit of the spectrometer at 200 nm, the FWHM for 193 nm cannot be determined.

The wavelength and spectral bandwidth for second, third and fourth harmonics are measured by using a commercial compact spectrometer (Ocean Optics, HR2000CG-UV-NIR). These spectra are shown in Fig. 2.4.1(e). In order to measure wavelengths lower than 300 nm, a fiber optic on the spectrometer is removed. The whole spectrometer entrance is directly coupled to attenuated harmonic beams. The measured bandwidths (FWHM) of second and third harmonics are $4.0\pm(0.2)$ nm and $1.3\pm(0.1)$ nm, respectively. The spectrometer has a designed

detection limit at 200 nm; therefore, the bandwidth of the fourth harmonic (at 193 nm) cannot be determined. The measured spectral width provides a lower bound for the pulse duration of the second and third harmonics. This is presented in Sec. 2.4.3.

2.4.2 Conversion efficiency

The conversion efficiency for the two different crystal setups is tabulated in follows. All crystals are purchased from Eksma Optics Company. The clear apertures of the crystals are 10 mm in diameter with designed thickness for better conversion efficiency. The selection guide for the BBO crystals thickness is presented in Sec. 2.4.3. A prism pair dispersion compensation (Thorlabs, ASF-CAF) made of CaF₂ is placed in the third harmonic beam path to compress the pulse width. The distance (260 mm) between the two prisms is optimized for the best fourth harmonic generation efficiency. The initial NIR input power at 780 nm is 1.48 mJ (4.45 W) for collinear THG and 1.5 mJ (4.5 W) for non-collinear THG. After all the conversion processes and reflection loss, the remaining NIR power for the fourth harmonic generation is 2.3 W. In the collinear setup, an α -BBO of 1.00 mm thick at a cut angle of 60° is installed for traveling time compensation between the NIR beam and the second harmonic. Both crystal surfaces have P-coatings for the best transmission at the NIR beam and at 393 nm.

By comparison between Tables 2.4.2(a) and 2.4.2(b), the third harmonic generation efficiency is two times higher even when the type-I β -BBO thickness is 0.1 mm thinner in the non-collinear setup. The obtained pulse intensity at 263 nm is ~130 μ J. The increased photon intensity at 263 nm does not improve the conversion efficiency equally in FHG process. The conversion efficiency for the fourth harmonic in the non-collinear configuration is 0.69 %. This is only 0.22 % higher than the collinear setup. Using a thicker BBO crystal for THG (type-I β -BBO thickness 0.3 mm, θ =44.3°) in the non-collinear geometry can produce 200 μ J at 263 nm.¹³ This should be able to improve the overall FHG photon intensity.

	780 nm	393 nm	263 nm	193 nm
Power (W)	4.45	1.1	0.170	0.021
Conversion (%)	NA	24.7	3.8	0.47
Crystals (β- BBO)	NA	Type-I 0.5 mm (29.2°)	Type-II 0.3 mm (57.2°)	Type-I 0.15 mm (71°)

 Table 2.4.2(a) Conversion Efficiency in Collinear Geometry for THG (3kHz)

Table 2.4.2(b)	Conversion Efficienc	y in Non-Collinear	Geometry for THG	(3kHz)
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	780 nm	393 nm	263 nm	193 nm
Power (W)	4.5	1.1	0.385	0.031
Conversion (%)	NA	24.7	8.6	0.69
Crystals (β -BBO)	NA	Type-I 0.5 mm (29.2°)	Type-I 0.2 mm (44.3°)	Type-I 0.15 mm (71°)

2.4.3 Estimated temporal width of third and fourth harmonics

The temporal widths of the third and fourth harmonics can be estimated by taking into account the group velocity mismatch (GVM) and group velocity dispersion (GVD) of optics at different wavelengths.¹⁰⁷ GVM is the group velocity difference between two wavelengthes λ_1 and λ_2 , travelling in the medium for the sum frequency generation. GVM is defined in Eq. 2.4.3(a).

$$GVM = \frac{1}{v_g^{\lambda_1}} - \frac{1}{v_g^{\lambda_2}}$$
 2.4.3(a)

where the group velocity at wavelength λ_1 is defined as $V_g^{\lambda_1} = (\partial k/\partial \omega)^{-1}$ and $k = n(\omega) \times \omega/c_0$. The parameters ω , $n(\omega)$ and c_0 are the angular frequency, refractive index at angular frequency ω and the vacuum speed of light, respectively. The temporal overlap of the two beams constantly changes along their path through the BBO crystal. Once the two beams are completely separated, there is no sum frequency generation, but the pulse duration is continuously broadened due to the group delay dispersion. In order to avoid the unwanted pulse stretching during the sum frequency generation (SFG), the interaction length, L_{GVM}, is used to determine the best crystal thickness. L_{GVM} is the ratio Δt_1 over GVM (Eq. 2.4.3(b)), where Δt_1 is the longer pulse duration in the two mixing components.

$$L_{\rm GVM} = \frac{\Delta t_1}{\rm GVM}$$
 2.4.3(b)

If the crystal thickness (L) used in the generation is larger than the L_{GVM}, a slightly increased conversion efficiency can be obtained. However, a pulse stretching of the generated beam can happen. This indicates that the temporal separation between two components ($\Delta t = L \times GVM$) is larger than Δt_1 , and the broadening of the pulse duration can occur. An example will be given in the estimation of the generated harmonic pulse duration.

The material GVD (fs²/mm) of a medium with thickness L (mm) stretches the pulse duration due to dispersion. A resulting pulse width Δt of a pulse with an original duration Δt_0 , can be estimated by using Eq. 2.4.3(c). (ln2=0.6931)

$$\Delta t = \Delta t_0 \sqrt{1 + \left(\frac{4 \ln 2 \times GVD \times L}{\Delta t_0^2}\right)^2}$$
 2.4.3(c)

The TH and FH pulse durations based on the non-collinear THG configuration can be estimated as follows. The initial NIR pulse duration from the Red-Dragon laser system is 25 fs (Δt_0) . Table 2.4.3(a) lists the GVDs for a type-I BBO crystal, fused silica, BK7 and SF10 optical materials at different wavelengths. Appendix B also lists GVDs for other materials. The calculation of GVD is through the second-order derivative of the refractive index n, see Appendix B for more details. Table 2.4.3(b) lists the GVMs for different harmonic wavelengthes in a type-I BBO crystal. Assuming a common sech² shape for a femtosecond laser pulse, the

convolution equation is shown in Eq. 2.4.3(d).¹⁰⁷ Δt_1 and Δt_2 represent the pulse durations of the mixing components.

$$\Delta t_3 = \sqrt[a]{\Delta t_1^{a} + \Delta t_2^{a}}$$
, a = 1.615 for sech² pulse 2.4.3 (d)

GVD (fs ² /mm)	780	393 nm	263 nm	193 nm
Type I BBO	75	106	125	1345
Fugad Silian	26	08	202	500
Fused Silica	30	98	205 NIA	300 NIA
BK /	40	123	NA	NA
SF 10	163	740	NA	NA

Table 2.4.3(a) List of Group Velocity Dispersion (GVD) for Optical Materials

Table 2.4.3(b) List of Group Velocity Mismatch (GVM) for BBOs

Type-L BBO	SHG	THG	FHG
Type T BBO	780 nm	780 nm + 393 nm	780 nm + 263 nm
GVM (fs/mm)	194	737	2074
Thickness (mm)	0.5	0.2	0.15
L _{GVM} (mm)	NA	0.132	0.03

In this section, an estimate of the pulse durations for the non-colinear THG setup is presented in this section. A 0.5 mm thick doubling crystal is employed for the 393 nm generation. The increased second harmonic intensity from doubling can help improve the THG process. An increase of 263 nm can also increase the overall fourth harmonic photon intensity. The estimated 393 nm pulse width from a 0.5 mm type-1 BBO crystal is 97 fs (194 fs/mm \times 0.5 mm) due to GVM between the 780 nm and SH light. The NIR pulse duration has stretched from 25 fs to 33 fs after travelling through the first BBO (0.5 mm), two dichroic mirrors (2 mm each) and one zero-order half wave plate (0.8 mm). Mixing of the NIR and the 393 nm laser pulses yields a pulse duration of 107.2 fs $(1.615\sqrt{33^{1.615}+97^{1.615}})$ at 263 nm if the second crystal thickness is equal to L_{GVM} ($L_{GVM} = 97/737 = 0.132$ mm). However, a crystal of 0.2 mm is used to increase the third harmonic photon intensity. This value is larger than L_{GVM}, indicating that the actual pulse duration of the third harmonic should be longer than 107.2 fs due to the GVM and GDD of the crystal. Based on the spectral bandwidth $\Delta \lambda = 1.3 \ nm$ of the TH signal in fig. 2.4.1(e) and the time-bandwidth product $\Delta t \times \Delta \lambda = 0.351$ for a sech² laser pulse, the shortest pulse duration that can be reached is 62 fs. As a consequence, employing a prism pair dispersion compensation on the third harmonic beam path to compress the pulse duration can help increasing the FHG efficiency.

In the NIR path, the overall thickness of the optics before reaching the FHG crystal is 12.3 mm. This includes two zero-order HWPs, two β -BBOs, and four dichroic mirrors. These optics stretch the NIR pulse duration to 55 fs. Assuming the pulse duration of the third harmonic

is fully compressed to 62 fs by the prism pair compressor, the pulse duration of the fourth harmonic would be equal to ~90 fs ($^{1.615}\sqrt{55^{1.615} + 62^{1.615}}$). This is the estimated minimum temporal width of the 193 nm pulses generated in the non-collinear FHG system described above. A thicker crystal (0.15 mm) for FHG is used for a higher conversion efficiency. This crystal is five times thicker than L_{GVM} (L_{GVM} = 62/2074 = 0.03 mm). A pulse temporal stretching in the crystal may occur. Additionally, the FH pulse duration in the interaction region will be broadened due to traveling through the air, a vacuum window (1mm) and a focal lens (3.5 mm). The actual instrumental temporal resolution is determined experimentally as discussed in Chapter 5.

2.5 Alignment of the Red Dragon laser system

This section presents experience-based descriptions of the optics alignment for the Red Dragon laser system. A standard detailed procedure is explained in the operation manual. In general, a few optical mirrors are adjusted from time to time to optimize the laser system. This reduces a significant amount of time on laser maintenance. The alignment of the laser system can vary from person to person. Several basic points are mentioned in following subsections that are useful for quick and efficient laser alignment. The most important work for the Red Dragon laser system is a regular check of the green pump laser power. This should be repeated every three months to insure the proper laser system performance. Please refer to detailed Red Dragon layout for the alignment optics.

2.5.1 Femtosecond Red Dragon laser system layout

The Red Dragon laser system delivers a maximum power of 15 W at a repetition rate of 3 kHz. This corresponds to 5 mJ per pulse. The NIR pulse duration and center wavelength are 25



Fig. 2.5.1

Layout of the Red Dragon laser system. The system contains four green pump lasers, three Ti-Sapphire crystals and two cryostats for crystal cooling. The system is a two-stage amplifier that delivers a maximum power of 15 W at a repetition rate of 3 kHz. The center wavelength is at 780 nm and the pulse duration is 25 fs. The green and red boxes represent the green pump lasers and the near infrared seed/amplifier systems, respectively. The black boxes represent periscopes and laser beam tubes.

fs and 780 nm, respectively. The output laser beam diameters $(1/e^2)$ are 12 ± 1 mm and 11 ± 1 mm in the horizontal and vertical planes. Fig. 2.5.1 shows a simple layout of the Red Dragon laser system. The laser is a two-stage amplifier system. The Red Dragon contains four green pump lasers, three Ti-Sapphire crystals, two of which are maintained at cryostatic temperatures (-217 °C) during operation. The first green laser (Verdi, Coherent Inc.) serves as a pump laser for an air-cooled Ti-Sapphire crystal to generate a seed laser beam. This seed beam is amplified in the two stages. The second green laser (LDP-200MQG, Lee Inc.) is used for the 1st amplifier stage. This laser is marked as P1 in Fig. 2.5.1. The P1 laser is used to pump the second TiSapphire crystal mounted on a cryostat (PT60 for the 1st stage and PT90 for the 2nd stage, Cryomech) system in a vacuum chamber. The second stage amplifier contains two pump lasers (DM30-527, Photonic Industries). These two green lasers are P2 and P3, respectively. P2 and P3 pump the third Ti-Sapphire crystal. The third crystal is mounted in a cryostatically cooled vacuum system. The cryorefrigerator mechanism is a high-pressure helium (99.999%) compression-expansion cooling process. The water-cooled helium compressor removes the heat that is generated in the amplifier crystals by the green lasers. The cooling reduces the impact of the thermal lensing effects on the amplified NIR pulses. Details are shown in the following sections.

2.5.2 Laser oscillator for the seed beam

Please see the manual for the detailed oscillator layout of the Red Dragon laser system. A common problem with the oscillator is a variation of the spectral bandwidth and center wavelength. This usually causes a change and instability of the amplification in the whole laser system. There are several reasons that lead to the instability. First, temperature fluctuations in the laboratory slightly change the cavity in the oscillator, which makes it unstable. The cavity is also sensitive to the ground and table vibrations in the laboratory. This can cause the loss of modelocking in the oscillator. Stable cavity and laboratory temperatures can also minimize this problem. Secondly, damage of the Ti-Sapphire crystal surface can change the spectrum and center wavelength. The damage of the crystal happen on the crystal surface at very low green pump power. Green scattered light from the front crystal surface indicates that damage on the surface has occurred. Shifting the crystal sideways can temporarily solve this problem. No green scattered light will occur from a new crystal spot. The crystal surface should be periodically cleaned with high purity methanol and acetone (water free). Be careful with the indium foil on the edge of the crystal mount; do not wipe any indium debris onto crystal surface, since debris increases the damage rate on the crystal surface. Finally, damage and dirt on the other optics can also cause instability. A regular cleaning process in the oscillator chamber (optics and housing) can maintain the operation of the laser cavity. Keeping the laboratory floor clean can also helps preventing dirt from getting into the laser system.

A periodic adjustment of the oscillator is necessary to insure cavity stability. Once the oscillator is mode-locked and stable even with the intentionally created ground/table vibrations, the whole laser amplification efficiency should be the same in comparison to previous outputs. This indicates that the mode-locking of the oscillator can serve as a good alignment guide for the following amplifiers. Adjusting two prisms and shifting of the crystal can fix the daily change of the spectrum (center wavelength and bandwidth). These adjustments are usually small. The amplification in the 1st and 2nd stages by the green lasers can be performed, and require a slow increase rate of the green powers. The NIR powers of the first and second stage can also give a good indication about the alignment of the laser in the amplifiers after slight tuning of the oscillator. If the NIR power in the first stage is lower than previous power by a significant amount, re-alignment in the 1st stage and 2nd stage amplifier is necessary. If the NIR power from

the first and the second stages is similar to previous measured output powers, no further alignment is needed. This procedure can minimize the amount of time in re-aligning the laser system due to a small shift and change on the oscillator spectrum.

Re-alignment of the whole Red Dragon laser system is necessary every three to four months. This is also a good moment to check the power of all green pump lasers (P1, P2 and P3). A check on the oscillator alignment (spectral bandwidth, center wavelength and cavity stability) should be performed before optimizing the amplifier systems (1st and 2nd stage). The alignment of the amplifier and the test of the green pump lasers are presented in following sections.

2.5.3 First stage amplifier system

Please see the manual for the laser paths in the first stage amplifier. The first stage amplifier is a seed beam multi-pass and green beam single-pass amplification system. The detailed steps of the alignment are given in the operation manual. This section presents some basic experience in the alignment of the first stage amplifier. Optimization of the 1st stage amplifier system can be performed by simply adjusting several key mirrors. The first two irises used to insure the alignment into the pulse stretcher are D-I1 and D-I2. The stretcher contains a grating that is passed four times by the seed beam. This layout introduces a significant amount of positive chirp on the seed pulse, corresponding to an extension of the pulse duration from 12 fs to 200 ps before the seed is coupled into the amplifier system. The alignment through D-I1 and D-I2 insures that the seed beam is properly adjusted. Use D-M1 and D-M2 to align the beam through irises D-I1 and D-I2, respectively (D-M1 for D-I1 and D-M2 for D-I2). By opening and closing the irises, diffraction fringes become apparent on camera 4 that may be used to fine tune the alignment. The diffraction patterns of the seed beam should be uniformly centered on camera 4. No optics in the stretcher system should be tuned. Never touch the S-M1 mirror. This is a coupled-mirror that sends the seed beam into the stretcher and bounces the seed beam out of the stretcher system. A misalignment in the stretcher system can introduce a spatial chirp that may significantly reduce the amplification efficiency. Alignment of the stretcher needs significant skill and possibly support by the vendor.

After the alignment of the stretcher, the alignment into the multi-pass amplification system can be simply achieved by tweaking the other two mirrors to the mask (A-A1). The two mirrors for the adjustment are D-M4 and D-M5, respectively. The mask is on the multi-pass ring amplification system. Set up an external CCD camera to monitor the alignment of the seed beam on the mask. The D-M4 and D-M5 mirrors are used to align to the 1st and last path of the ring on the mask. Note that for the alignment of the ring, two half-wave plates (P-HW and 2P-HW1) should be flipped up in order to by pass the Pockel cells. After the seed beam on the mask is properly aligned, the output seed beam power at the end of the 1st stage is approximately 5 mW (before entering the 2nd stage).

After the seed beam is aligned in the first stage, pulse-train mode amplification can be performed. Pulse-train mode is achieved while the two half-wave plates are on the seed beam path. This produces a seed beam pulse sequence at 80 MHz. In this moment, whether the pockel cell (P-P3 and 2P-P1, and PC1 & PC2 for short names) is on or off does not have any difference in the amplification. (The pockel cell serves as a frequency divider that reduces the seed beam frequency from 80 MHz down to 3 kHz.) In the 80 MHz pulse-train mode, the amplification of each pulse by the green pump laser is small and the peak intensity of the amplified NIR is relatively low. This mode is used to fine-tune the spatial overlap between the green pump and the seed beams on the cryo-cooled Ti-Sapphire crystal in the vacuum chamber (A-C1). Wait for a few minutes for the green pump laser to warm up. Set the green pump power to have a stable NIR amplification power. Note that a power meter (PM10) is placed at the end of the first stage for the measurement of the seed and its amplification. Mirror G-M3 is used to tune the green laser alignment on the crystal. Camera 3 can be used to monitor the green spot on the crystal surface. Adjustment of the big reflective mirror in the multi-pass ring (A-M8) can also optimize the amplified NIR beam. Several iterations of the adjustments on the G-M3 and A-M8 mirrors can optimize the power in the pulse-train amplification mode. Note that in order to reach the G-M3 mirror from the right side, it is very easy to knock the A-M1 mirror.

