Imaging Electronic Structure and Dynamics of Molecules through Strong-Field Ionization, Rescattering and Holography

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Summary

This dissertation describes the design and construction of a velocity-mapimaging spectrometer (VMIS) and its application to four different experiments that explored the structure and dynamics of molecules by means of strong-field ionization (SFI). The main components of the spectrometer are an electrostatic lens system and a position-sensitive detector. Ions or electrons generated in the focus of the VMIS through photoionization are accelerated by the static field of the lens system towards the detector. The initial momentum and the mass-to-charge ratio of the accelerated particles can be retrieved from the position of impact on the detector and the time of flight. As a result one obtains a three-dimensional momentum-distribution spectrum. In the first experiment a mixed electronic-rotational wave packet in nitric oxide was measured using impulsive stimulated Raman scattering as pump and SFI as probe. We found the low-energy photoelectron momentum distribution to be very sensitive to the evolution of the electronic wave packet through holographic interferences whereas the high-energy electron momentum distribution was mainly influenced by the rotational wave packet. In a second experiment isotope effects on the tunneling-ionization and dissociative ionization rates of $\mathrm{H}_2,\,\mathrm{D}_2,\,\mathrm{CH}_4$ and CD_4 were measured and compared with theoretical results. A strong dependence of the tunneling-ionization rate on the nuclear dynamics as predicted by theory has not been conclusively identified. The accuracy of the measurement was limited by the knowledge of the sample density in the detection volume. However, isotope effects on the dissociative ionization of the molecules were observed. In the third experiment, we have attempted to observe nuclear dynamics based on laser-induced photoelectron diffraction. To this end the angle-resolved photoelectron momentum spectra of H_2 , D_2 , CH_4 and CD_4 were measured and compared. Differences in the spectra of the corresponding isotopologues were observed but we could not exclude contributions of laser intensity variations to the observed differences. Nevertheless, theoretical results obtained in the framework of this thesis predict observable effects. Finally, we studied the dissociative ionization of methyl halides in a phase-controlled two-color laser field. We found that tunneling ionization leading to the Coulomb explosion of CH₃F is faster if the electric field amplitude points from the methyl group to the halogen atom. For CH_3Cl , CH_3Br and

 $\rm CH_3I$ the asymmetry is opposite when $\rm CH_3^{+}$ ions with low kinetic energies are formed. However, for the dissociative ionization leading to high-energy $\rm CH_3^{+}$ fragments different asymmetries were observed.

Zusammenfassung

In dieser Arbeit werden der Entwurf und Aufbau eines Velocity-Map-Imaging (VMI) Spektrometers beschrieben und die Resultate von vier verschiedenen Experimenten vorgestellt. Diese Experimente untersuchten die elektronische Struktur und Dynamik von Molekülen mittels Ionisation im starken Laserfeld und winkelaufgelöster Detektion von Ionen und Elektronen im VMI Spektrometer. Die wichtigsten Bauteile des Spektrometers sind ein elektrostatisches Linsensystem und ein positionsempfindlicher Detektor. Ionen oder Elektronen, die im Fokus des VMI Spektrometers durch Photoionisation entstehen, werden vom statischen Feld des Linsensystems in Richtung des Detektors beschleunigt. Aus der Position, an der die Partikel auf den Detektor auftreffen und der Flugzeit können anschliessend der Impuls und das Masse-zu-Ladungsverhältnis bestimmt werden. Daraus ergibt sich ein dreidimensionales Impulsspektrum. Im ersten Experiment wurde mittels impulsiver stimulierter Raman-Streuung ein gemischtes Elektronen-Rotationswellenpaket in Stickstoffmonoxid angeregt und durch Ionisation im starken Laserfeld abgefragt. Wir fanden heraus, dass die Impulsverteilung der Photoelektronen mit niedriger Energie wegen holographischer Interferenzen stark von der Zeitentwicklung des elektronischen Wellenpakets abhängig ist, wohingegen die Impulsverteilung der hochenergetischen Elektronen empfindlicher auf das Rotationswellenpaket ist. Im zweiten Experiment wurden Isotopeneffekte auf die Tunnelionisationsrate und dissoziative Ionisation von H₂, D₂, CH₄ und CD₄ gemessen und mit Berechnungen verglichen. Die theoretisch vorausgesagte starke Abhängigkeit der Tunnelionisationsrate von der Kerndynamik konnte jedoch nicht eindeutig bestätigt werden. Die Messung war limitiert durch die Genauigkeit in der Bestimmung der Probengasdichte im Detektionsvolumen. Es konnten hingegen Isotopeneffekte auf die dissoziative Ionisation nachgewiesen werden. Im dritten Experiment haben wir versucht, Kerndynamik basierend auf laserinduzierter Photoelektronenstreuung zu beobachten. Zu diesem Zweck wurden winkelaufgelöste Impulsspektren von Photoelektronen von H₂, D₂, CH₄ und CD₄ aufgenommen und verglichen. Zwischen den Spektren der entsprechenden Isotopologen wurden zwar Differenzen beobachtet, jedoch konnten wir nicht endgültig ausschliessen, dass die Unterschiede von Intensitätsfluktuationen des Lasers verursacht wurden. Allerdings deuten Berechnungen, die im Rahmen dieser Arbeit