After the optimization of the power in the pulse-train mode (low peak intensity mode), the amplified mode at 3 kHz can be performed. This is achieved by turning on the two pockel cells and flipping down the two half-wave plates. The seed beam frequency after the first pockel cell is at 3 kHz. The amplification of the seed beam at 3 kHz should result in an average power of 4.5 W to 5 W measured at the end of the first stage. Fine-tuning on the G-M3 and A-M8 can help optimizing the NIR output. At this moment, the adjustments should be made with extreme care because the peak power is much higher. Tuning the timing of the P1 laser relative to the seed beam may be necessary to find the best temporal overlap for the amplification. Note that the timing of the P1 pulses changes with the output power of the pump laser, i.e. the correct timing has to be tuned under the conditions that are used during the experiment. If the first stage power is lower than 4.5 W after careful alignment and timing adjustment, the green pump power should be checked. A decreased amplified NIR power may be simply due to a decrease of the green power.

Before sending any amplified NIR beam into the second stage, the non-amplified seed beam should be used to align the second stage. If the seed beam has been aligned through the second stage, the Red Dragon output power after the second stage is approximately 2.5 W from a full power of 5 W measured in the first stage, i.e. the transmission of the NIR laser power from the first stage through the second stage is ~54 %. The decrease of the NIR laser power is mostly due to losses in the grating compressor. A clean grating compressor system has an average transmission efficiency of 65 %. The transmission efficiency decreases over time due to photochemistry on the grating surface that reduces the reflectivity. Regular cleaning of the grating surface with distilled warm water, optics methanol (water-free) and dried nitrogen restore the original reflectivity. The other sources of the NIR laser power loss are the optical components in the second state. The alignment of the second stage is presented in next section.

2.5.4 Second stage amplifier system

The alignment in the second stage amplifier system is simpler. A schematic of the second stage is shown in the manual. Before optimizing the second stage at full power, an unamplified seed beam is used for the coarse alignment (with two half-wave plates up in the first stage, i.e. in a pulse-train mode). Two mirrors in the first stage (2P-M1 and 2P-M4) are used to align the beam through the two irises 2A-1I1 and C-I2, respectively, in the second stage. The 2P-M1 is tuned for the iris 2A-1I1, and 2P-M4 for C-I2. This ensures a good alignment of the seed beam through the second stage Ti-Sapphire crystal and the grating compressor. A careful check of the NIR beam path on the Brewster windows of the crystal housing should be performed. Avoid any clipping of the NIR beam on the edge of the windows as otherwise the window seal may be damaged, leading to air leaking into the vacuum chamber, ice built-up on the cryogenically cooled crystal and ultimately crystal damage.

After the seed beam is aligned, the ASE (amplified spontaneous emission) mode of the first stage can be used for aligning the second stage under low amplification conditions. ASE originates from spontaneous NIR fluorescence of the green pumped Ti-Sapphire crystal that is self-amplified in the ring system. The peak intensity of ASE is much lower than that of amplified seeded NIR beam due to a longer pulse duration and lower average power. This mode is activated by switching off the first Pockels cell (PC1), effectively block the seed beam from entering the first amplifier stage. The second Pockels cell (PC2) is still on. The two half-wave plates are flipped down in this mode. The full-amplified first stage can be switched to ASE mode by simply turning off the PC1 voltage without damaging the laser system. Never switch off PC2 while operating the first stage in pulse amplification mode. This will damage the polarizer behind the PC2, which would absorb the entire pulse energy.

In ASE mode, the second stage can be operated in full power amplification mode using the two green lasers P2 and P3. Using ASE instead of seeded pulse mode avoids high peak intensities in the crystal chamber that may damage the crystal if the crystal housing and/or the heat-conducting indium foil are hit and debris is deposited on the crystal surface. Place a power meter (PM30, Coherent) in front of the mirror 2T-M2. The power meter is used to measure the ASE power amplified by P2 and P3 to optimize the spatial overlap between the green laser beam and the NIR beam in the Ti-Sapphire crystal. Camera 1 in the second stage helps to find the coarse spatial overlap, which is then fine tuned using output power. There are two separated NIR spots on the crystal due to the bowtie configuration of the NIR laser beam passes through the second stage crystal. These two paths cross the crystal in the horizontal plane. The green laser beams from P2 and P3 also cross the crystal but in the vertical plane. Before tuning the second stage with amplified ASE, a careful check of the green beam alignment through the crystal chamber Brewster windows should be performed at very low power. Make sure there is no clipping of the green beam on the edge of the window for the reasons described above.

Before the green laser amplification, the ASE power from the first stage should be recorded (PM30 in front of 2T-M2 mirror). While using P2 and P3, increase the power slowly. This protects the diodes and the gain medium (Nd-YLF rod) in the green laser cavities. Note that the amplification by the green laser should be performed on one laser at a time. At full power of P2 or P3, the ASE power should be recorded again. From the ASE powers before and after amplification, the ASE amplification ratio for P2 and P3 can be calculated. The amplification ratios for the P2 and P3 lasers are usually in the range between 5 and 6. This ratio can be tuned by moving the green focal lens. While changing the lens position, very low green power should be used to prevent damage on the crystal. Note that the green laser (P2 and P3) foci have to be located behind the Ti-Sapphire crystal in each beam path in order to avoid crystal damage.

To optimize the ASE power, the spatial overlaps between the green laser beams and the NIR beam on the crystal is fine tuned by using mirrors 2G-2M1 and 2G-3M3 for P2 and P3, respectively. Note that mirror 2G-3M3 is very close to the NIR beam path (right at the bottom). Do not clip the NIR beam while tuning 2G-3M3. Camera 1 of the Red Dragon system helps to monitor the positions of the green beams on the crystal. Do not move the green spot to the edge of the crystal mount. This will burn off some indium foil from the crystal mount and damage the crystal surface. Record the optimized ASE power and calculate the amplification ratio. This helps to evaluate any shifts of the seed beam alignment from small adjustments in the oscillator and first stage amplifier. Generally, only very small adjustments of the beam paths in the second stage should be required after the first stage is properly aligned. After a spatial optimization in the amplification of P2 and P3 in ASE mode, slowly decrease the powers of P2 and P3 to warm up conditions (~4 A diode current). At these settings (P2 and P3), the ASE mode can be switched to the amplified mode in the first stage (PC1 on). This will change to a full power of the first stage. Never switch from ASE mode to amplified mode (in the 1st state) while P2 or P3 are operating at amplifying intensities in the 2nd stage. This will damage the 2nd stage crystal. The power meter (PM30) is still in front of mirror 2T-M2 (before the grating compressor). The measured NIR power ranges from 4 W to 4.8 W.

Note that the next step operates at the highest NIR peak power in the Red Dragon laser system. The increase rate of the pump powers (P2 and P3) should be slow. The high peak intensity of the NIR laser can easily damage the Ti-Sapphire crystal. At the full powers of P2 and P3 lasers (and amplified 1st stage), the amplified NIR is at the maximum power of the Red Dragon laser system. The power should be approximately 23 W before the grating compressor (i.e. measured in front of mirror 2T-M2). This number is used for later comparison. The next step is to measure the laser power after the grating compressor. The power meter (PM30) should be placed at the Red Dragon laser output. The full power of the compressed NIR is 15 W. This corresponds to 65 % transmission of the grating compressor. If the transmission is lower than 58 %, one or both of the compressor gratings should be cleaned. The cleaning procedure is described in the operating manual (or contact KM Lab company).

2.5.5 General knowledge of the green pump lasers

The green lasers that pump the two amplifier stages are high power diode-pumped nanosecond laser systems. The diode array has a working lifetime that varies from company to company. A warm up period of the laser systems is required to protect the diode arrays and the gain medium (Nd-YAG or Nd-YLF rod) from damage due to overshoot in the pump current. Try to minimize dry runs of the pump lasers (leaving lasers unsupervised and not running experiments). These reduce the lifetime of diode. Pump laser currents should always be raised slowly. This will also protect the pump lasers and the Ti-Sapphire. During the past 6 years, we have spent a tremendous amount of time replacing green pump lasers (~20 times replacements and repairs). An experienced operator can replace one pump laser within a half day (P2 and P3), including the recovery of the Red Dragon laser system back to the full power. A regular check on the green laser power is very important. The following lists the places where the power meter (PM30) is placed in order to ensure reproducible readings.

- (1) P1 (Lee laser): between G-M3 and A-M4 mirror.
- (2) P2 (PI laser): after the first periscope. The beam tube between the periscope and the amplifier housing should be removed for the measurement.
- (3) P3 (PI laser): before mirror 2G-3M1. This place is very crowded. Avoid knocking other mirrors.

The green laser power should be recorded at the same currents as previous measurements. Also record the diode working hours, since this can help to calculate the green power drop rate and predict when a laser should be replaced. In each measurement, also write down the lab book page numbers of previous measurements so that you can refer quickly to them for laser maintenance.

2.6 Data acquisition and analysis

The experimental results for the static absorption and pump-probe transient absorption spectra are given in optical density (OD) and difference of optical density (Δ OD), respectively. OD is defined as:

$$OD = -\log[I_s^{\rm pr}/I_0^{\rm pr}]$$
 2.6(a)

where I_s^{pr} and I_0^{pr} represent the transmitted XUV intensity with and without the sample in the gas cell, respectively. Both transmission spectra are acquired while the pump beam is blocked. Each transmission spectrum, I_s^{pr} and I_0^{pr} , is obtained from an average of 20 sets of data. Each data set is accumulated for of 2.5 seconds. The average of these spectra yields a statistical standard deviation of mean (σ). An error propagation through Eq. 2.6(a) gives the final error bars as shown in the experimental results. The error bars are in the 95% confidence levels (1.96 σ).

 Δ OD is defined according to Eq. 2.6(b). It is the difference between the OD's of the sample with and without the pump laser beam.

$$\Delta OD(t) = OD_{pp(t)} - OD_{pr} = \log \left[I_0^{pr} / I_{s(t)}^{pp} \right] - \log \left[I_0^{pr} / I_s^{pr} \right] = -\log \left[I_{s(t)}^{pp} / I_s^{pr} \right]$$
 2.6(b)

where $I_{s(t)}^{pp}$ represents the transmission intensity in the presence of target sample at pump-probe time delay t. Note that the spectra I_{s}^{pr} and $I_{s(t)}^{pp}$ are acquired in a condition without the influence of the background from the pump laser beam. A positive pump-probe delay corresponds to a pulse sequence where the pump beam arrives at the gas target cell before the XUV probe laser beam.

In the experiments, a small contribution of scattered pump beam background (I_{BG}) overlaps with the transmission spectrum $(I_{s(t)}^{pp})$ at all time delays. Therefore, the experimentally observed transmission spectrum $(I_{s(t)}^{pp'})$ is equal to the sum of the time-independent background from the pump laser beam (I_{BG}) and a background-free transmission spectrum $(I_{s(t)}^{pp})$. This modifies the observed change in optical density to $\Delta OD(t) = \log [I_{s}^{pr}/(I_{s(t)}^{pp} + I_{BG})]$, precluding the use of I_{s}^{pr} as a reference spectrum for the ΔOD . In order to compensate for the influence of the background in the transmission spectrum, a reference spectrum recorded at large negative delay without temporal pump-probe overlap is used instead of a reference spectrum without pump laser light. The time-dependent change in optical density is then defined as:

$$\Delta OD(t) = \log \left[I_{s(t_{ref.})}^{pp'} / I_{s(t)}^{pp'} \right] = \log \left[(I_{s(t_{ref.})}^{pp} + I_{BG}) / (I_{s(t)}^{pp} + I_{BG}) \right] \cong \log \left[I_{s}^{pr} / I_{s(t)}^{pp} \right]$$
 2.6(c)

where $I_{s(t,ref.)}^{pp'}$ and $I_{s(t)}^{pp'}$ represent the XUV transmission spectra with a contribution of background at pump-probe delay time t_{ref} and t, respectively. At far negative delay time without temporal overlap between the pump and probe beams, the transmission spectrum $I_{s(t,ref)}^{pp}$ is equal to I_{s}^{pr} . This reduces Eq. 2.6(c) to $\Delta OD(t) = \log \left[(I_{s}^{pr} + I_{BG}) / (I_{s(t)}^{pp} + I_{BG}) \right] \cong \log \left[I_{s(t)}^{pr} / I_{s(t)}^{pp} \right]$ while I_{BG} is small compared to I_{s}^{pr} . The approximation in Eq. 2.6(c) is valid since the background signal from the pump beam is small (<5 %) compared to the XUV signals. Thus, the final $\Delta OD(t)$ can be calculated by using a reference spectrum at far negative delay time. The derivation of Eq. 2.6(c) is presented in Appendix A. The pump-probe data set is obtained by averaging ten to twenty scans. Each scan contains tens of pump-probe delay points. Each delay point has an accumulation time of 2.5 second on the CCD camera. The overall data accumulation time for the experimental pump-probe scans is between four and five hours. Two to three repeated experiments under the same conditions are performed in order to confirm the existence of transient signals. The error bars correspond to 95 % confidence intervals and are the result of propagating the statistical uncertainties of the 10-20 scans through Eq. 2.6(b).

Chapter 3

Light-Induced XUV Transmission and Multiplet Splitting in $4d^{-1}6p$ Core-Excited Xenon

The content and figures in this chapter are adapted with permission from M.–F. Lin, Adrian Pfeiffer, Daniel M. Neumark, Stephen R. Leone and Oliver Gessner, "Strong-field induced XUV transmission and multiple splitting in 4d⁻¹6p core-excited xenon studied by femtosecond XUV transient absorption spectroscopy," Journal of Chemical Physics, 2012, **137**, 244305, Copyright 2012 The American Institute of Physics

3.1 Introduction

Optical control of the properties of matter in the extreme ultraviolet (XUV) energy regime is an active field of research. 52,56,57,108-112 In the infrared (IR), visible, and ultraviolet, light induced manipulation of the optical properties of matter has been demonstrated by a wide variety of effects, including coherent population trapping,¹¹³ Autler-Townes splittin electromagnetically-induced transparency (EIT),^{58,60,115} lasing without inversion,¹¹⁶ splitting.¹¹⁴ and "stopping" of light.¹¹⁷ All of these phenomena can be described and understood in the picture of light-coupled few-level quantum systems.^{59,60} However, there are fundamental differences between strong-field control mechanisms in the optical and the XUV regimes that arise from different lifetimes of the relevant electronic states. The XUV probe field can induce transitions into core-hole states or doubly-excited states that have lifetimes of only a few femtoseconds. As a consequence, the NIR field must be extraordinarily strong to induce coherent coupling. Femtosecond laser pulses can achieve the necessary field strengths, but the laser field becomes so strong that it couples the excited states to the ionization continuum by multiphoton ionization,¹¹² tunneling ionization,¹¹⁸ or Coulomb-barrier suppression.¹¹⁹ It is therefore important to gain a detailed understanding of strong-field induced coupling and ionization effects in highly excited states in order to be able to manipulate the optical properties of matter in the XUV in a controlled fashion.

Transient XUV absorption experiments, where the delay between the coupling pulse and the probe pulse is scanned while the transmitted spectrum of the probe pulse is recorded, are particularly well suited to study the physics that governs strong-field induced ionization and the coupling of core-excited states.^{11,61,108} In this chapter, an ultrafast XUV transient absorption measurement on Xe atoms exposed to an intense NIR laser field is performed using broadband femtosecond XUV pulses with photon energies extending from 50 eV to 72 eV. The XUV pulses are generated by high harmonic generation (HHG). The inherent broadband nature of HHG light eliminates the need to scan the probe frequency, enabling laboratory-based XUV transient absorption experiments despite the relatively modest photon fluence of HHG based light sources. The impact of the NIR laser field on the electronic structure and the XUV optical properties of Xe is traced by changes in the XUV absorption spectrum as a function of the delay between the

XUV probe pulse and the NIR coupling pulse. The measurements reveal a variety of effects such as strong-field induced XUV transmission and absorption, NIR coupling induced multiplet splitting, and core-hole alignment in strong-field ionized atoms.

Strong-field induced transmission and absorption are observed for photon energies in the vicinity of the transitions from the ${}^{1}S_{0}$ ground state to the $4d^{-1}({}^{2}D_{5/2})6p({}^{2}P_{3/2})$ and $4d^{-1}({}^{2}D_{3/2})6p({}^{2}P_{1/2})$ core-excited states of atomic Xe at 65.1 eV and 67.0 eV, respectively. The most prominent features can be described by the near-resonant coupling of the $4d^{-1}6p$ states to nearby $4d^{-1}6s$ and $4d^{-1}6d$ states (Autler-Townes doublet).^{50,57} Near the peak of the NIR field, additional absorption features are observed in the spectral region between 60 eV and 65 eV. These features can principally be modeled by either near-resonant or off-resonant coupling to neighboring Rydberg states at sufficiently high coupling field intensities such that the Rabi frequencies of the coupling transitions exceed the NIR frequency.⁵³ Under these conditions, the field-free absorption lines split into multiple branches, spanning a range between 62 eV and 65 eV at the low energy side of the field-free resonances. As a specific showcase example for this effect, theoretical evidence for multiple branches in near-resonant Autler-Townes splitting is presented by numerical integration of the von Neumann equation. The results indicate that the light-induced absorption between 60 eV and 63 eV may be due to a breakdown of the rotating wave approximation (RWA).⁵³

Furthermore, the alignment of the $5p^{-1}$ valence hole of Xe⁺ ions created by strong-field ionization is revisited. Femtosecond transient XUV absorption spectroscopy has previously been used as a powerful tool to probe the electronic alignment of cationic states of atoms created by strong-field ionization.^{11,61,120} In this chapter, the measured degree of hole-alignment for the transitions at 55.4 eV and 57.3 eV is in reasonable agreement with previous experiments and, in particular, confirms a lower degree of alignment than predicted by theory.^{61,121}

3.2 Experimental method

The XUV transient absorption spectroscopy setup is shown in Fig. 3.2.1. It is similar to that in Fig. 2.1 in Chapter 2. The laser is a commercial high power femtosecond laser system that provides pulses with a center wavelength of 775 nm. For the transient absorption experiments in this study, the grating compressor of the laser system is adjusted to chirp the laser pulse. This detuning leads to a broadening of discrete harmonics in order to generate a quasi-continuous HHG spectrum⁹⁸ with photon energies that span a wide range of the





Apparatus for transient XUV absorption experiments. Red and blue colors represent the NIR and XUV beams, respectively. An 200 nm thick aluminum filter is placed between the target and grating chambers to reduce the NIR scattering light. BS: beam splitter, HHG: high harmonic generation cell, TM: toroidal mirror, HWP: half wave plate, RM: recombination mirror, and MCP: microchannel plates.

Xe $4d^{-1}$ inner-shell absorption spectrum. It also results in a temporal broadening of the coupling pulse to 100 ± 10 fs (FWHM).

A 50/50 beam splitter is used to split the original NIR pulse into a "pump" pulse for strong-field coupling and ionization and the driver pulse for HHG, which produces the XUV "probe" pulse. HHG is performed in a 25 mm long gas cell filled with neon gas at a pressure of 3.33 kPa, tuned for optimal phase matching.¹²² The 1.3 mJ HHG driving pulses are focused to a 90 μ m (1/e²) spot size with an f/30 lens. A 300 nm thick aluminum foil is used to remove the residual NIR light from the XUV pulse. A toroidal mirror is used to focus the transmitted XUV light into the interaction region inside a 3 mm long target cell filled with xenon gas at a pressure of 2.53 kPa. The beam diameter (1/e²) of the XUV light in the interaction region is 100 ± 10 μ m. After passing through the absorption cell, the XUV light is dispersed by a constant line spacing spherical grating (1200 lines/mm) and detected by a chevron-mounted pair of microchannel plates (MCPs) coupled to a phosphor screen. The resulting two-dimensional image is read out by a CCD camera and then transferred to a computer for analysis. The XUV flux at the entrance of the absorption cell is ~10⁵ photons per pulse in the spectral region between 50 eV and 72 eV.



Fig. 3.2.2

Absorption peaks due to transitions to different core-excited states of neutral xenon. The vertical bars correspond to the experimental data with error bars. The solid black line represents the simulated absorption profile using a natural linewidth of 0.11 eV (Refs. 123, 124, 126) convoluted with an instrumental energy resolution of 0.37 eV. The broad thin line represents a nonresonant background due to ionization. Its contribution to the spectrum in (a) is estimated by a broad Gaussian peak that is centered at the maximum of the Xe^+ (4 d^{-1}) giant resonance and for which the ratio of OD's at 64.4 eV and 67.8 eV is the same as the ratio between the ionization cross sections at these energies. (b) Emergence of xenon ions monitored by the transient absorption signal at 55.4 eV corresponding to the $5p^{-1}({}^{2}P_{3/2})$ $\rightarrow 4d^{-1}(^{2}D_{5/2})$ transition in Xe⁺. The solid line is the result of a fit to an error function, giving a rise time of 70 ± 10 fs (FWHM).

The NIR pump pulse is focused into the target cell by an f/40 lens. The pump and probe pulses are combined by an annular mirror that is placed in front of the target cell. The XUV probe beam passes through the center hole of the mirror, while the NIR pump beam is reflected by the mirror to achieve pump-probe overlap in the interaction volume. The angle between the pump and probe beams is approximately 1.3°. The measured beam diameter $(1/e^2)$ of the focused NIR beam at the target cell position is 150 ± 10 um. This results in a peak intensity of the NIR pump beam on the order of 10^{14} W/cm². The estimated NIR peak intensities are 0.5×10^{14} W/cm^2 for the induced XUV transmission/absorption measurements and 1 \times 10^{14} W/cm^2 for valence hole-alignment measurements.

The experimental energy resolution is derived by modeling the static field-free XUV absorption spectrum of xenon atoms through a convolution of the literature spectrum¹²³⁻¹²⁵ with Gaussian functions. The peaks in Fig. 3.2.2 (a) correspond to inner-shell excitations from the ${}^{1}S_{0}$ ground state to the $4d^{-1}({}^{2}D_{5/2})6p({}^{2}P_{3/2})$, $4d^{-1}$

 ${}^{1}({}^{2}D_{5/2})7p({}^{2}P_{3/2})$, and $4d^{-1}({}^{2}D_{3/2})6p({}^{2}P_{1/2})$ core-excited states at energies of 65.1 eV, 66.3 eV, and 67.0 eV, respectively. 123,124,126,127 The experimental data are shown as vertical lines that represent the error bars. The solid line represents the convolution model described above, corresponding to an instrumental energy resolution of 0.37 eV.

An upper bound of 70 fs for the duration of the chirped XUV pulse is derived from the rise time of the strong-field ionization signal. Fig. 3.3.2 (b) shows the pump-probe time-delay dependent change in the XUV absorbance at 55.4 eV, corresponding to the emergence of the $(5p_{3/2}^{-1})^2 P_{3/2} \rightarrow (4d_{5/2}^{-1})^2 D_{5/2}$ transition in xenon ions that are created by strong-field ionization.¹²⁸ Here, nlj^{-1} represents a valence hole in the nl orbital with total angular momentum j. Fitting the absorption trace with an error function leads to a rise time of 70 ± 10 fs.

The transient spectra shown in Secs. 3.3 and 3.4 are obtained by using spectra collected at -280 fs delay time as a reference.¹²⁹ Zero delay between pump and probe pulses is defined by the maximum induced transmission of the neutral xenon signal at 67.0 eV. A positive time delay corresponds to a pulse sequence where the NIR pump pulse arrives at the sample before the XUV probe beam. A zero-order half-wave plate is placed into the path of the pump beam to vary the relative polarization of pump and probe beams in the ion alignment experiments. The experimentally confirmed polarization purity of the NIR beam is $\geq 100:1$. The uncertainty of the relative angle between the pump and probe beam polarizations in the interaction volume is $\pm 2^{\circ}$. It is determined by using a combination of a polarizer and a half-wave plate independently for both the NIR pump beam and the NIR driver of the XUV probe beam at the location of the interaction volume. The NIR driver and XUV probe beam polarizations are parallel by virtue of the HHG process in an isotropic medium.¹³⁰ The error bars in all figures denote 95% confidence intervals unless otherwise noted.

3.3 Laser induced transmission and absorption

Fig. 3.3.1 (a) shows the static absorption spectrum of neutral xenon from a synchrotronbased study. The peaks at 65.1 eV and 67.0 eV (marked with asterisks) correspond to transitions from the ${}^{1}S_{0}$ ground state to the $4d^{-1}({}^{2}D_{5/2} 6p({}^{2}P_{3/2})$ and $4d^{-1}({}^{2}D_{3/2})6p({}^{2}P_{1/2})$ core-excited states, respectively, that decay to form Xe⁺ and Xe⁺⁺ ions.¹²⁶ Fig. 3.3.1 (b) displays the NIR induced time- and energy-resolved change in the XUV optical density of the gas cell (Δ OD). The quantity Δ OD is defined in Eq. 3.3 as the difference in optical density with and without laser dressing. The latter condition is represented by data recorded at a large negative delay tref = -280 fs in order to account for a small constant background from scattered NIR light.¹²⁹ This background signal could not be completely eliminated in the experiment. A detailed description is presented in Sec. 2.5 in Chapter 2. The background is taken into account in the analysis by using the spectrum that is recorded when the XUV pulse precedes the NIR pulse by 280 fs as a reference for the sum of the time-independent NIR background and the XUV spectrum without laser dressing. Modification of the NIR background by XUV absorption can be neglected since the number of core-excited Xe atoms (<10⁵) is ten orders of magnitude lower than the number of NIR photons (~10¹⁵/pulse).

$$\Delta OD(t) = \log\left[\frac{I(t_{ref})}{I(t)}\right] = \log\left[\frac{I_0}{I(t)}\right] - \log\left[\frac{I_0}{I(t_{ref})}\right] = OD(t) - OD(t_{ref})$$
(3.3)

Here, I₀ represents the transmitted XUV intensity without Xe gas and the dressing NIR field. I(t) and I(t_{ref}) denote the transmitted XUV intensity with Xe gas in the target cell at pump-probe delays of t and t_{ref} = -280 fs, respectively. Note that at t_{ref} = -280 fs, the XUV and NIR pulses have no temporal overlap. For a thin target, Δ OD is linearly proportional to the product of the number density of transient species and their absorption cross-section. Fig. 3.3.1 (c) shows the photoionization yield spectrum of Xe⁺ ions.¹²⁸ The absorption peaks at 55.4 eV, 56.2 eV, and 57.3 eV correspond to the 4*d* inner-shell to 5*p* valence hole excitations $5p_{3/2}^{-1}(^{2}P_{3/2}) \rightarrow 4d_{5/2}^{-1}(^{2}D_{5/2})$, $5p_{1/2}^{-1}(^{2}P_{1/2}) \rightarrow 4d_{3/2}^{-1}(^{2}D_{3/2})$, and $5p_{3/2}^{-1}(^{2}P_{3/2}) \rightarrow 4d_{3/2}^{-1}(^{2}D_{3/2})$. The absorption peak at 71 eV has previously been assigned to a $4d \rightarrow 4f$ transition in Xe⁺.^{128,131}



Fig. 3.3.1

(a) Static absorption spectrum of neutral Xe atoms from a previous study,¹²⁵ containing two different spin-orbit series of $4d^{-1} \rightarrow np$ inner shell excitations.^{123,124,126} (b) Transient XUV absorption spectra of neutral and ionized xenon atoms. The time- and energy-resolved change in the XUV optical density (Δ OD) reveals that the NIR pump pulse simultaneously induces both enhanced absorption (Δ OD > 0) and enhanced transmission (Δ OD < 0) in the vicinity of 65.1 eV and 67.0 eV. (c) Static photoionization yield spectrum of Xe⁺ ions in the range of $4d^{-1} \rightarrow 5p, 4f$ inner-shell excitations.¹²⁸

Pump-Probe Delay Time [fs] The transient absorption data in Fig. 3.3.1 (b) reveal that the NIR pump pulse simultaneously induces both enhanced absorption ($\Delta OD > 0$) and enhanced transmission ($\Delta OD < 0$) in the vicinity of the neutral xenon XUV absorption resonances. The split features at 65.1 eV to 67.0 eV extend significantly toward negative (XUV first) pump-probe time delays. The strong-field induced absorption features associated with transitions involving 6p excitations obscure minor features from absorption to the 7p state at 66.3 eV. The extended absorption feature between 60 eV and 65 eV does not have a direct correspondence to features in the static absorption spectra. Its origin will be discussed in Sec. 3.4. The narrow enhanced transmission features at 56.4 eV, 59.6 eV, 62.8 eV, 69 eV, and 72 eV are artifacts due to small denominator values in Eq. 3.3. These are caused by small high harmonic intensities in the minima of the HH spectrum, which exhibit the same energy spacing as the HH maxima (3.2 eV).

Fig. 3.3.1 (b) also shows the emergence of xenon ions for positive pump-probe delays as a consequence of strong-field ionization by the NIR pump pulse. Note that strong-field ionization is a nonlinear process, which leads to a delayed onset of the ion signals below 58 eV compared to the signals from the neutral excited states above 60 eV. The deep blue area spanning 67 eV to 72 eV for positive delays is due to depletion (Δ OD<0) of neutral xenon atoms by strong-field ionization. The emergence of the Xe⁺ ion signal at 71 eV exhibits a 70 fs delay relative to the ion signals at other energies. The generated ions include singly and doubly charged states as can be

seen in Fig. 3.3.2 (a). All spectra in Fig. 3.3.2 are generated by averaging the transient absorption data over a delay range of 25 fs to 250 fs. The ion signals between 55 eV and 58 eV reach their asymptotic values at a delay of 25 fs. Three spin-orbit transitions involving the promotion of an electron from a 4*d* orbital to a 5*p* hole of Xe⁺ can be seen at 55.4 eV, 56.2 eV and 57.3 eV. Minor contributions from transitions in Xe²⁺ ions are also shown. Fig. 3.3.2 (b) shows the same spectral features as Fig. 3.3.2 (a) recorded for parallel (red) and perpendicular (black) alignment of the NIR and XUV polarizations at a nominal NIR power density of 10^{14} W/cm². The transition intensities at 55.4 eV and 57.3 eV exhibit a strong polarization dependence with opposite signs as illustrated by the difference plot in Fig. 3.3.2 (c). No polarization dependence is observed for the transition at 56.2 eV, as expected for a J=1/2 state.⁶¹



Fig. 3.3.2

 Xe^+ ion absorption spectra for different relative polarizations of the NIR and XUV pulses. The spectra are averaged over pump-probe delays between 25 fs and 250 fs. (The ion signals in this energy range are constant for delays beyond 25 fs.) (a) Perpendicular polarization of XUV and NIR laser field. The underlying spectra contain contributions from singly and doubly charged xenon ions. Black vertical bars represent the experimental data with error bars. The dashed red line is the sum of all individually fitted ionic species shown as black solid lines. (b) Polarization dependence of xenon ion absorption spectra. Red dashed and black dashed lines are measured with parallel and perpendicular polarizations of the XUV and NIR fields, respectively. (c) Difference of spectra in (b). Note the opposite signs at 55.4 eV and 57.3 eV.

Fig. 3.3.3

Laser-induced transmission of neutral xenon at 65.1eV and 67.0eV after correcting for the depletion in the pump-probe interaction volume due to strong-field ionization of neutral molecules. (a) $4d^{-1}({}^{2}D_{5/2})6p({}^{2}P_{3/2})$ core-excited state at 65.1 eV. (b) $4d^{-1}({}^{2}D_{3/2})6p({}^{2}P_{1/2})$ core-excited state at 67.0 eV. The transmission far from time zero is described by the optical density of xenon atoms in a field-free environment. While approaching the maximum of the NIR envelope, the transmission increases gradually by a factor of three.

Pump-Probe Delay Time [15] The strong NIR field manipulates the electronic properties of the Xe atoms, which results in a change of XUV transmission at 65.1 eV $(4d^{-1}(^{2}D_{5/2})6p(^{2}P_{3/2}))$ and at 67.0 eV $(4d^{-1}(^{2}D_{3/2})6p(^{2}P_{1/2}))$ through field-induced coupling among core-excited states. The field-strength dependent effect of the NIR pump pulse on the core-excited states is obtained by monitoring the change of transmission at the field-free resonance energies. The time-dependent transmission curves, after correcting for neutral xenon depletion by strong-field ionization,¹³² are shown in Fig. 3.3.3. Long before time zero, the constant transmission is determined by the field-free neutral xenon absorbance as shown in Fig. 3.2.2 (a). The transmittance at 67.0 eV returns to its field-free value at long time delays, while at 65.1 eV it is slightly lower due to a residual effect of the NIR at the longest time delays as can be seen in Fig. 3.3.1 (b). The NIR laser field changes the transmission at 65.1 eV and 67.0 eV from $3.2 \pm 0.4\%$ and $5.9 \pm 0.5\%$ (field-free) to $9 \pm 2\%$ and $22 \pm 5\%$, respectively, i.e., by approximately a factor of 3 to 4. The induced transmission curve in Fig. 3.3.3 (b) is 100 ± 10 fs, which is longer than the xenon ion rise time of 70 ± 10 fs derived from the traces in Fig. 3.2.2. This effect is probably due to the nonlinear character of strong-field ionization and ionization saturation in the leading edge of the NIR pulse.

3.4 Simulation of light-induced structures

The induced transmission and absorption in the vicinity of the neutral xenon XUV absorption resonances are modeled in the framework of a few-level quantum system. The basis for the simulations is described in Refs. 51 and 53. In principle, both near-resonant coupling as well as off-resonant coupling to nearby core-excited states may contribute to the observed effects. Here, we discuss the specific example of near-resonant (Autler-Townes) coupling of the $4d^{-1}(^{2}D_{5/2})6p(^{2}P_{3/2})$ and $4d^{-1}(^{2}D_{3/2})6p(^{2}P_{1/2})$ states to the $4d^{-1}(^{2}D_{5/2})6s(^{2}S_{1/2})$, $4d^{-1}(^{2}D_{3/2})6s(^{2}S_{1/2})$, $4d^{-1}(^{2}D_{5/2})6d(^{2}D_{5/2})$, and $4d^{-1}(^{2}D_{3/2})6d(^{2}D_{3/2})$ states by the intense NIR field (Fig. 3.4.1).



Fig. 3.4.1

Reduced level scheme for strong-field coupling. The left side of the figure shows the levels that are most important for the coupling of the $4d^{-1}(^{2}D_{5/2})6p(^{2}P_{3/2})$ core-excited states. On the right, the coupling levels for the $4d^{-1}(^{2}D_{3/2})6p(^{2}P_{1/2})$ core-hole state are shown. The vertical widths of the horizontal black and red bars represent the natural and effective linewidths, respectively. The numbers on the levels represent excitation energies in eV.

This coupling scheme is expected to contribute significantly to the light-induced effects described above due to relatively large oscillator strengths and the near resonant character of the NIR transitions. However, contributions from other transitions involving, for example, 7s states cannot be excluded. The following Hamiltonian is introduced to describe the strong-field induced coupling in the dipole approximation.⁵³

$$\mathbf{H} = \mathbf{H}_0 + \mathbf{D}\mathbf{F} \tag{3.4.1}$$

where \mathbf{H}_0 is the Hamiltonian of the unperturbed system, **D** is the dipole transition matrix, and F is the electric field of the laser pulse. The parameters of the electric field are matched to the

experimental conditions: the infrared pulse has a center wavelength of 775 nm and a transform limited pulse duration of 25 fs. The intentionally imposed linear chirp of the NIR pulse is included in the model, leading to an effective pulse duration of 100 fs. The peak intensity is 0.5×10^{14} W/cm². The XUV field is modeled by a pulse train consisting of 15 pulses, each with a duration of 0.1 fs and a center energy of 61 eV. The spatial intensity profile of the coupling laser is not included in the calculation.

Two cases are considered in the simulations in order to address the broad induced absorption feature in Fig. 3.3.1 (b) that extends from 60 eV to 65 eV. First, as previously shown, the RWA is applied, such that F is replaced by the complex field values for the off-diagonal entries of **H** and the rapidly oscillating terms are neglected.⁵³ Second, no approximation is made with respect to the electric field. The absorbance is calculated from the density matrix assuming a thin gas target. The absorbance is predicted to show multiple lines for high field strengths,⁵³ a phenomenon that can only be described without the RWA.

The simulation from Ref. 53 is generalized to include lifetime effects. The time evolution of the density matrix of the states is calculated by a numerical integration of the von Neumann equation with the inclusion of phenomenological decay rates as shown in Eq. 3.4.2.

$$i\dot{\rho} = [\mathbf{H}, \rho] + i\boldsymbol{\Gamma} \tag{3.4.2}$$

Here, ρ is the density matrix and Γ is a matrix that contains the decay rates of the states. The decay matrix Γ accounts for the natural lifetime of the core-hole states and for strong-field ionization of the ground state. The inclusion of ionization broadening in the decay matrix of the core-excited states is discussed in the next section.

Fig. 3.4.2 shows a comparison of the experimental Δ OD (black curve) with the simulations, convoluted with the experimental energy resolution of 0.37 eV, at a pump-probe delay of 0 fs. In Fig. 3.4.2 (a), the blue and red curves correspond to the simulations with and without the RWA, respectively. In both simulations, the $4d \rightarrow 6p$ transitions at 65.1 eV and 67.0 eV are split due to coupling to nearby $4d^{-1}6s$ and $4d^{-1}6d$ states. A significant difference between the simulations with (blue) and without (red) applications of the RWA in Fig. 3.4.2 (a) is found in the spectral region between 60 eV and 65 eV. The simulation that makes use of the RWA exhibits a sharp cutoff at 63 eV, whereas the absorption features in the simulation without the RWA extend down to 60 eV. A qualitative interpretation for this observation can be given if the model is restricted to a three-level system. If only one XUV transition and one NIR coupling transition are considered, the field-free XUV absorption line is split into a doublet for moderate intensities, which is characteristic for Autler-Townes splitting in the visible regime. At higher intensities, for which the Rabi frequency exceeds the frequency of the coupling laser field, the NIR coupling induces a multiplet splitting that is not captured within the RWA.⁵³ For the coreexcited states with the strongest coupling, $(4d^{-1}(^{2}D_{5/2})6p(^{2}P_{3/2}))$ and $4d^{-1}(^{2}D_{5/2})6s(^{2}S_{1/2}))$, this condition is fulfilled for NIR intensities beyond 0.16×10^{14} W/cm².