durchgeführt wurden, auf beobachtbare Unterschiede hin. Zuletzt haben wir die dissoziative Ionisation von Methylhalogeniden in einem phasenkontrollierten Zweifarbenfeld untersucht. Wir fanden heraus, dass die Tunnelionisation, die zur Coulomb-Explosion des CH₃F führt, schneller abläuft, wenn das elektrische Feld des Lasers vom Methylrest in Richtung des Halogenatoms zeigt. Für CH₃Cl, CH₃Br und CH₃I ist dies für die entgegengesetzte Richtung der Fall, wenn CH₃⁺ Fragmente mit geringer kinetischer Energie entstehen. Für die dissoziative Ionisation, die zu hochenergetischen CH₃⁺ Ionen führt, wurden jedoch andere Richtungspräferenzen beobachtet.

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Chapter 1 Introduction

The interpretation of the photoelectric effect based on energy quanta by Albert Einstein was an important milestone in the development of quantum mechanics at the beginning of the last century [1]. The photoelectric effect was first observed by Heinrich Hertz in 1887. In his experiment, Hertz showed that the sparking between two electrodes is enhanced if the electrodes are illuminated with ultraviolet light [2]. This result demonstrated that electrons can overcome the Coulomb force and detach from the atomic nucleus through the absorption of photons. For weak electromagnetic fields this process can only occur if the photon energy exceeds the ionization potential. In strong fields, however, ionization is also possible when the photon energy is less than the ionization potential. In this case the electron has to absorb several photons to reach the continuum. Such transitions become only relevant if the photon flux is very high. Therefore, multiphoton experiments were not possible with the light sources available before the invention of the laser. But with the development of high-performance laser systems in the 1970's multiphoton experiments became feasible. In an experiment realized by Agostini et al. [3] in the late 1970's it was observed that the photoelectrons can absorb more photons than actually necessary to overcome the ionization potential. Today, this process is called above-threshold ionization (ATI). Fourteen years later Yang et al. [4] measured ATI peaks up to the 30th order from xenon and krypton for a laser intensity exceeding 10^{13} W/cm². This was an amazing result because, according to Newton's equation of motion, a free electron in a laser field can only gain a maximum kinetic energy of $2U_{\rm p}$ where $U_{\rm p}$ represents the ponderomotive energy (quiver energy). It is defined as $U_{\rm p} = e^2 I/2c\epsilon_0 m\omega^2$ with the electric permittivity of free space ϵ_0 , the speed of light c, the charge e and mass m of the electron and the laser intensity I and frequency ω . The highest observed ATI peaks, however, were near an energy of $9U_{\rm p}$. Yang and co-workers have further measured the angular distribution of the high-energy electrons and found that some electrons are emitted under an angle of $\sim 45^{\circ}$ with respect to the z axis, the polarization axis of the laser beam. They concluded that the high energy as well as the angular distribution are the result of a scattering process of the photoelectron with the parent ion.

Today, the complete process is often explained using the three-step model introduced by Corkum [5] in 1993. The first step involves the ionization of the atom or molecule. Depending on the ionization potential, the laser frequency and the intensity this process can be assigned to the multiphoton or to the tunneling regime. The assignment is made using the parameter $\gamma = \sqrt{I_{\rm p}/2U_{\rm p}}$ introduced by Keldysh in 1964 [6], where $I_{\rm p}$ stands for the ionization potential of the target. For $\gamma > 1$ the ionization process is assigned to the multiphoton regime and for $\gamma < 1$ to the tunneling regime. The two regimes differ only in how the ionization process is described. In the multiphoton regime the electron absorbs several photons till it reaches a continuum state. In the tunneling regime, however, the electron reaches the continuum state by tunneling through the strongly-distorted Coulomb potential. When $\gamma < 1$ it follows that this process becomes the most adequate description which applies to atoms or molecules with a high ionization potential in an intense, low-frequency laser pulse. Thus, ionization induced by an intense infrared laser is well described by the tunneling model. The second step describes the free motion of the photoelectron in the oscillating field. In the simplest approximation one can neglect the influence of the Coulomb potential of the parent ion and describe the electron trajectories based on Newton's equation of motion. The electron tunnels through the barrier when the field is maximal, reaches a continuum state and is then pulled away from the ion. As the amplitude of the field changes its sign the electron is slowed down and driven back to its starting position where it arrives just one period later. For this trajectory the kinetic energy accumulated at the time of return will be zero. If the electron tunnels through the barrier just a bit later it will have a nonzero kinetic energy when it returns to the parent ion. The maximum energy is limited to $3.17U_{\rm p}$. Upon return the electron can recombine with the ion under the emission of a photon or it can undergo an inelastic or elastic scattering process. Within the threestep model these processes belong to the third step.