In Fig. 3.4.2, the splitting due to coupling to the $4d^{-1}6s$ and $4d^{-1}6d$ states is so large that it exceeds the energy gap between the two $4d^{-1}6p$ states. Hence, the split peaks overlap and cannot be assigned to a specific XUV transition. The exact shape of the experimental Δ OD curve is not reproduced by the simulation. This finding is not surprising, because the simulation is based on a highly simplified level scheme in Fig. 3.4.2 where many electronic states are neglected. Additionally, the NIR intensity distribution across the interaction volume is neglected.

Due to the several contributing levels, the Δ OD curve does not exhibit clear side branches, but rather a variety of absorption features appear in the spectral region from 60 eV to 65 eV. This structure is qualitatively reproduced in the simulation without the RWA, whereas it is missed entirely if the RWA is made. The observation of side branches is not restricted to the lower energy side of the XUV absorption energy, but can also occur to the higher photon energy side.⁵³ However, experimental observation in the higher photon energy regime is hindered here by the contribution of higher lying Rydberg levels and the continuum (see Fig. 3.3.1 (a)).

We also performed calculations based on coupling of the field-free core-excited states to far off-resonance states with, for example, $4d^{-1}7s$ electronic configurations. Discrete structures



Fig. 3.4.2

Comparison of the experimental change in optical density $\triangle OD$ with simulations at a pump-probe delay of 0 fs. In (a) and (b), the top figures represent the field-free neutral xenon absorption spectrum from Ref. 125. In the bottom of (a) and (b), the black solid curve shows the experimental result where the statistical error is indicated by the grey area (2σ) . (a) The simulations with and without the RWA are shown as blue and red curves, respectively, without the inclusion of ionization broadening. (b) The green and red curves show the simulation with and without ionization broadening, both without the assumption of the RWA. The simulated curves are convoluted with the experimental energy resolution of 0.37 eV.

from off-resonant coupling have recently been observed in a combined experimental and theoretical study of atomic helium.⁵¹ Qualitatively, the spectral features in all simulations are similar but differ in the magnitude of the energy splitting and the intensities of the lightinduced structures. A common phenomenon, however, is that absorption features below 62 eV only emerge from calculations that go beyond the RWA, indicating observed absorption that the features in this energy range may indicate a breakdown of this frequently applied approximation.

Under the influence of the strong NIR field, the dressed coreexcited states are expected to have a shorter lifetime and thus a broader resonant linewidth.⁵⁴ In the absence of theoretical values, this broadening is estimated by the contribution of strong-field ionization of the core-excited states.

The estimate of the effective linewidth is based on a theoretical study of neon atoms,^{50,57} where the effective lifetime of the core-excited states $1s^{-1}3s$ $(1s^{-1}3p)$ at a field intensity of 10^{13} W/cm² is 0.54 eV (0.68 eV), and the field-free core-hole linewidth is 0.27 eV (2.4 fs) in both cases. The contribution of the laser ionization process in neon is estimated to be 0.54 (0.68) eV – 0.27 eV = 0.27 eV (0.41 eV) for the $1s^{-1}3s$ $(1s^{-1}3p)$ core-excited states, respectively. The ionization potential (IP) of the $1s^{-1}3s$ $(1s^{-1}3p)$ core-hole state is 4.54 eV (2.85 eV). These IP's are similar to the IP's of the core-excited states of xenon. Therefore, we adapt the values from neon to address the ionization broadening of the core-excited states in xenon. For lower field strengths, the contribution of the laser ionization process is calculated from ADK tunneling ionization rates.¹¹⁸ For higher field strengths, where the ADK rates exceed the ionization broadening of xenon atoms. This approach is similar to the one applied in the work by Loh et al.¹⁰⁸

In Fig. 3.4.2 (b), the results of the non-RWA simulations with (green) and without (red) additional broadening due to the laser ionization of the core-hole states are shown. It can be seen that the impact of the additional broadening mechanism on the extended absorption features in the energy region from 60 eV to 65 eV is relatively small. Studies including more levels will be valuable to determine if better agreement could be achieved.

3.5 Hole-alignment of xenon ions generated by a strong laser field

We briefly revisit the hole-alignment in xenon ions generated by strong-field ionization.⁶¹ Note that only ionization from the electronic ground state has to be taken into account because the number of XUV photons is very small and therefore very few ions are produced by the XUV excitation of 6p states and subsequent ionization by the NIR light. Mechanisms leading to multiply charged ions are also neglected because their yield is very low in this experiment.

By definition, the $5p^{-1}_{1/2}({}^{2}P_{1/2})$ ionic state cannot exhibit any orbital alignment since it has only two magnetic sublevels $m_{J} = \pm 1/2$.¹³³ However, for the case of J = 3/2, theory predicts a greater population in the $m_{J} = \pm 1/2$ sublevels than in the $m_{J} = \pm 3/2$ sublevels of the $5p^{-1}_{3/2}({}^{2}P_{3/2})$ hole state.^{61,11,120,121} In order to compare the theoretical predictions with the experiment, the parameters shown in Eqs. 3.5 (a) through 3.5 (e) are derived from standard angular momentum algebra.

$$R = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}} \tag{3.5 a}$$

$$R_{1} = \frac{1}{10} \frac{\rho_{3/2,|\pm 1/2|} - \rho_{3/2,|\pm 3/2|}}{\rho_{3/2,|\pm 1/2|} + \rho_{3/2,|\pm 3/2|}}$$
(3.5 b)

$$R_2 = 0$$
 (3.5 c)

$$R_3 = \frac{2}{5} \frac{\rho_{3/2,|\pm 3/2|} - \rho_{3/2,|\pm 1/2|}}{\rho_{3/2,|\pm 3/2|} + \rho_{3/2,|\pm 1/2|}} \tag{3.5 d}$$

$$r = \frac{I_{3/2 \to 5/2}}{I_{1/2 \to 3/2}} = 1.6 \frac{3\rho_{3/2,|\pm 1/2|} + 2\rho_{3/2,|\pm 3/2|}}{5\rho_{1/2,|\pm 1/2|}}$$
(3.5 e)

Equation 3.5 (a) denotes the absorption anisotropy for the two different polarization schemes (parallel and perpendicular) obtained from the experimental results. In Eqs. 3.5 (b) to 3.5 (d), R₁, R₂, and R₃ represent the polarization anisotropies for transitions at 55.4 eV, 56.2 eV, and 57.3 eV, respectively. The r value in Eq. 3.5 (e) denotes the ratio of the transition strengths at 55.4 eV and 56.2 eV.⁶¹ $\rho_{J,|\pm mJ|}$ is the probability of finding the xenon ion in a 5p_{J,mJ} or 5p_{J,-mJ} hole state.⁶¹ Note that according to the theory of tunneling ionization with the inclusion of spin-orbit coupling, $\rho_{3/2,|\pm 1/2|}$ is larger than $\rho_{3/2,|\pm 3/2|}$. The values for R₁, R₃, and r obtained from the data shown in Fig. 3.3.2 are 0.04 ± 0.02, -0.24 ± 0.08, and 5.5 ± 0.6, respectively. The quantum state distributions for the resonances at 55.4 eV and 57.3 eV are shown in Table 3.5 along with the experimental results of Loh et al. at 55.4 eV and a theoretical calculation.⁶¹

The quantum state distribution derived from R_1 and R_3 in this work is similar to the one measured by Loh et al. with $R_1 = 0.07 \pm 0.01$. Both experiments yield a lower degree of alignment than predicted by theory with the inclusion of spin-orbit interaction.^{61,11} The discrepancy between theory and experimental results cannot be explained by the finite degree of linear polarization in the experiment ($\geq 100:1$) or the small uncertainty ($\pm 2^\circ$) in the relative angle between the pump and probe beam polarizations. A 2° mismatch between the polarization axes would lead to a lowering of the intensity ratio R_1 from the predicted value $R_1 = 0.0930$ to a measured value $R_1 = 0.0928$. The relative angle between the polarization axes would have to be off by 32°, i.e., more than an order of magnitude beyond the experimental uncertainty, to explain the difference between the predicted value of R_1 and the measured value $R_1 = 0.04$.

Loss of alignment through electron-ion collisions seems unlikely. Taking the value of electron-ion collision induced spin-orbit state transitions for similar quantum states in krypton ions,¹³⁴ the estimated dealignment time constant for Xe ions would be on the order of 15 ps at 2.53 kPa of xenon in the gas cell. Therefore, dealignment from electron-ion collisions within 300 fs is negligible. Other possible mechanisms for the loss of electronic alignment include a breakdown of the adiabatic approximation,^{61,120} multielectron effects,^{63,67} and re-collision of tunnel-ionized electrons with the parent ion core.^{135,136} Theoretical studies that go beyond the adiabatic approximation do not explain the lower degree of alignment.^{41,45} Thus, multielectron effects during the ionization and/or strong-field induced electron-ion recollision may be responsible for the lowering of the hole-alignment of atomic xenon under strong-field ionization

as observed in the experiments.

TABLE 3.5. Hole-alignment in xenon ions. Comparison of quantum state distributions retrieved from the measured polarization anisotropies at 55.4 eV and 57.3 eV, results from Loh. et al. at 55.4 eV and the theoretical calculation in Ref. 61. The error bars in this work are the statistical errors of 95% confidence intervals after propagating through Eq. 3.5.

Quantum States	This work (55.4 eV/57.3 eV)	Loh et al. (55.4 eV)	Theoretical Calculation
$r_{3/2, \pm 3/2 }$	$26/17 \pm 9$	13 ± 6	3
$r_{3/2, \pm 1/2 }$	$60/69 \pm 9$	75 ± 6	83
$r_{1/2, \pm 1/2 }$	$14/14 \pm 2$	12 ± 3	14

3.6 Conclusion

Femtosecond XUV transient absorption spectroscopy is employed to monitor the impact of an intense NIR pulse on core-level transitions in xenon. Coupling of core-excited states by a strong NIR field induces both enhanced absorption and enhanced transmission around photon energies of 65.1 eV and 67.0 eV, corresponding to transitions from the ground state to $4d^{-1}$ $(^{2}D_{5/2})6p(^{2}P_{3/2})$ and $4d^{-1}(^{2}D_{3/2})6p(^{2}P_{1/2})$ core-hole states, respectively. The threefold enhancement of XUV transmission by the NIR field leads to an ultrashort enhancement of the transmitted XUV light, effectively creating a "femtosecond XUV light switch." This ability to control XUV pulses in the time domain may enable new possibilities for ultrafast pump-probe experiments at synchrotrons.^{50,52,56,57}

The observations are described in the picture of NIR-induced coupling between coreexcited states within few-level quantum systems. Extended transient absorption features between 60 eV and 65 eV are interpreted as multiple absorption branches that emerge when the Rabi frequencies of the NIR coupling transitions exceed the NIR laser frequency. In particular, the example of Autler-Townes multiplet splitting due to near-resonant coupling of the $4d^{-1}6p$ coreexcited states to $4d^{-1}6s$ and $4d^{-1}6d$ states is discussed in detail based on a numerical solution of the von Neumann equation. The results indicate that the rotating wave approximation for the description of the light-induced coupling breaks down for NIR peak intensities of $\sim 5 \cdot 10^{13}$ W/cm².

The strong NIR field also generates Xe^+ ions in different fine-structure states, and the polarization anisotropy of the corresponding core level transitions is determined. The transition at 57.3 eV reveals an opposite polarization anisotropy, as expected, compared to the transition at 55.4 eV. The extracted quantum state distributions from the transitions at 55.4 eV and 57.3 eV both reveal a similar core-hole alignment as determined in previous measurements and a lower degree of alignment than predicted by theory.^{62,67}

Chapter 4 Ionization and dissociation Dynamics of Vinyl Bromide Probed by XUV Transient Absorption Spectroscopy

4.1 Introduction

Static XUV and X-ray absorption spectroscopy has been widely applied to studies of polyatomic molecules in gas, liquid and surface environments.^{16,17,137-139} Core-to-valence transitions can be used to selectively probe the chemical composition, oxidation states, valence orbital symmetries, and alignment of molecules. With the development of time-resolved methods utilizing XUV and X-ray light sources,^{18-25,29,42,48,122,129,140-143} investigations using core-to-valence transitions can be extended to the time domain. Ultrafast dynamics in the vicinity of specific chemical elements and reaction centers in transient species can now be monitored in real-time.^{18,19,21,22,24,26,27} Ultrafast electronic motion and structural relaxation can be explored with atomic site specificity.^{11,144-147} Recently, table-top high harmonic sources with attosecond and femtosecond time resolution have been used to investigate ultrafast physics and chemistry of helium, neon, argon, krypton, xenon, CH₂Br₂ and Br₂.^{11,61,104,108,148-157} These high-harmonic light sources enable novel research in which one probes ultrafast electronic wavepackets, vibrational wavepackets and dissociative ionization of polyatomic molecules prepared by coherent strong-field laser ionization.

Strong-field ionization (SFI) of polyatomic molecules accesses multiple electronic continua corresponding to different ionized molecular valence orbitals,^{63,158,159} i.e. the ionization process simultaneously generates ions in several electronic states, some of which can dissociate. However, the relation between the molecular fragments and the parent ionic states is rarely explored in SFI. In addition, the multielectron response in a nonresonant strong-field leads to complex ionization mechanisms. For example, nonadiabatic multielectron (NME) excitation^{63,159,160} can generate ions preferentially in electronically excited states and can greatly affect the molecular dissociation pathways.^{160,161} SFI-induced relaxation and dissociation dynamics in polyatomic molecules are often difficult to trace in experiments that detect only the asymptotic dissociation products with techniques such as time-of-flight (TOF) mass spectrometry.

Here, femtosecond time-resolved XUV (50 eV to 72 eV) transient absorption measurements are performed on vinyl bromide molecules (CH₂=CHBr) that are ionized by an intense NIR laser field (10^{13} to 10^{14} W/cm², λ =775 nm). The strong NIR field ionizes electrons from both the highest and the second highest occupied molecular orbitals (HOMO and HOMO-1), producing the ionic \tilde{X} and \tilde{A} states, respectively. The valence hole configurations are probed

by XUV light that promotes electrons from the Br (3*d*) inner-shell to partly filled valence orbitals at transition energies between 64 eV and 69 eV, the $M_{4/5}$ edge. The transient XUV absorption spectrum direct monitors and distinguishes among parent ions with HOMO and HOMO-1 valence holes, atomic Br fragments, and doubly charged ions, all of which generated by the NIR pulse.

We analyze the formation and dissociation dynamics of strong-field induced vinyl bromide ions ($C_2H_3Br^+$) from the two ionic states (\tilde{X} and \tilde{A}). Formation of the $C_2H_3Br^{++}$ dications is also observed. An ultrafast transient XUV absorption energy shift in the singly charged ionic \tilde{A} state is observed, suggesting a possible correlation with the C-Br bond dissociation that produces free atomic Br (${}^2P_{3/2}$). In contrast, ions in the ionic \tilde{X} ground state and doubly charged ions ($C_2H_3Br^{++}$) appear to be stable and do not dissociate into fragment ions. Electronic structure calculations are performed to elucidate the stability of doubly charged ions. The results offer new insights into the temporal evolution of parent ions in different ionic states and their correlation to emerging molecular fragments.

4.2 Experimental and theoretical methods

A schematic of the tabletop XUV transient absorption setup is shown in Fig. 2.1. A detailed description of the experiment is provided in Chapter 2. Briefly, a high power NIR femtosecond laser system provides pulses with a center wavelength of 775 nm. A 50/50 beam splitter is used to divide the initial NIR energy into a "pump beam" for NIR strong-field ionization and a "probe beam" for high harmonic generation (HHG). Both beams are combined in the 10 mm long absorption cell that is filled with 0.27 kPa of vinyl bromide. The measured XUV and NIR beam diameters ($1/e^2$) at the focus (i.e. target cell position) are $100\pm10 \mu m$ and $150\pm10 \mu m$, respectively. In the pump-probe experiment, a positive time delay indicates that the NIR pump pulse arrives before the XUV probe pulse at the sample. All experiments are performed with parallel pump and probe beam polarizations.

The peak intensity of the NIR pump beam for strong-field ionization ranges from 140 TW/cm² to 290 TW/cm². The laser peak intensities used in this study correspond to a Keldysh parameter γ <1, indicating that ionization proceeds in the tunneling regime.¹⁶² Note that the intensity profile of the NIR beam and the longitudinal extent of the focal volume result in a broad distribution of power densities; the peak values are quoted. The XUV probe beam is generated in a 25 mm long gas cell filled with neon gas at a pressure of 3.3 kPa.¹²² The generated XUV light with energies between 50 eV and 72 eV has an overall flux of ~10⁵ photons per pulse at the sample cell. The energy calibration of the spectrometer is performed using the characteristic XUV absorption lines of laser-produced Xe⁺ ions at transition energies of 55.4 eV and 71 eV.^{123,128,131} A combination of a half-wave plate and a thin film polarizer is used to vary the power of the NIR pump beam.

All transient absorption spectra (delta optical density Δ OD) presented here are obtained by using a transmission spectrum collected at a delay time of -550 fs as a reference.^{104,129} The transient optical density is defined as Δ OD(E,t)=log [I(E, t = -550 fs)/I(E, t)], where I(E,t) represents the transmission spectrum at pump-probe time delay t and XUV photon energy E. A small time-independent background from scattered NIR pump photons precludes the use of the pump-off transmission spectra as a reference. Using the transmission spectrum at -550 fs removes the unavoidable small NIR background that occurs in each pump-probe transient absorption spectrum. The pressure in the pump-probe experiments is kept low to prevent clogging of the sample cell. This results in a typical Δ OD \leq 0.1. The spectrum for each time delay is averaged for ten scans resulting in a total data acquisition time of 250 seconds per delay. This yields a signal-to-noise ratio of ~5 after ~10⁶ pump-probe pulses. The pulse-to-pulse fluctuations of the XUV photon intensity are the major source of noise in the experiments. Error bars presented in the figures represent 95% confidence intervals unless otherwise noted.

Quantum chemistry calculations were carried out for doubly charged $C_2H_3Br^{++}$ ions. Density functional theory (DFT) calculations are performed using the GAUSSIAN 09 program package.¹⁶³ The hybrid functions of Becke, 3-parameter, Lee-Yang-Parr (B3LYP) for exchangecorrelation energies with the 6-311++G(3d,2p) basis set are employed in the calculations. The calculations yield vertical ionization energies (IE's) for the transition from the ground state of C_2H_3Br to $C_2H_3Br^{++}$ ions. The results are tested by comparing calculations for other organic molecules (e.g. ethene, 2-butene and benzene) with available experimental results.¹⁶⁴ The agreement is within 0.6 eV, verifying the accuracy of the calculations for single and double ionization energies. In addition, the transition state for the dissociation of $C_2H_3Br^{++}$ into $C_2H_3^+$ + Br^+ is characterized. All reported results from this calculation (Section 5B) include corrections for zero point energy.

4.3 Results

4.3.1 Static and transient absorption spectra

Fig. 4.3.1(a) shows a static absorption spectrum of neutral vinyl bromide. The absorption spectrum is obtained from two XUV transmission spectra with and without the gas sample in the target cell. The conversion from transmission to absorption spectra is performed according to $OD = -\log [I(E)/I_0(E)]$, where I(E) and I₀(E) represent the XUV transmission spectrum with and without vinyl bromide in the sample cell. The open squares and red solid line represent the experimental data and overall fit results, respectively. The spectrum is fit to two Gaussian features centered at 71.1 eV and 71.9 eV that have been previously assigned to the spin-orbit split transitions from Br (3*d*) inner-shell orbitals to the LUMO+1 orbital (σ^* , C-Br antibonding).¹⁶⁵



Fig. 4.3.1(a)

The static absorption spectrum of neutral vinyl bromide. The transitions correspond to the excitation of Br (3d) electrons to the LUMO+1. Experimental result is shown in black open squares with error bars. Red solid line represents the overall fitting. The features are fit to two Gaussian functions with fixed centers at 71.1 eV and 71.9 eV. The resulting FWHMs are equal to 1.0 eV and 0.7 eV, respectively.

Fig. 4.3.1(b) shows a transient absorption spectrum at a pump-probe delay

of +5 ps. The Δ OD scale on the vertical axis is proportional to the concentration of transient species in the pump-probe interaction volume. Positive and negative values of Δ OD in Fig. 4.3.1(b) represent the production of transient species and the depletion of ground state neutral molecules, respectively. Several distinct features are seen and marked with numbers from 1 to 7. Negative Δ OD's for peaks 6 and 7 correspond to the reduction of resonant absorption according to Fig. 4.3.1(a), i.e. a depletion of the neutral parent molecule. The inset in Fig. 4.3.1(b) shows the extension of a broad, featureless depletion signal at energies below 64 eV. The assignments of peaks 1-5 and further data analysis for Figs. 4.3.1(a) and 4.3.1(b) are presented in Sec. 4.4.1.



Fig. 4.3.1(b)

Transient absorption spectrum at +5 ps. The transient peaks are marked with numbers from 1 to 7. The peaks 6 and 7 represent the neutral vinyl bromide depletion as shown in Fig. 4.3.1(a). The inset shows the next section of depleted non-resonant continuum below 64 eV. The vertical bars represent the statistical 95 % confidence interval.

Fig. 4.3.1(c) shows a two-dimensional false color map of the transient absorption spectra (Δ OD) versus time delay and XUV photon energy at a NIR peak intensity of

 $220\pm90 \text{ TW/cm}^2$. The transient species are labeled according to the peaks shown in Fig. 4.3.1(b). In Fig. 4.3.1(c), the formation of peaks 2 to 5 and the depletion of peaks 6 and 7 occur promptly. The rise time of the leading edges of these signals reflects the temporal resolution (instrument response function, IRF 61 ± 11 fs) of the experiments. However, peak 1 exhibits a slower rise time of 330 ± 150 fs. Moreover, the absorption maximum of peak 2 evolves from 65.5 eV to 65.1 eV within the rise time of peak 1. This shifting implies that some ultrafast dynamics are imprinted in the XUV absorption profile. The transition energies for all other peaks remain constant for all pump-probe time delays. Further analysis of Fig. 4.3.1(c) will be presented in Sec. 4.4.1.



4.3.2 Power dependence measurements of transient species

Fig. 4.3.2 shows transient spectra taken at 10 ps pump-probe time delay at three different NIR peak intensities ranging from 140 TW/cm² to 290 TW/cm². The vertical and horizontal axes represent the densities of the transient species and the XUV energies, respectively. The spectra displayed as recorded with varying NIR intensities and constant XUV intensities; they are not normalized to one another. In the spectra, the amplitudes of peak 1 and peak 2 hardly change with the NIR peak intensity. However, a strong dependence of peaks 3, 4, and 5 on the NIR peak intensity is observed. The depletion of neutral C₂H₃Br at peaks 6 and 7 increases markedly when going from 140 TW/cm^2 to 220 TW/cm², but remains virtually constant upon further increase of the peak intensity to 290 TW/cm².



Power dependence measurements over three different NIR peak intensities at pump-probe delay time +10 ps. The transient species are labeled accordingly as described in Fig. 4.3.1(b). Some intensity correlations in the transient species are observed.

4.3.3 Calculated molecular orbitals of vinyl bromide molecule

Fig. 4.3.3 shows the calculated molecular orbitals (MO) of neutral vinyl bromide using the same theoretical methods described in Sec. 4.2. The lowest-lying empty molecular orbitals are the LUMO (lowest unoccupied MO) and LUMO+1 (2^{nd} lowest unoccupied MO), as shown in Fig. 4.3.3(a) and Fig. 4.3.3(b), respectively. The electron density located on the bromine atom is

very small in the LUMO. In contrast, the LUMO+1 has significant density on the bromine atom and antibonding character along the C-Br bond. The valence orbitals subjected to NIR strongfield ionization in this work are the HOMO and HOMO-1. Fig. 4.3.3(c) shows the HOMO, which has π bonding character between two carbon atoms and π^* antibonding character between the carbon and bromine atoms.¹⁶⁶⁻¹⁶⁹ The electron densities are located above and below the molecular plane and the wavefunctions have opposite signs around the C-C bond and the bromine atom. Fig. 4.3.3(d) shows the HOMO-1, which has a lone pair of electrons localized on the bromine atom with maximum density in the molecular plane.¹⁶⁶⁻¹⁶⁹ The HOMO-2 is shown in Fig.4.3.3(e) for later comparison. This orbital has strongly delocalized electron density above and below the molecular plane.



Fig. 4.3.3

The molecular orbitals of neutral vinyl bromide calculated by using Gaussian 09 Program package. (a) LUMO orbital. This orbital possesses an electron density mainly localized on carbon atoms. The electron density on the bromine atom is small. (b) LUMO+1 orbital. It possesses a σ antibonding along the C-Br bond. (c) HOMO orbital. The π bonding is between two carbon atoms and the π^* antibonding is between the carbon and bromine atoms, (d) HOMO-1 orbital. This corresponds to p shell lone-pair electrons on the bromine atom in the molecular plane. (e) HOMO-2 orbital. The orbital shows a delocalized electron distribution over the whole molecule.

4.4 Data analysis

4.4.1 Spectroscopic assignments of static/transient absorption spectra

Neutral vinyl bromide has previously been studied by using inner-shell electron energy loss spectroscopy (ISEELS) in the vicinity of the Br (3*d*) absorption edge.¹⁶⁵ The static absorption spectrum in Fig. 4.3.1(a) is free fit to two Gaussian peaks. The resulting centers are at 71.1 eV and 71.9 eV, respectively. The obtained full widths at half maximum (FHWM) are 1.0 eV and 0.7 eV. The lower energy component is broader than the higher energy component due to the ligand-field splitting (molecular field splitting) of the Br (3*d*) inner-shell.¹⁷⁰ The valence spin-orbit splitting of LUMO+1 is on the order of ~0.05 eV.¹⁷¹ Vibrational progressions also contribute to the broadening of each absorption peak in the Br (3*d*)-to-LUMO+1 transition. Note that the static absorption lines in Fig. 4.3.1(a) are not assigned to Br (3*d*)-to-LUMO transitions as a consequence of negligible spatial overlap between the initial and final molecular orbitals and therefore negligible oscillator strengths of the corresponding transitions.^{15,165} The LUMO has very little electron density in the vicinity of the bromine atom (Fig. 4.3.3(a)), and thus the Br (3*d*)-to-LUMO transition probability is very small.

The transient spectrum shown in Fig 4.3.1(b) is simultaneously fit with multiple Gaussian peaks. The fit results and assignments are shown in Fig. 4.4.1(a). These peaks represent inner-shell to valence transitions in atomic Br (${}^{2}P_{3/2}$), singly charged parent ions (C₂H₃Br⁺) in the \tilde{X} and \tilde{A} states, doubly charged parent ions (C₂H₃Br⁺⁺), and neutral vinyl bromide depletion. Each feature comprises a pair of inner-shell excited spin-orbit states representing the $3d^{1}_{3/2}$ (${}^{2}D_{3/2}$) and $3d^{-1}_{5/2}$ (${}^{2}D_{5/2}$) configurations separated by approximately 0.9 eV. The relative absorption strength and width of each inner-shell excited spin-orbit component are free fit parameters. The peak centers of atomic Br (${}^{2}P_{3/2}$), C₂H₃Br and C₂H₃Br⁺⁺ ions are obtained from the literature.^{148,172} For the C₂H₃Br⁺ ions in the \tilde{X} and \tilde{A} states, the estimate of the absorption energies (i.e. peak center) is described in the following paragraph. The experimental values are determined from the free fit within the range of the prediction.



Fig. 4.4.1(a)

Transient absorption spectrum at +5 ps. Solid and dash color lines represent the transient species of different inner-shell spin-orbit states. In the spectrum, the atomic Br (${}^{2}P_{3/2}$), the singly charged ionic A state, ionic X state and doubly charged $C_{2}H_{3}Br^{++}$ ions are shown. The depletions of the neutral vinyl bromide at resonance (solid/dash magenta lines) and non-resonant continuum (black solid line) are considered in the spectra as well. The inset shows the next section of depleted non-resonant continuum from 56 eV to 64 eV. The inset suggests that there are no electronic states higher than the ionic A state are observed.

There are no experimental values available for the Br (3*d*) inner-shell absorption energies of $C_2H_3Br^+$ parent ions in the ionic \tilde{X} and \tilde{A} states. These two ionic states correspond to the ionization of electrons from the HOMO and HOMO-1 orbitals, respectively. The inner-shell to valence level transition energies within the two ionic states are estimated by the difference



between the binding energies of Br (3*d*) inner-shell electrons and the IE's of the HOMO and HOMO-1 valence electrons, using the energy diagram shown in Fig. 4.4.1(b). The previously measured inner-shell electron binding energies for vinyl bromide are 76.4±0.3 eV and 77.3±0.3 eV for the spin-orbit-split inner-shell states $3d_{5/2}^{1}(^{2}D_{5/2})$ and $3d_{3/2}^{1}(^{2}D_{3/2})$, respectively.^{148,165,170} The IE of electrons

Fig. 4.4.1(b)

Predicted inner-shell absorption energies for the Br (3*d*)-to-valence transitions. The energies at 66.6 eV and 67.5 eV represent the transition of two inner-shell excited spin-orbit series of configurations $3d^9$ with term symbols of ${}^{2}D_{5/2}$ and ${}^{2}D_{3/2}$, respectively. The red arrows represent the ionization of electrons from the HOMO, HOMO-1 and HOMO-2 to the ionization continuum that generates the ionic \tilde{X} , \tilde{A} and \tilde{B} states. Green arrows represent the excitation of the ionic states to the inner-shell excited state by promoting a Br (3*d*) electron to the valence holes.

in the HOMO is 9.8 eV.¹⁶⁶⁻¹⁶⁹ Within a simple Koopmans' picture and Fig. 4.4.1(b),^{173,174} Br (3*d*)-to-HOMO transition energies of 66.6 ± 0.3 eV and 67.5 ± 0.3 eV are obtained. These values supports the assignment of the absorption peaks at 66.4 eV and 67.3 eV to the Br (3*d*)-to-HOMO transitions in the parent C₂H₃Br⁺ ion.

Following the same procedure as for the HOMO vacancy, the Br (3d)-to-HOMO-1 and Br (3d)-to-HOMO-2 energies are derived as the difference between the Br (3d) ionization energies noted above and previously determined inner valence ionization energies, as discussed next. From VUV experiments on neutral vinyl bromide,¹⁶⁶⁻¹⁶⁹ the IE's of valence electrons in the HOMO-1 and HOMO-2 are 10.9 eV and 12.3 eV, respectively, as indicated by the red arrows in Fig. 4.4.1(b). This yields inner-shell to valence absorption energies of 65.5 ± 0.3 eV and 66.4 ± 0.3 eV for the Br (3d)-to-HOMO-1 transition, and 64.1±0.3 eV and 65.0±0.3 eV for Br (3d)-to-HOMO-2 transitions. Note that the ionization of electrons from the HOMO-1 and HOMO-2 orbitals produces the ionic \tilde{A} and \tilde{B} states, respectively. As shown in Fig. 4.3.1(b) and 4.3.1(c), the lack of any clear time-dependent absorption peak centered at 64.1eV indicates that the amount of ions in the B state (i.e. a HOMO-2 hole) may be negligible. The agreement between the predicted and the experimental results for the Br (3d)-to-HOMO-1 transition (i.e. the innershell transition of ions in the \tilde{A} state) is within ~0.2 eV. This value is also within the error bars $(\pm 0.3 \text{ eV})$ from the previous study.¹⁶⁵ The difference between prediction and observation can be accounted for by the simplified estimate of inner-shell to valence transition energies from the difference of inner-shell IE's and valence IE's. Moreover, the vibrational internal energy of parent ions may also have a small effect on the origins of the XUV absorption peaks.^{170,175} From the fit results shown in Fig. 4.4.1(a), the absorption ratios of the inner-shell-excited spin-orbit component $(3d_{5/2}/3d_{3/2})$ for the ionic \tilde{X} and \tilde{A} states are 1.7±0.1 and 2.7±0.2, respectively. The featureless character of the signal below 64 eV indicates that no ionic states higher than the \tilde{A} state are observed at a NIR peak intensity of 220 ± 90 TW/cm².

There are no experimental values available for the Br (3*d*) inner-shell absorption energies of $C_2H_3Br^{++}$ ions. The absorption peaks in the spectral range between 68 eV and 70 eV have previously been assigned to doubly charged ground state $CH_2Br_2^{++}$ and Br^{++} ions.^{148,172} thus, the absorption peak in this energy region is assigned to the dication.

The inner-shell absorption energies of atomic Br (3*d*) are obtained from the literature.¹⁷² From the free fit in Fig. 4.4.1(a), the ratio of absorption strengths obtained from the fit for atomic bromine at 64.4 eV (${}^{2}P_{3/2} \rightarrow {}^{2}D_{5/2}$) and 65.4 eV (${}^{2}P_{3/2} \rightarrow {}^{2}D_{3/2}$) is equal to 5. This value is consistent with existing literature.¹⁷⁶ An experimental energy resolution of ~0.45 eV is derived by deconvoluting the atomic Br (3*d*) line at 64.4 eV, taking into account the natural linewidth (~0.1 eV).¹⁷² There is no clear evidence for atomic Br production in the valence excited spin-orbit state (${}^{2}P_{1/2}$) from C₂H₃Br⁺ ions.¹⁷⁷ According to a series of photoelectron-photoion coincidence experiments, the breakdown diagram of vinyl bromide parent ions correlates directly to the formation of the Br (${}^{2}P_{3/2}$) spin-orbit ground state of the bromine atom.^{178,179} This indicates that the fragmentation of the ionized vinyl bromide molecules with sufficient internal energy leads predominately to the production of the C₂H₃⁺ + Br (${}^{2}P_{3/2}$) channel.

4.4.2 Ultrafast dynamics of $C_2H_3Br^+$ and $C_2H_3Br^{++}$ ions

Figs. 4.4.2.1(a) to 4.4.2.1(c) show the pump-probe traces for the production of singly charged ions in the \tilde{X} state (black), the depletion of neutral vinyl bromide (blue) and the emergence of doubly charged ions (red) over time delays ranging from -0.6 ps to 2.5 ps. Figs. 4.4.2.1(d) and 4.4.2.1(e) display the pump-probe traces for the emergence of atomic Br (²P_{3/2}) and singly charged ions in the \tilde{A} state and, respectively. Fig. 4.4.2.2 shows the pump-probe traces for all transient species over time delays ranging from -5 ps to 20 ps, using coarser time intervals. All the pump-probe traces shown in Figs. 4.4.2.1 and 4.4.2.2 represent the areas of the Gaussian peaks that are used to model the different transient signals according to Fig. 4.4.1(a) (Sec. 4.4.1).

In Fig. 4.4.2.1(a), the singly charged ions in the \tilde{X} state (HOMO hole) are produced promptly by the strong laser field. The time constant of the rising edge in Fig. 4.4.2.1(a) is obtained by fitting the data with an error function with a FWHM of 65±14 fs (black line). The depletion of neutral molecules shown in Fig. 4.4.2.1(b) occurs promptly, too, and can be



Fig. 4.4.2.1(a) to (c)

The pump-probe transient traces for (a) singly charged ions in the ionic \tilde{X} state (black color), (b) the depletion of neutral C₂H₃Br molecules (blue color), and (c) the doubly charged C₂H₃Br ions (red color). The rising and depletion edges are fitted with error functions of FWHM equal to 65 ± 14 fs and 55 ± 17 fs, respectively. A weighted average IRF of 61 ± 11 fs is derived. A red simulation curve with rinsing-edge of IRF is plotted over the doubly charged ions to show а promptly production of this transient species.

described by an error function with a FWHM of 55±17 fs (blue line). We take the weighted average of these values to be the instrumental response functions (IRF), 61±11 fs. In Figs. 4.4.2.1(c), a simulation of the rising edge with an IRF of 61 fs is shown as a red solid line in comparison to the $C_2H_3Br^{++}$ ion signals (red markers). This indicates that the doubly charged ions $(C_2H_3Br^{++})$ are generated instantly within the time resolution of this experiment. A close inspection of the data at the rising edge reveals that the signal rises promptly within two adjacent time delays (30 fs). This indicates that the signal rise time is shorter for dications than for singly charge ions. The effective experimental time resolution strongly depends on the number of NIR photons required to produce different types of ions. Highly non-linear processes require the highest peak intensities and proceed efficiently only during the fraction of the NIR pulse with intensities above a relatively high threshold value. Double ionization requires more NIR photons than single ionization, which may lead to a more pronounced non-linear behavior and a shorter effective NIR pulse duration for the production of $C_2H_3Br^{++}$ dication compared to $C_2H_3Br^+$ ions. A shorten rise time in the generation of doubly charged ions has been reported in other works.¹²⁹ We are not able to distinguish the subtle difference between sequential and non-sequential double ionization in this experiment. In addition, the small overshoot signal on top of the constant plateau indicates that some dications dissociate into fragment ions within the first few hundred femtoseconds. The majority of dications,

however, are longlived. This will be discussed in Sec. 4.5.2.

shows

Fig. 4.4.2.1(d)

the pump-

Fig. 4.4.2.1 (d) to (e) The pump-probe transient traces for (d) the atomic Br $({}^{2}P_{3/2})$. The red curve represents a free fit of an exponential growth and an instantaneous rise, both convoluted with an IRF of 61 fs. The exponential rising time constant is 330 ± 150 fs. (e) The pump-probe transient traces of singly charged ions in the ionic \tilde{A} state. The time trace can be described by the red curve comprising an exponential decay component (330 fs) and constant ion intensity both convoluted with an IRF (61 fs) at rising edge.

probe trace for the emergence of atomic Br (${}^{2}P_{3/2}$). The trace is fitted to a single exponential growth function convoluted with the IRF. The resulting time constant of the single exponential growth is 330±150 fs (red line). Fig. 4.4.2.1(e) shows the transient intensity trace for the ionic \tilde{A} state at short pump-probe time delays. The \tilde{A} state signal exhibits a small but noticeable overshoot at early times that decays rapidly to its asymptotic value. The limited signal-to-noise ratio of the pump probe trace prevents a completely free fit from using a kinetic model composed of an exponential decay and a constant value. However, the pump-probe trace can be well approximated by a fit curve (red) that represents the sum of an exponential decay with a fixed



Transient pump-probe traces of vinyl bromide from -10 ps to 25 ps. Generation of (a) ions in the ionic \tilde{X} state, (b) the depletion of neutral vinyl bromide, (c) the doubly charged C₂H₃Br⁺⁺ ions, (d) in the ionic \tilde{A} state, and (e) the atomic Br (²P_{3/2}) formation. There is no dynamic change of the transient species after 5 ps. The solid lines represent extended curves that describe the pump probe traces shown in Fig. 4.4.2.1.

time constant of 330 fs chosen to match the Br rise and instantaneously rising, constant value, an both convoluted with the IRF (61 fs). This suggests an instantaneous production of the A state ions within the time resolution of the experiment that either remain stable within the first few picosecond or decay into other products within ~330 fs. The obtained free fit ratio of amplitudes for the decaying vs. constant components is approximately 0.37 ± 0.25 . Figs. 4.4.2.2(a) to 4.4.2.2(e) show the pump-probe traces of transient species at time delays ranging from -5 ps to 20 ps. There are no amplitude changes of the transient species from 5 ps to 20 ps. The solid curves represent extended plots of the fit results shown in Fig. 4.4.2.1 to guide the eyes.

Figs. 4.4.2.3(a) and 4.4.2.3(b) show a series of transient spectra recorded with pump-probe time delays ranging from -50 fs to 300 fs and 0 ps to 15 ps,


respectively. Each spectrum is fit with six Gaussian functions that represent the inner-shell excited spin-orbit components $(3d^{-1}_{3/2,5/2})$ for the atomic Br $({}^{2}P_{3/2})$ and the ionic \widetilde{A} and \widetilde{X} states, as shown in Fig. 4.4.1(a). Free fit parameters are the ion/neutral peak intensities, widths, and positions. The relative absorption strength of each inner-shell excited spin-orbit component is



Fig. 4.4.2.3 (a) and (b)

Transient spectra of vinyl bromide ions at different pump-probe delay windows. (a) From -50 fs to 300 fs (top to bottom). Each spectrum is simultaneously fitted with six Gaussian peaks in order to deconvolute the absorption shifts of ions in the ionic à state. (b) From 0 ps to 15 ps (top to bottom). The ions in the \tilde{A} state have presumably reached equilibrium through the dissociation and vibrational relaxation at 5 ps. No changes of absorption energy are observed at delay times from 5 ps to 15 ps. Note that at time-zero in (a) and (b) the absorption energy of ions in the ionic A state can be subjected to the influence of the NIR field. However, this is limited to the temporal overlap between the XUV and NIR pulses (~61 fs).

state peak. Note that at time zero in Fig. 4.4.2.3(a) and Fig. 4.4.2.3(b), the transient ions could be subjected to an AC stark effect that results in a shift in the absorption energy. However, this effect is limited to the temporal overlap between the XUV and NIR pulses (IRF 61 fs) and thus cannot be responsible for the longer-time dynamics seen here.

4.4.3 Correlated densities of transient species

Fig. 4.4.3 displays the areas of the Gaussian peaks that are used to model the transient species versus the NIR peak intensity in Fig. 4.3.2. Each spectrum is fit

the quantifies time-dependent energy shift of the ionic \tilde{A} state signal within the first ~300 fs as noted in Sec. 4.3.1 (Fig. 4.3.1(c)). The time-dependent peak maximum position of the A state signal that results from the fit is indicated by a series of small dots in Fig. 4.4.2.3(a); its temporal evolution is shown in Fig 4.4.2.3(c). The absorption energies of ions in the \tilde{X} state and atomic Br $({}^{2}P_{3/2})$ remain constant. For time delay beyond ~ 1 ps, the XUV absorption energies of all transient ions and fragments remain constant (Fig. 4.4.2.3(b)). The red solid line in Fig. 4.4.2.3(c) is derived by an exponential fit of the energy shift and it represents a guide for the energy shift of the \widetilde{A}





The deconvoluted absorption energy of ionic A state versus the pump-probe delay time (black open circles). A clearly change of the absorption energy is observed. The red solid line represents a guide for the eye.

with multiple Gaussian peaks as described in Sec. 4.4.1. The ion signals related to the \tilde{X} state and the doubly charged C₂H₃Br⁺⁺ dications increase markedly with increasing NIR peak intensity. However, the signal intensities for the ionic \tilde{A} state and the atomic Br (²P_{3/2}) remain constant. According to Figs. 4.3.2 and 4.4.3, the depletion of the neutral molecules seems to saturate at a NIR peak intensity of 220 TW/cm² but the Δ OD's of the ionic \tilde{X} state and C₂H₃Br⁺⁺ ions still increase with NIR peak intensity.



Fig. 4.4.3

Area-integrated intensities of transient species versus the NIR peak intensities. The experimental results are shown in open squares and circles. The solid color lines represent a guide for the eye. The intensity correlations are observed between the ionic \tilde{X} state and the doubly charged ions, and between the atomic Br (${}^{2}P_{3/2}$) and the ionic \tilde{A} state.

4.5 Discussion and theoretical calculations

4.5.1 Ultrafast dynamics of $C_2H_3Br^+$ ions in the ionic \tilde{A} state

Figs. 4.4.2.1(d) and 4.4.2.1(e) demonstrate that the decaying fraction of the \tilde{A} state signal can be characterized by the time constant (330 fs) obtained from the fit of the emerging atomic Br (${}^{2}P_{3/2}$) signal. These observations suggest that some of the C₂H₃Br⁺ ions formed in the \tilde{A} state dissociate along the C-Br bond to form atomic Br (${}^{2}P_{3/2}$). In Figs. 4.4.2.3(a) and 4.4.2.3(c), a continuous shift of the XUV absorption peak (~0.4 eV) associated with the \tilde{A} state of the parent ion is observed. Such an XUV spectral shift has been observed in Br₂ as the result of a vibrational wavepacket produced by SFI.¹⁴⁹ The evolution of the \tilde{A} state absorption energy occurs within the time window that the C-Br bond breaks. The energy shift of the XUV absorption maximum may therefore indicate a vibrational energy redistribution in the \tilde{A} state that is followed by the C-Br bond dissociation. The ionic \tilde{A} state has been implicated with respect to the C-Br bond dissociation in a previous study involving single photon ionization.¹⁷⁹

The relevant energetics for dissociative ionization and ionic dissociation are¹⁷⁹

- $C_2H_3Br \rightarrow C_2H_3 + Br^+$ 15.4 eV (1)
- $C_2H_3Br \rightarrow C_2H_3^+ + Br(^2P_{3/2})$ 11.9 eV (2)
- $C_2H_3Br^+(\tilde{X}) \rightarrow C_2H_3^+ + Br(^2P_{3/2}) = 2.1 \text{ eV}$ (3)
- $C_2H_3Br^+(\widetilde{A}) \rightarrow C_2H_3^+ + Br(^2P_{3/2}) = 1.0 \text{ eV}$ (4)

Eq. (1) contains a much higher dissociation threshold in comparison to Eq. (2). Thus, the formation of Br^+ ions should be much less likely than that of neutral Br atoms. Eqs. (3) and (4) show the energies required for the formation of atomic Br (${}^2P_{3/2}$) relative to the ionic \tilde{X} and \tilde{A} states, respectively.¹⁸⁰⁻¹⁸² The dissociation threshold of the \tilde{X} state is twice as high as that of the \tilde{A} state. Hence, if SFI creates ions in the \tilde{X} and \tilde{A} states with comparable levels of internal excitation, one can envision that some of the \tilde{A} state ions but none of the \tilde{X} state ions will have enough energy to dissociate, leading to a depletion of the \tilde{A} state population and a shifting of its XUV electronic band at short pump-probe delay times, as the hotter ions fall apart. However, without a better understanding of the vibrational energy distribution produced by SFI, one cannot say if this simple energetic suffices to explain the differences in the temporal behavior of the \tilde{X} and \tilde{A} state ions.

In principle, the atomic Br (${}^{2}P_{3/2}$) can be produced from the dissociation of neutral vinyl bromide along the C-Br bond. Such an excitation process would require four NIR photons to reach the neutral excited state at 6.4 eV (${}^{1}\pi\pi^{*}$).¹⁶⁹ This excited state may cross to a lower energy state that breaks the C-Br bond.¹⁶⁹ However, as noted above, the NIR peak intensities in this experiment are in the tunneling ionization regime with a Keldysh parameter $\gamma < 1$.¹⁶² The power dependence of both the atomic Br (${}^{2}P_{3/2}$) and the ionic \tilde{A} state yields is strongly saturated (Fig. 4.4.3), supporting the picture of tunneling ionization of vinyl bromide leading to the C-Br bond dissociation from the ionic \tilde{A} state. The saturation of ion production as a function of NIR peak intensity in the tunneling ionization regime has previously been reported.¹⁸³ The tunneling ionization process would have ionized neutral vinyl bromide molecules before the C-Br bond dissociation occurs. Therefore, the contribution of atomic Br (${}^{2}P_{3/2}$) from the dissociation of neutral vinyl bromide is unlikely.^{148,184}

4.5.2 Generation and stability of $C_2H_3Br^{++}$ ions

In Fig. 4.4.2.1(c), the small overshoot signal on top of the plateau indicates that some dications with enough internal energy may dissociate into fragments. In Fig. 4.4.2.2(c), however, shows that nearly all the doubly charged $C_2H_3Br^{++}$ ions are long-lived and do not undergo dissociation through Coulomb explosion. Metastable dications of unsaturated hydrocarbons with lifetimes on the order of nanoseconds have been observed in several TOF studies.^{185,186} According to Gaussian 09 calculations for vinyl bromide, removing two electrons from the HOMO orbital requires the lowest total ionization energy for the generation of the dication (27.2 eV). Under the assumption that the lowest energy state of $C_2H_3Br^{++}$ dications is generated, we perform DFT calculations to estimate the stability of this ion. A theoretical calculation shown in Fig. 4.5.3 presents several possible dication dissociation pathways following the dissociative ionization of vinyl bromide that leads to the possible dication dissociation pathways. The appearance potentials for three different dissociation channels (Eqs. (5) and (6)) are considerably higher in energy and thus much less likely to play a role in the dication dissociation dynamics, so we focus solely on Eq. (7).



Dissociative ionization channels of vinyl bromide dications. The dications are generated by ionizing two electrons from the HOMO orbital. The red and black color lines represent the low energetic dissociation and high energetic dissociation channels. The double ionization and dissociative ionization energies are obtained by performing calculations with B3LYP DFT exchange /correlation and 6-311++G (3d, 2p) basis sets. A transition state is found for $C_2H_3Br^{++} \rightarrow C_2H_3^{+} +$ Br⁺ channel. This dissociation barrier at 28.9 eV supports the stability of the C₂H₃Br⁺⁺ parent ions without dissociation in the pump-probe delay time window of 20 ps. The numbers on the molecular structures denote the bond distance in Å.

$C_2H_3Br \rightarrow C_2H_3 + Br^{++}$	36.8 eV	(5)
$C_2H_3Br \rightarrow C_2H_3^{++} + Br$	31.6 eV	(6)
$C_2H_3Br \rightarrow C_2H_3^+ + Br^+$	23.9 eV	(7)

As shown in Fig. 4.5.3, the vertical ionization energy for the generation of C₂H₃Br⁺⁺ dications is 27.2 eV. This energy is higher than that required to produce $C_2H_3^+$ + Br^+ ions. Table 4.5.3 summarizes the dication bond angles and bond lengths for the local minimum at 26.6 eV, ground state dications at 26.2 eV, and transition state the dissociation channels structures along according to Eq. (7). The optimized structure for free $C_2H_3^+$ ions is also listed in the table. Right after vertical double ionization within the NIR pulse, the molecular ions elongate along the C-C bond to a local minimum at 26.6 eV. This stretching enables a rotation around the C-C bond toward a structure that has staggered geometry at 26.2 eV. Elimination of the Br^+ ion would proceed through a transition state at 28.9 eV that is marked by a Y-shaped $C_2H_3^+$ radical ion. The 1.7 eV higher energy of this transition state compared to the initial Franck-Condon active dication state may explain the long lifetime of the majority of dications produced by SFI. However, some

dications with enough internal energy may dissociate to form fragment ions.

Table 4.5.3

Optimized structures parameters for the $C_2H_3Br^{++}$ dications at local minimum (26.6 eV), ground state (26.2 eV) and transition state (28.9 eV). The optimized structure for $C_2H_3^+$ ion is also shown. The bond angle and bond length are in degree and Å, respectively.

$C_2H_3Br^{++}$	Local minimum	Ground state	Transition state	$C_2H_3^+$
\rightarrow C ₂ H ₃ ⁺ + Br ⁺	at 26.6 eV	at 26.2 eV	at 28.9 eV	ground state
r (CBr)	1.770	1.792	3.5	NA
r (CC)	1.482	1.418	1.274	1.253
θ (CCH)	121.12	136.2	170.67	179.99
θ (HCH)	119.49	118.76	116.26	117.33

In our measurements, we do not probe dynamics beyond 20 ps, where dissociation of dications into $C_2H_3^+ + Br^+$ ions may occur. This would appear as an isotropic distribution of atomic Br^+ ions as observed in a previous SFI study¹⁸⁷ that used ion TOF spectroscopy to collect the dissociation products in a time window of a nanosecond. The dissociation lifetime of dications strongly depends on the internal energy that is deposited by the strong laser field. Unfortunately, the amount of internal energy in the ions is unknown. For the uneven charge separation channels ($C_2H_3^{++}$ + Br and C_2H_3 + Br^{++}), the dissociation thresholds are several eV higher (Fig. 4.5.3). These channels are negligible in the pump-probe time window of 20 ps.

4.6 Conclusions and outlook

The ultrafast dissociative ionization and relaxation dynamics of vinyl bromide exposed to a strong NIR laser field has been studied with a table-top femtosecond XUV transient absorption setup. The NIR field removes electrons both from the HOMO and HOMO-1 of neutral vinyl bromide (C₂H₃Br), corresponding to the generation of ionic \tilde{X} and \tilde{A} states, respectively. The ions in the \tilde{X} state are long lived with lifetimes longer than 20 ps. Most of the ions in the \tilde{A} state do not dissociate in the time window of 20 ps. However, some ions with high internal energy in the \tilde{A} state appear to relax and dissociate within a few hundred femtoseconds, leading to a decay of the ionic \tilde{A} state population and a dynamic shift of the XUV absorption energy of ~0.4 eV. The time scales for the decay of the \tilde{A} state ions and their dynamic energy shift are well approximated by the time constant of the atomic Br (²P_{3/2}) emergence (330±150 fs), suggesting that the C-Br bond dissociation occurs from the ionic \tilde{A} state.

The NIR power dependence measurements also show an ion/fragment density correlation between the ionic \tilde{A} state and atomic Br (²P_{3/2}), supporting the formation of free atomic Br from the \tilde{A} state. Moreover, from the results of electronic structure calculations suggests that an energy barrier along the dissociative ionization reaction coordinate of C₂H₃Br⁺⁺ to form C₂H₃⁺ + Br⁺ may prevent a direct dissociation of the dication, indicating the production of stable ions upon ionizing two electrons from the HOMO orbital.

The current study demonstrates that a tabletop femtosecond XUV light source can be used to probe the ultrafast relaxation and dissociation dynamics of ions by monitoring changes in the XUV absorption strength and energy. The dynamics of vinyl bromide molecular ions with broad internal energy distribution have been investigated. In future studies, the method will be applied to molecules excited by one-photon excitation processes and with known internal energies. Dynamics around conical intersections, internal conversion and ring-opening dynamics of excited polyatomic molecules will be explored with femtosecond time resolution and element specificity.

Chapter 5 Toward Spin-Orbit Wavepackets of Carbon Disulfide and Ultrafast Dissociation Dynamics of Thiophene Molecules

5.1 Introduction

This chapter describes an ongoing study of CS₂ and thiophene molecules. The first part of this chapter presents the studies toward spin-orbit wavepackets of carbon disulfide ions generated by the highly non-linear strong-field ionization process. In the past, the atomic spinorbit wavepacket of krypton ions has been studied to explore coherent electron motion by using a sub-femtosecond XUV probe.¹¹ In this previous study, quantum beating in the absorption signal of the inner-shell to empty valence transitions demonstrated that a coherence of two spin-orbit states can be produced by strong-field ionization of an atomic system. However, an open question is whether or not we can detect the coherence of an electronic wavepacket in polyatomic molecules. The molecular spin-orbit splitting of carbon disulfide ions in the first ionic \tilde{X} state is 60 meV (484 cm⁻¹).⁷⁷⁻⁷⁹ This energy gap corresponds to a beating period of 69 fs, a factor of three longer than our NIR pulse duration. The equilibrium structure of the first ionic state is similar to the neutral ground state, which would result in relatively little vibrational wavepacket excitations. The vibrational periods of the ground state ions are 28 fs, 54 fs and 100 fs for the asymmetric stretch, symmetric stretch, and degenerate bend modes, respectively. These time scales can be distinguished from the expected electronic wavepackets within our instrumental time resolution.

The second ionic state of carbon disulfide ions is 2.6 eV higher than the ionic ground state. By applying a higher NIR laser field, the ionic \tilde{A} state can be populated. In contrast to the ionic ground state, the equilibrium structure of the ionic \tilde{A} state is displaced along the CS bond, leading to vibrational excitation in the symmetric stretch mode, with a vibrational period of 60 fs. The molecular spin-orbit splitting of 22 meV has been reported for the ionic \tilde{A} state, indicating the possibility to observe a spin-orbit wavepacket (~188 fs) and a vibrational wavepacket (~60 fs) at the same time.⁷⁸

The XUV absorption energies of sulfur 2p electrons to the ionic \tilde{X} and \tilde{A} states are separated by the difference of the valence ionization energies (~ 2.6 eV). The resolved transient absorption signal can provide an opportunity to explore and study the interaction between the vibrational and electronic coherent motions in different ionic states generated by the strong laser field. The following sections present preliminary experimental results toward the study of spinorbit and vibrational wavepackets of carbon disulfide ions by using the newly developed XUV transient absorption spectroscopy technique. The second half of this chapter presents first steps toward the study of ultrafast photodissociation of electronic excited thiophene molecules. Ring opening of thiophene (C_4H_4S) is one of the dissociation processes related to photodamage of organic solar cells that degrades the efficiency of charge separation and propagation.^{82,83} This tremendously reduces the average working lifetime of these devices in comparison to the inorganic silicon-based solar cells. However, the advantages of low-cost and flexible geometry hold promise to make organic photovoltaics one of the next generation portable sunlight energy conversion technologies. The photo-excited component of these solar cell devices often consists of the P3HT (Poly(3-hexylthiophene)) compound that can transfer the electronic energy to oxygen molecules ($^{3}O_{2}$), leading to the formation of reactive singlet oxygen. $^{1}O_{2}$ molecules, in turn, can react with thiophene rings, ultimately breaking them apart and forming radical fragments that result in more chemical bond dissociations. More research efforts are required in order to optimize the basic design of thiophene-based organic solar cells and to improve the cell lifetime under exposure to sunlight.

The removal of thiophene derivatives is an important step in the oil refinery industry.⁸⁴⁻⁸⁸ The reduction of sulfur compounds in petroleum can significantly reduce deleterious combustion products, for example SO₂ emission and H₂SO₄ formation ("acid rain"). Sulfur compounds in oil refinery processes can passivate catalyst metal surfaces by the bonding sulfur atoms to the available reactive sites on the metal surface. In order to efficiently remove sulfur-containing compounds in the oil refinery process, a hydrodesulfurization (HDS) process is applied. The fundamental reaction mechanism is to use molybdenum disulfide (MoS₂) catalyst to bond sulfur-containing molecules and to initiate the ring-opening dissociation pathway. The open ring product can then degrade to form hydrocarbons. However, the sulfur atoms are strongly bonded to the catalyst surface. The ring-opening dissociation of thiophene, however, is a predicted pathway that is used to understand the photochemical reactions before and after the catalytic process. A more straightforward detection technique should be applied to understand these in situ chemical reactions.

Several studies have focused on the photodissociation of thiophene that leads to the formation of $C_4H_4 + S$, $C_2H_2S + C_2H_2$, HCS+C₃H₃, CS+C₃H₄, HS + C₄H₃ and H₂ + C₄H₂S.^{89,90} From the translational kinetic energy distributions of these photofragments, information on the photolytic process through hot molecules in the ground electronic state can be obtained. Note that all the fragmentation channels involve the dissociation of two chemical bonds. A detailed experimental and theoretical study of ultrafast thiophene ring opening dynamics has been reported.^{91,92} However, a real-time observation of the C-S bond dissociation in the gaseous thiophene molecules is still to be achieved. Newly developed tabletop XUV light sources based on high harmonic generation can provide a unique chemically specific probe for the study of dynamics in polyatomic molecules. The light sources provide attosecond to femtosecond temporal resolution that can be utilized to probe ultrafast dissociation and relaxation in the vicinity of a chemical reaction center. Here, a tabletop femtosecond XUV light source with up to 180 eV photon energy is demonstrated that will enable time-domain inner-shell studies of thiophene molecules. The sulfur 2p absorption edge is located at 165 eV. The absorption of one XUV photon promotes the S (2p) inner-shell electrons to the empty valence orbitals. A UV pump laser pulse (193 nm) excites the molecule before the XUV pulse arrives. The ring opening

dynamics of valence excited thiophene molecules will be studied by varying the time delay between the UV pump pulse and the XUV probe pulse. Dissociation of the C-S bond provides an empty orbital located on the sulfur atom, which can be detected by the XUV photons in the vicinity of the S (2p) absorption edge.

5.2 Experimental method

Several modifications to the instrumental setup are made for the studies of sulfurcontaining molecules using XUV transient absorption spectroscopy. The XUV optical layout for the sulfur-containing molecules was shown previously in Fig. 2.1 (c). Briefly, an f/20 lens is used to focus the NIR beam with pulse energies of 1.4 mJ into a gas cell, enabling femtosecond XUV pulse generation with photon energy up to 180 eV. The estimated NIR focus beam diameter in HHG cell is ~60 μ m (1/e²). The pressure in the cell is tuned to produce the highest XUV cut-off energy. An optimized neon gas pressure of 0.7 kPa is obtained. A silver filter of 200 nm thickness is inserted at 0.9 m behind the HHG cell to block residual NIR light. A toroidal mirror is used to focus the XUV laser beam into the sample gas cell. The XUV light emerging from the sample cell is dispersed by a spherical variable line-spacing (VLS) imaging grating with a center groove density of 1200 lines/mm. The VLS grating produce a flat-field tangential focus at the detector plane. The estimated photon flux in the spectral region between 140 eV and 180 eV is approximately two orders of magnitude lower than the photon flux in the spectral region from 50 eV to 72 eV. The spectrometer system is equipped with two different detectors. The first one is chevron-type microchannel-plates with a phosphor screen. The resolving power of the spectrometer with this detector is $E/\Delta E\approx 170$, the absolute energy resolution is ~1 eV at 165 eV. The spin-orbit splitting of the sulfur 2p absorption edges is barely resolved. An X-ray CCD will be installed in the future to achieve higher energy resolution and detection efficiency.

An f/30 lens is used to focus the NIR pump pulse into the sample cell for the spin-orbit and vibrational wavepacket studies on CS_2 ions. The NIR peak intensity of $\sim 10^{14}$ W/cm² produces sufficient pump-probe ion signal to overcome the fluctuation noise in the XUV absorption signal at 165 eV. A flow of argon gas in front of the recombination mirror is used to purge the mirror surface, suppressing the photochemical reactions of molecules on the mirror surface that otherwise change the focal property and flux of the NIR beam at the target cell position. The background pressure of the purge gas in the sample chamber is approximately 0.13 Pa. Including the continuous CS_2 sample flow in the experiment, the overall background pressure in the experimental chamber is ~ 0.3 Pa.

The low pump-probe signal intensities in the strong-field ionization experiment on CS_2 molecules require a new approach to achieve the spatiotemporal pump/probe overlap in vacuum before a long transient absorption scan. The spatial overlap is optimized by tuning two attenuated NIR beams to overlap each other on a webcam (in air). The webcam is placed at the target sample cell position. The NIR laser beams have to be attenuated by neutral density (ND) filters before being sent onto the webcam. The overall ND of 10 is used. When temporal and spatial

overlap is reached, interference fringes will be observed. However, the temporal overlap under the ambient pressure conditions is not preserved under vacuum since the NIR laser pulse travels faster in vacuum than in air (travel time difference: 0.92 fs/mm). As a consequence, the timezero defined in air will be slightly different from that in vacuum. A new approach is used to find the exact time-zero in vacuum that imitates the whole transient absorption experiments. The key idea is to perform HHG in the sample cell (not in the XUV generation cell) by combining the NIR pump beam and the NIR driver of the XUV probe pulses in the sample cell region. The NIR intensities are chosen such that the two NIR beams have to overlap spatially and temporally in the sample cell in order to produce detectable amount of XUV light. The sample cell is filled with the xenon or other gases. The NIR and XUV propagation speeds in vacuum are assumed to be identical. After the coarse spatiotemporal alignment in air by using a webcam, the XUV intensity emerging from the target sample cell is used as a pump-probe cross correlation signal. When the spectrometer is set up for the detection of high-energy photons (110 eV to 180 eV), the low energy cross correlation of XUV harmonics are not directly imaged but appears as a scattering background. Fig. 5.2.1 shows a cross correlation scan obtained from the collection of the background signal as a function of the pump-probe delay time. This can help to characterize the exact time-zero quickly before a long scan transient absorption experiment. The measured time-zero difference between vacuum and ambient pressure conditions is 1.613 ps. This corresponds to a travel distance of 1754 mm for the NIR probe beam in vacuum. The exact travel distance of the probe beam in vacuum is 1870 mm. The difference is approximately 6.2%. The difference cannot be accounted for by the error in the measurement of the probe beam distance. The source of the difference can be from the imprecise refractive index of 780 nm in air.



Fig. 5.2.1

Cross-correlation signal from HHG in the sample cell filled with atomic xenon. The pump and probe beams are both NIR laser beams. The signal appears as a uniform background on the MCP detector. The black circles are the experimental results. The red curve is from a Gaussian fit, resulting in a FWHM of 16.5 fs. The FWHM of the cross correlation single is expected to be smaller than that of a linear convolution of two identical ~25 fs NIR pulses since HHG is a highly nonlinear process that emphasizes the pulse regions with the highest intensities. The time zero has been calibrated in this figure.

For thiophene ring opening studies, a femtosecond 193 nm light source with pulse energies of 10 μ J is assembled for the excitation step in the thiophene ring opening studies. The detailed layout of the 193 nm generation setup using BBO crystals is discussed in Chapter 2. An f/5 lens is installed to focus the 193 nm laser beam into the sample cell or ionization cell. All optics in the vacuum chamber are purged with argon gas to prevent photochemical deposition on the mirror surfaces. This keeps the VUV mirrors at high reflectivity without degradation.

A webcam (Logitech) is placed at the target cell position to optimize the spatial overlap between the pump and probe beams. An ionization cell is employed to characterize the temporal overlap between the XUV and the 193 nm laser pulses under vacuum. This cell is also used to measure the duration of the 193 nm pulses. Since the generated XUV light propagates with the NIR pulse with a sub-femtosecond delay due to an extra thin metal filter, the NIR pulse can be used to imitate the XUV laser beam for the time-zero calibration. The temporal width of 193 nm pulses is characterized by using a "one-193 nm-photon pump" and "multi-780 nm-photon probe" scheme in an ionization cell. The setup makes use of the enhanced multiphoton ionization yield of electronically molecules. The design of the ionization cell to collect the generated ions is shown in Fig. 5.2.2. The cell contains two parallel stainless steel electrodes spaced by 3 mm (Fig. 5.2.2.b). One electrode is biased at ~200 V relative to ground. The other electrode is connected to the oscilloscope set to high input impedance. The estimated pressure in the ion cell is approximately 0.13 Pa (1 mtorr) to avoid discharging between the two electric plates. The 193 nm pulse duration is measured using CS₂ and thiophene molecules in the ionization cell. The instrument response function is independent of the molecular system. The experimental results are discussed in Sec. 5.3.3.



Fig. 5.2.2

Design of the ionization cell for the pump-probe time zero calibration and pulse duration measurement with 193 nm pump pulse. (a) The cell is placed at the sample cell position as shown in Fig. 2.1. The incoming pump (193 nm) and probe (780 nm) laser beams both enter from the left side. The cell length is approximately ~50 mm. Two electrodes in the cell are supported by two plastic spacers. The spacers are drilled through ((\emptyset =3 mm) for the beam path. Transparent teflon tubes are used to insulate the electric wires connected to the plates. (b) Cross section of ionization cell. The blue and orange lines represent the pump and probe beams, respectively. The 193 nm pump laser beam is focused by an f/5 lens. The NIR probe beam is focused by the toroidal mirror.

The static XUV absorption spectra for CS_2 and thiophene molecules are averaged over 2 minutes exposure times on the CCD camera. In the transient absorption spectra, a positive delay time corresponds to a setting in which the "pump" laser pulses arrives at the target sample cell

position before the "probe" laser pulses. All error bars shown in the results correspond to a statistical 95% confidence interval unless otherwise noted.

5.3 Results and Analysis

5.3.1 Static absorption spectra of thiophene and carbon disulfide



Fig. 5.3.1 (a)

Static absorption spectrum of thiophene molecules in 2 mm sample cell. The spectrum is obtained from 1st order diffraction off the variable line spacing grating. The assignment of the spin-orbit series is obtained from the literature. The red solid line represents the experimental results. The vertical bars represent the statistical error bars at 95 % confidence interval. The grey curve shows the inner shell electron energy loss spectrum from Ref. 188.

In the thiophene absorption spectrum shown in Fig. 5.3.1 (a), the pre-edge features cannot be resolved. The unresolved broad absorption peak in the spectral range from 164 eV to 170 eV corresponds to transitions of inner-shell sulfur (2p) electrons to valence $\sigma^*(C-S)$ and π^* antibonding orbitals.¹⁸⁸ In the absorption spectrum of carbon disulfide shown in Fig. 5.3.1 (b), the broad absorption peak at 164 eV contains two spin-orbit peaks at 163.3 \pm 0.1 eV and 164.5 \pm 0.1 eV, respectively. These correspond to transitions of inner-shell sulfur 2p electrons to the valence $3\pi_u$ orbital.¹⁸⁹

Figs. 5.3.1 (a) and 5.3.1 (b) show the static absorption spectra of thiophene and carbon disulfide molecules recorded with 4 mm and 2 mm long absorption cells, respectively. The spectra are obtained by using a spectrometer equipped with an MCP detector. The data acquisition time for the static absorption spectra is approximately 2 minutes. In each spectrum, the inner-shell spin-orbit absorption series are assigned according to the literature. The grey curves show literature spectra recorded at higher resolution for comparison.^{188,189}





A static absorption spectrum of CS₂ molecules recorded in second order diffraction off the VLS grating is shown in Fig. 5.3.1 (c). Here, the spin-orbit doublet of the sulfur 2*p* electrons to valence $3\pi_u$ orbital transition is well resolved due to the higher energy resolution in 2nd order diffraction geometry. According to the grating equation shown in Eq. 2.1 in Chapter 2, the spectral energy resolution in 2nd order diffraction (m=2) is two times higher than in the first order diffraction (m=1). The spectra shown in Figs. 5.3.1(b) and 5.3.1(c) demonstrate that the higher energy resolution available in 2nd order diffraction should be utilized for the pump-probe experiments. However, the XUV photon intensity in the 2nd order diffraction features is reduced by about a factor of 10 compared to those in the 1st order diffraction features, requiring longer data acquisition times to achieve the same signal-to-noise ratio. Spectra in both diffraction orders (m=1, 2) are recorded simultaneously on the same position sensitive detector.



Fig. 5.3.1 (c)

Static absorption spectrum of carbon disulfide recorded in second order diffraction (m=2). Spectra in both diffraction orders (m=1, 2) are recorded simultaneously on the same position sensitive detector. The spin-orbit peaks are resolved in 2^{nd} order diffraction of the grating. The red solid line represents the experimental results. The vertical error bars represent the statistical 95% confidence interval. The grey curve shows the absorption spectrum of carbon disulfide obtained from Ref. 189.

The energy resolutions of the spectrometer in 1st and 2nd order diffraction are 1.11 eV and 0.47 eV, when using the MCPs-based detector. The energy resolution has been determined by taking into account the intrinsic line widths of the CS₂ absorption features at 163.3 eV and 164.5 eV obtained from high-resolution absorption data.¹⁸⁹ The spectrometer energy resolution for 1st order diffraction is approximately two times lower than for 2nd order diffraction as predicted by the grating equation. The obtained value for the resolution in 1st order diffraction is close to the prediction presented in Chapter 2.

5.3.2 Transient Absorption Experiments of Carbon Disulfide (CS₂)

This section presents preliminary results for the study of strong-field ionized CS₂ molecules by XUV transient absorption spectroscopy in the vicinity of the S (2*p*) edge. The strong 780 nm laser field (780 nm) removes the valence electrons from the HOMO and HOMO-1 orbitals, generating ions in the ground (\tilde{X}) and first excited (\tilde{A}) states, respectively. The ionization energies for electrons from the HOMO and HOMO-1 are 10.1 eV and 12.7 eV, respectively. The inner-shell ionization energies for the sulfur 2*p* electrons are 169.9 eV (²P_{3/2}) and 171.1 eV (²P_{1/2}). The splitting of two S (2*p*) spin-orbit states (²P_{3/2} and ²P_{1/2}) is approximately 1.2 eV. Fig. 5.3.2.1 illustrates the predicted transition energies for the inner-shell

S (2p) electrons to the partially empty HOMO and HOMO-1 orbitals. The absorption energies are shown by the green arrows. This prediction can help assign the newly formed transient absorption peaks from the experiments.

Some calculated molecular valence orbitals of the CS_2 molecule are shown in Fig. 5.3.2.2. The calculations are performed with the Gaussian 09 package using density functional theory with



Fig. 5.3.2.1 Estimate of the S 2p to the HOMO and ĤOMO-1 transition energies in CS₂. The red arrows represent the ionization energies of the HOMO and HOMO-1 orbitals, corresponding to the generation of the ionic ground (\widetilde{X}) and excited (\widetilde{A}) states, respectively. The green arrows show the innershell absorption energies for the ionic ground and first excited states.

B3LYP exchange/correlation energies and the 6-311+G(2d) basis set. The LUMO, HOMO and HOMO-1 orbitals are shown for comparison. All the molecular orbitals are doubly degenerated. The LUMO orbital possesses antibonding character. The HOMO orbital consists predominately of lone-pair electrons located on the sulfur atoms. The HOMO-1 orbital is delocalized over the carbon and sulfur atoms. Under the influence of a strong laser field, the ionization efficiency of electrons from the HOMO and HOMO-1 orbitals should be different due to the differences in the orbital symmetry and ionization energy.



Fig. 5.3.2.2

Calculated molecular orbitals for the CS₂ molecule. All the orbitals are two-fold degenerate. Here, only one orbital is shown. The orbital symmetries for the LUMO, HOMO, and HOMO-1 are $3\pi_u$, $2\pi_g$ and $2\pi_u$, respectively.

Fig 5.3.2.3 shows transient absorption spectra of CS₂ molecules at a NIR peak intensity of 9×10^{13} W/cm² in two different pump-probe delay time ranges. The spectra are obtained by averaging 40 pump-probe time delay scans. Both transient spectra exhibit a prompt depletion of neutral CS₂ molecules in the spectral region from 163 eV to 173 eV. The formation of transient species is observed at 176 eV (indicated by red arrow). The predicted absorption energies of the singly charged CS₂⁺ ions in the \tilde{X} and \tilde{A} states are located between 157 eV and 161 eV (Fig. 5.3.2.1). No clear transient absorption signal is observed in this region. However, the CS₂⁺ ions have been measured in previous studies by using mass spectrometer.^{190,191} The lack of transient absorption signal in the predicted spectral energy region may be due to a low oscillator strength for transitions from the S(2*p*) inner-shell to vacancies with a strong contribution from S(3*p*) orbital.

The CS_2^+ and CS_2^{2+} ground state ions are both long-lived.¹⁹⁰⁻¹⁹² The appearance potentials for the $CS_2^+ \rightarrow CS + S^+$ and $CS_2^+ \rightarrow CS^+ + S$ channels are 14.8 eV and 15.75 eV, respectively.¹⁹³ These energies are approximately 4.8 eV to 5.75 eV higher than the ionization

energy for the production of the ionic \tilde{X} state. The high dissociation thresholds indicate that fragmentation of the parent CS_2^+ ions may be small. The double ionization threshold of the neutral CS_2 molecule to form CS_2^{2+} ions is 27 eV.¹⁹² The appearance potential for the dissociation of CS_2^{2+} is 30 eV,¹⁹² and there are indications of stable dications without further fragmentation. Thus, the transient absorption peak at 176 eV is most likely from parent ions $(CS_2^+ \text{ and/or } CS_2^{2+})$ involving transitions from the S (2*p*) orbital to vacancies in valence molecular orbitals. Minor contributions from CS, CS^+ , CS^{2+} , S, S⁺, and S²⁺ fragment species may be possible as well. Further theoretical calculations are needed to assign these transient species.



Fig. 5.3.2.3

The transient absorption spectra of CS_2 molecules at a NIR peak intensity of 9×10^{13} W/cm² in two different pump-probe delay time ranges. A prompt depletion of the neutral CS_2 absorption features is observed, indicating the ionization of molecules to the ionic states by the NIR field. The positive absorption feature at 176 eV (red arrows) may be due to the innershell to valence hole transition in parent ions and ionic fragments.

Fig. 5.3.2.4 shows a comparison of two transient spectra recorded in first and second order diffraction geometry from the grating. The black and red lines represent the background



and transient pump-probe spectra, respectively. Note that at the second order region, the exact XUV energy corresponds to the axis XUV energy \times 2. The two orange regions mark the depletion peaks that correspond to

Fig. 5.3.2.4

The comparison of transient absorption spectrum at the 1st and 2nd order diffraction of grating. The black solid line represents the background spectrum without pump beam. The red line shows the transient spectrum at 1ps at 1st and 2nd order diffractions from the grating. Three different energy regions are labeled with color bars. The second order has higher energy resolution compared to 1st order.

transitions from the sulfur 2p inner-shell to the $3\pi_u$ valence orbital. The pink regions contain transitions from the S 2p to 7_{σ_g} orbitals and other Rydberg states. The blue regions contain positive features, indicating the formation of transient species produced by the strong laser field. The reduced XUV photon flux in the 2^{nd} diffraction order results in a noisier transient signal than in the 1st order but the energy resolution of the 2^{nd} order diffraction spectrum is two times higher. This trend can be used to resolve overlapping absorption peaks in the first order diffraction. The estimated flux in the 2^{nd} order is approximately one order of magnitude lower than in the 1st order.

5.3.3 Toward ultrafast dissociation dynamics of thiophene and CS₂

This section presents work toward transient XUV absorption studies of ultrafast dissociation dynamics in thiophene molecules. The concept of the experiment is to initiate intramolecular dynamics by 193 nm (6.4 eV) one-photon excitation and to probe these dynamics by XUV transient absorption in the vicinity of the sulfur 2p edge (~165 eV). Ring opening at the C-S bond produces a partially filled valence orbital located on the sulfur atom. Electron vacancies in the vicinity of the sulfur atom can be detected by XUV transitions corresponding to the promotion of inner-shell S (2p) electrons to the holes in the valence orbitals. The currently achieved pulse energy of the 193 nm pump beam in the interaction region is estimated to be 3 μ J. At this low pump fluence, the estimated pump-probe signal is close to the noise level for a one-hour pump-probe integration time. The shot-to-shot XUV intensity fluctuations are higher near the cut-off at ~180 eV than in lower energy region, making these measurements particular challenging. Due to these difficulties, 193 nm-pump and XUV-probe experiments on the ring opening of thiophene molecules have not yet been performed. Methods for achieving spatiotemporal overlap and for measuring the temporal width of the pump pulse are described in the following paragraph.



Fig. 5.3.3.1

The pump-probe schemes and energy levels for thiophene $(1+2^{\circ})$ and carbon disulfide $(1+3^{\circ})$ molecules. For the excited state of thiophene, it takes two NIR photons to overcome the ionization energy. The excited CS₂ molecule needs three NIR photons to overcome the ionization energy. Both molecules in the excited state can lead to the C-S bond dissociation.

The spatiotemporal overlap between the pump (193 nm) and probe (XUV) beams is characterized by replacing the XUV beam with the 780 nm HHG driving beam. The NIR driver and XUV pulse propagation times are assumed to be the same for the purpose of this calibration The 780 nm beam for HHG imitates the XUV beam with a few femtoseconds traveling time difference. Thus, the NIR from the HHG can be used as a good reference to search for spatial and temporal overlap. Spatial overlap is achieved by replacing the interaction cell with a webcam or CCD camera. Note that the unwanted residual NIR light from the BBO frequency up-conversion system may propagate along with the 193 nm, which can result in an erroneous time zero calibration. A caution should be made in order to identify the 193 nm beam on the webcam properly. Blocking the third harmonic (263 nm) in the 193 nm generation system is used for this purpose. The temporal overlap can be measured by using the ionization cell as described in Sec. 5.2. The temporal width of the 193 nm laser pulse is measured by using thiophene and CS₂ molecules in the ionization cell. The ionization energies for thiophene and CS₂ molecules are 8.86 eV and 10.1 eV, respectively. Correspondingly, UV-excited thiophene and CS₂ molecules require two and three NIR photons to overcome the ionization thresholds, respectively. This corresponds to (1+2') and (1+3') pump-probe schemes for thiophene and CS₂ molecules. The 193 nm excitation of thiophene molecules corresponds to a promotion of the HOMO π electrons to the σ^* antibonding orbital that leads to a ring opening process in the five-membered ring.^{91,92} 193nm excitation of the CS₂ molecule can also break the C-S bond. The dissociation products are CS (X) + S (¹D, ³P).^{194,195} Fig. 5.3.3.1shows the energy levels and pump-probe schemes for thiophene and CS₂ molecules. The NIR peak intensity of the probe beam in the ionization cell is ~10¹³ W/cm².

The pump-probe ion traces for thiophene and CS_2 molecules are shown in Figs. 5.3.3.2(a) and 5.3.3.2(b), respectively. Note that the offset of the ordinate scale from zero. The majority of the ions in the ionization cell are from two-photon ionization at 193 nm and multiphoton ionization at 780nm. These processes contribute nearly equally to a time independent ion background signal The time dependent signal amounts to approximately 3% compared to the ion background signal.





Pump-probe ion signal for thiophene molecules. The red solid line represents a fit corresponding to Eq. 5.1. The resulting IRF and exponential decay time constants are 290 ± 30 fs and 200 ± 30 , respectively. The time dependent signal amounts to approximately 2.7% of the background ion signal. The pump-probe trace is obtained by averaging over six scans with a total data integration time of one hour.





Pump-probe ion signal for CS_2 molecules. The red solid line represents a fit corresponding to Eq. 5.1. The resulting IRF and exponential decay time constants are 260 ± 40 fs and 730 ± 180 , respectively. The time dependent signal amounts to approximately 3.2% of the background ion signal. The pump-probe trace is obtained by averaging over 8 scans with a total data integration of 0.8 hours (48 minutes).

The rising edges of the ion signals are independent of the molecular species. However, the ultrafast dynamics of the excited states are different. The pump-probe ion traces are fit with a convolution (*) of a Gaussian response function (instrument response function, IRF) and an exponential decay function as shown in Eq. 5.1. The parameters S, τ , and t_o are the standard

deviation, pump-probe delay time and time zero offset for the Gaussian response function, respectively. The parameter t1 is the time constant of the exponential decay function. This convolution function can be solved analytically. The first term in the analytical formula is an error function with a small time zero shift $(S^2/t1)$. The second term only rescales the overall signal intensity. The third term describes the exponential decay of the ions signal.

$$I_{(\tau)} = IRF * e^{-\frac{t}{t_1}} = \int_{-\infty}^{\tau} e^{-\frac{(t-t_0)^2}{2S^2}} \times e^{-\frac{\tau-t}{t_1}} dt$$
$$= \frac{1}{2} \left[1 + erf\left(\frac{\tau - \left(t_0 + \frac{S^2}{t_1}\right)}{\sqrt{2}S}\right) \right] \times e^{\frac{1}{2}(\frac{S}{t_1})^2} \times e^{\frac{-(\tau-t_0)}{t_1}}$$
Eq. 5.1

The resulting IRF widths from the thiophene and the CS_2 ions traces are 290 ± 30 fs and 260 ± 40 fs, respectively. These two values agree within error bars. A fixed weighted average IRF width of 280 ± 30 fs is derived. The resulting time constants for the ultrafast decay of the excited thiophene and CS₂ signals are 200 ± 30 fs and 730 ± 180 fs, respectively. These two values are consistent with the results of previous photoelectron and photoion experiments.^{92,19} The relaxation time scale of 200 ± 30 fs of the thiophene signal may represent dynamics involving ring opening and electronic state relaxation processes. This value can provide a reference point for femtosecond XUV transient absorption experiments that probe the dissociation dynamics locally on the sulfur atom. The excited CS₂ molecule relaxes and dissociates on a time scale of 730 ± 180 fs into CS + S (¹D, ³P) fragments. This value can be compared to the time constant of the appearance of free atomic sulfur as measured by XUV transient absorption spectroscopy at the S (2p) edge. The measurement involving a local reporter atom may provide additional insight into the electronic dynamics that ultimately result in the elimination of the sulfur atom. The interaction between the carbon and sulfur atoms in the dissociation process may also alter the transition from which a time dependent XUV absorption energy may change with pump-probe delay time. These two perspective experiments for thiophene and CS₂ molecules in the XUV transient absorption spectroscopy will be able to demonstrate a powerful detection on the reaction center with a femtosecond time resolution along the reaction coordinate.

5.4 Conclusion and future improvements

Efficient methods to find zero pump-probe time delay in experiment with weak transient absorption signal have been demonstrated. The approaches are based either on high harmonic generation or total ion yield detection in the sample cell. For experiments using 193 nm excitation, a 193 nm pump - multiphoton 780 nm probe total ion yield measurement provides the apparatus function and zero pump probe delay. This scheme has been demonstrated to work for both CS_2 and thiophene molecules.

Several difficulties have been encountered in the attempts to study spin-orbit wavepackets in CS_2 molecular ions and ultrafast dissociation dynamics of thiophene molecules. Sample cell clogging is the main issue. It precludes long scans for a better signal-to-noise ratio, which is particularly important for experiments with a weak XUV probe beam at photon energies up to 180 eV. A slit jet sample source may be a solution to avoid clogging issues.

The lack of any obvious transient absorption signal at the predicted XUV energies for CS_2^+ ions may indicate that the oscillator strength for the inner-shell to the valence orbital transitions is small. The transient absorption peak that appears at 176 eV for positive pump-probe delays is still to be assigned, indicating the need for more theoretical work that is essential for the interpretation of the experimental results.

For transient absorption experiments using 193 nm one-photon excitation, the pump pulse energy at the target cell position should be on the order of 10 μ J to overcome the noise from XUV intensity fluctuations at 170 eV photon energy

Several key steps to improve the experimental setup for future research are underway. A commercial X-ray CCD camera (Princeton Instruments PIXIS-XO:2048B) will be used to improve the energy resolution and detection efficiency. A longer IR driving wavelength (e.g. 1.6 μ m) for HHG can provide XUV pulses with up to 300 eV photon energy to complement experiments at the sulfur inner shell absorption edges with others at the carbon 1s edge in CS₂ and thiophene molecules. A higher flux of 193 nm light will improve the signal for the one-photon pump - XUV probe experiments for the thiophene ring opening dynamics.

Chapter 6 Summary and conclusion

A tabletop femtosecond XUV transient absorption spectroscopy based on high order harmonic generation is employed for the studies of ultrafast core-excited state coupling dynamics in atomic Xe and intramolecular dissociative ionization dynamics of vinyl bromide (CH₂=CHBr) ions in the two different ionic states. The preliminary results for CS₂ molecules under the influence of strong laser field are reported. The results using one-photon 193 nm excitation on CS₂ and thiophene molecules are also presented.

The core-excited states coupling in atomic Xe has been studied using femtosecond XUV transient absorption spectroscopy. Core-excited states of configurations $4d^{-1}6p$ are coupled to the states of $4d^{-1}6s$ and $4d^{-1}6d$ configurations at a NIR peak intensity of $\sim 10^{14}$ W/cm². The Xe⁺ ions are also produced at this peak intensity. Theoretical calculations using von Neumann equation supports the light induced features in the vicinity of the neutral transitions at 65.1 eV and 67 eV. These features are called Autler-Townes doublet splittings. However, the broad induced structures below 64 eV manifest an indication of breakdown of rotating wave approximation (RWA). This work indicates that RWA in a simulation involving the core-excited states in the strong-field regime may not be appropriate.

The dissociative ionization of vinyl bromide ions in the two different ionic states (\tilde{X} and \tilde{A}) are studied using femtosecond XUV transient absorption spectroscopy to probe the ultrafast dynamics in the vicinity of the atomic bromine. The ions in ionic ground state (\tilde{X}) are stable without further dissociation due to a deeper potential well. The first ionic excited state (\tilde{A}) dissociates in a time scale of 330 fs that leads to the formation of the free Br (${}^{2}P_{3/2}$) atom. The ultrafast dissociation process in the \tilde{A} state also manifests an XUV absorption energy shift by ~0.4 eV within the C-Br bond dissociation time window. Theoretical calculations are also performed to elucidate the stability of doubly charged ions. The results show a high dissociation barrier at transition state that explains the majority of the dications are stable without dissociation.

The preliminary results of CS_2 molecules under the influence of strong laser field shows the possibility of using HHG to probe the dynamics of CS_2 in the vicinity of the S (2*p*) absorption edge (~165 eV). Low oscillator strength in the XUV transitions of S (2*p*) to valence orbitals of 3*p* contribution from the sulfur atom may explain the absence of ion absorption signals. The 193 nm excitation of CS_2 and thiophene molecules is performed in an ionization cell. The resulting time constants of the excited states agree with the previous studies in literature.

Appendix

Appendix A

A derivation of Eq. 2.6(c) is shown in this Appendix. It shows that a use of a reference spectrum at far negative delay time can cancel out the unwanted NIR background in the calculation of Δ OD.

(a)

 $\Delta OD(t)$

$$= \log \left[I_{s(t_{ref})}^{pp'} / I_{s(t)}^{pp'} \right] = \log \left[\left(I_{s(t_{ref})}^{pp} + I_{BG} \right) / \left(I_{s(t)}^{pp} + I_{BG} \right) \right] = \log \left[(I_{s}^{pr} + I_{BG}) / (I_{s(t)}^{pp} + I_{BG}) \right]$$

Both divide by I_s^{pr} in the numerator and denominator in logarithm.

$$= \log\left[\left(1 + \frac{I_{BG}}{I_{s}^{pr}}\right) / \left(\frac{I_{s}^{pp}}{I_{s}^{pr}} + \frac{I_{BG}}{I_{s}^{pr}}\right)\right] = \log\left[1 + \frac{I_{BG}}{I_{s}^{pr}}\right] - \log\left[\frac{I_{s}^{pp}}{I_{s}^{pr}} + \frac{I_{BG}}{I_{s}^{pr}}\right]$$
$$= \log\left[1 + \frac{I_{BG}}{I_{s}^{pr}}\right] - \log\left[\left(\frac{I_{s}^{pp}}{I_{s}^{pr}}\right] \times \left[1 + \frac{I_{BG}}{I_{s}^{pp}}\right]\right]$$
$$= \log\left[1 + \frac{I_{BG}}{I_{s}^{pr}}\right] - \log\left[\frac{I_{s}^{pp}}{I_{s}^{pr}}\right] - \log\left[\frac{I_{s}^{pp}}{I_{s}^{pr}}\right] - \log\left[1 + \frac{I_{BG}}{I_{s}^{pp}}\right]\right]$$

Rearrange the equation (switch 1st and 2nd terms above)

$$= -\log\left[\frac{I_{s(t)}^{pp}}{I_{s}^{pr}}\right] + \log\left[1 + \frac{I_{BG}}{I_{s}^{pr}}\right] - \log\left[1 + \frac{I_{BG}}{I_{s(t)}^{pp}}\right]$$

Let $x = \frac{I_{BG}}{I_{s}^{pr}}$, and $y = \frac{I_{BG}}{I_{s(t)}^{pp}}$

$$= \log \left[\frac{I_s^{pr}}{I_{s(t)}^{pp}} \right] + \log[1 + x] - \log[1 + y]$$

In Taylor expansion, while -1 < x, y < 1

$$= \log\left[\frac{I_{s}^{pr}}{I_{s(t)}^{p}}\right] + \frac{1}{\ln 10}\left(x - \frac{x^{2}}{2} + \frac{x^{3}}{3} - \frac{x^{4}}{4}\dots\right) - \frac{1}{\ln 10}\left(y - \frac{y^{2}}{2} + \frac{y^{3}}{3} - \frac{y^{4}}{4}\dots\right)$$
$$= \log\left[\frac{I_{s}^{pr}}{I_{s(t)}^{p}}\right] + \frac{1}{\ln 10}\left((x - y) - \left(\frac{x^{2}}{2} - \frac{y^{2}}{2}\right) + \left(\frac{x^{3}}{3} - \frac{y^{3}}{3}\right) - \left(\frac{x^{4}}{4} - \frac{y^{4}}{4}\right) + \dots\right)$$

In the appearance of transient signal, I_s^{pr} is not equal to $I_{s(t)}^{pp}$. In order to approach the condition that $x \simeq y$, I_{BG} should be much smaller than I_s^{pr} and $I_{s(t)}^{pp}$. Therefore, the following term in x and y can cancel each other.

$$\therefore \Delta OD(t) = \log \left[I_{s(t_{ref})}^{pp'} / I_{s(t)}^{pp'} \right] = \log \left[\frac{I_s^{pr}}{I_{s(t)}^{pp}} \right]$$

(b)

If we use I_s^{pr} as a reference spectrum, an error in $\Delta OD(t)$ calculation will occur. Note that I_s^{pr} is the XUV transmission spectrum while pump laser beam is blocked.

$$\Delta OD(t) = \log \left[I_{s}^{pr} / \left(I_{s(t)}^{pp} + I_{BG} \right) \right] = \log \left[\frac{I_{s}^{pr} / I_{s(t)}^{pp}}{1 + I_{BG} / I_{s(t)}^{pp}} \right]$$

$$= \log \left[I_{s}^{pr} / I_{s(t)}^{pp} \right] - \log \left[1 + I_{BG} / I_{s(t)}^{pp} \right]$$

Let
$$x = \frac{I_{BG}}{I_{s(t)}^{pp}}$$

$$\Delta OD(t) = \log \left[I_s^{pr} / I_{s(t)}^{pp} \right] - \log \left[1 + x \right]$$

In Taylor expansion, while -1 < x < 1

$$\therefore \Delta OD(t) = \log \left[I_{s}^{pr} / I_{s(t)}^{pp} \right] - \frac{1}{\ln 10} \left(x - \frac{x^{2}}{2} + \frac{x^{3}}{3} - \frac{x^{4}}{4} \dots \right)$$

This indicates that the obtained $\Delta OD(t)$ deviates from the true signal $\log \left[I_s^{pr}/I_{s(t)}^{pp}\right]$ by the following term $-\frac{1}{\ln 10} \left(x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4}...\right)$. This deviation can be avoided by using a transmission spectrum at far negative delay time while pump and probe beam both exists at target cell without temporal overlap.

Appendix B

The phase of a wave propagation in a medium is equal $\varphi = n(\omega)k_0L = kL$, where $n(\omega)$, k and L are the refractive index at angular frequency ω , the wave vector k and the thickness of the medium L, respectively. k_0 is the wave vector in vacuum at wavelength λ_0 . Dispersion

effects are estimated by describing the spectral phase through a Taylor expansion around frequency ω_0 :

$$\varphi = kL = k(\omega_0)L + k'_{(\omega_0)}(\omega - \omega_0)L + \frac{1}{2}k''_{(\omega_0)}(\omega - \omega_0)^2L + high order.$$

$$k(\omega_0) = \frac{\omega_0}{v_{\varphi}}$$
 Phase delay

$$k'_{(\omega_0)} = \frac{1}{v_g(\omega_0)}$$
 Group delay

, where $v_g = \frac{c}{n - \lambda_0 \frac{\partial n}{\partial \lambda_0}}$ is the group velocity in mm/fs.

$$k''_{(\omega_0)} = \frac{\partial}{\partial \omega} \left(\frac{1}{v_g}\right)$$
 Group velocity dispersion, GVD

, where
$$\frac{\partial}{\partial \omega} \left(\frac{1}{v_g} \right) = \frac{\lambda_0^3}{2\pi c^2} \frac{\partial^2 n}{\partial \lambda_0^2}$$
 is the GVD in fs²/mm.

Group Delay Dispersion (GDD)=GVD×L in fs²

Therefore, GVD (fs²/mm) of all the materials can be calculated from the second-order derivative of refraction index. The wavelength dependent GVD for various materials is plotted in the figures below.



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