The recombination of the electron under the emission of a photon is called high-harmonic generation (HHG). In the past HHG spectroscopy has proven to be a versatile tool to observe nuclear and electronic dynamics even on the sub-femtosecond time scale. The high temporal resolution is achieved because the HHG generation process itself can be viewed as pump-probe experiment where the ionization corresponds to the pump and the recombination to the probe. Therefore, a single HHG spectrum contains information about the nuclear and the electronic dynamics. For example, the nuclear motion in H_2^+ and D_2^+ [7, 8] or the temporal evolution of an attosecond electron-hole wave packet in N₂ [9] or CO₂ [10] have been extracted from the HHG spectrum. In these experiments the nuclear and electronic motion is triggered by the tunneling ionization itself. In other experiments the coherence between different states is created by a preceding pulse where the subsequent dynamics is then probed by HHG spectroscopy. For example the dissociation of Br_2 , electronic and nuclear dynamics in the vicinity of a conical intersection in NO₂ or electronic coherence in NO have been studied using this method [11–13]. HHG is also a source of attosecond pulses [14–16] which again can be used to investigate ultrafast processes in atoms or molecules [17–19].

In fact the recombination process which leads to HHG is very unlikely. It is far more likely that the returning electron is scattered elastically at the parent ion. In principle the electron can be scattered in any direction. But generally forward scattering is dominant leading to electrons with a maximum energy of $2U_{\rm p}$. However, if the electron is backscattered it is further accelerated by the driving field and gains an energy of up to $10U_{\rm p}$ as observed by Yang et al. in 1993. Meanwhile, the spectroscopy of the photoelectrons has been refined and it was shown that it can be used to investigate the structure and dynamics of atoms and molecules similar to HHG spectroscopy. A very important conclusion was that the elastic differential scattering cross section (DCS) of the parent ion can be obtained from the angular distribution of the highenergy electrons [20–23]. This observation connects strong-field photoelectron spectroscopy with the well-established X-ray, electron and neutron diffraction techniques which are commonly used to determine the structure of molecules. It was indeed shown that photoelectron spectroscopy can also be used to obtain information about the structure of molecules [24, 25]. Therefore, this spectroscopy method is often referred to as laser-induced electron diffraction (LIED). But in contrast to the standard scattering experiments LIED comes with the advantage that the photoelectron spectrum also contains temporal information. Just recently Blaga *et al.* could show that it is possible to image nuclear dynamics induced by SFI with LIED [26]. Another important discovery was the observation of a holographic pattern in the photoelectron spectrum [27–29]. To explain this effect the photoelectron has to be described as a wave packet which starts to disperse as soon as it reaches a continuum state. Therefore, only a fraction of the wave packet is scattered upon return which leads to interference between the scattered "signal" and non-scattered "reference" waves. As a consequence of the interference between the two wave packets, the holographic pattern contains information about the scattering process and the initial electron wave packet after tunneling.

Encouraged by these observations we further developed strong-field photoelectron spectroscopy and used it to study dynamics in atoms and molecules based on LIED and photoelectron holography. A suitable tool to record a photoelectron spectrum is the velocity-map imaging spectrometer (VMIS) [30, 31]. A VMIS uses electrostatic lenses to guide the photoelectrons onto a position sensitive detector. In analogy with an optical lens where the transmissive object placed in the focus in front of the lens and the image obtained in the focus behind the lens are related through a Fourier transformation, the electrostatic lenses generate a velocity map image (or momentum distribution spectrum) of the photoelectrons on the detector. However, this also works for ions which is a real opportunity because ionization can also lead to the fragmentation of the molecule. With a VMIS one can thus study electronic structure and dynamics of molecules or atoms based on the angle-resolved momentum distribution spectrum of photoelectrons and ions.

1.1 Outline of this Thesis

The thesis starts with the description of the VMIS and the laser system. In the subsequent chapters the results of four different experiments are presented. Each of these chapters contains a short introduction followed by the specific experimental details. The chapters also contain further information which is necessary for the interpretation of the results. After the discussion of the results the chapters end with a conclusion. The content of the chapters are:

- **Chapter 3** In this chapter the result of a pump-probe experiment is presented where a mixed rotational-electronic wave packet in NO was measured using angle-resolved momentum spectroscopy of the photoelectrons.
- **Chapter 4** Motivated by theoretical results which predict a difference of the ionization rate of H_2 and D_2 caused by different nuclear dynamics we have studied the ionization and dissociation rate of H_2 , D_2 , CH_4 and CD_4 by means of ion time-of-flight spectroscopy.
- **Chapter 5** In this chapter the angle-resolved photoelectron momentum distribution spectra of H_2 , D_2 , CH_4 and CD_4 are presented and compared. The spectra were recorded for laser pulses with a center wavelength of 800 nm and 1800 nm. The goal was to observe sub-femtosecond nuclear dynamics using LIED.
- **Chapter 6** Based on the angle-resolved momentum distribution of positivelycharged fragments from methyl halides we have studied the angular dependence of the tunneling ionization.

This thesis ends with a general conclusion together with an outlook on future experiments and improvements.

Chapter 2

Spectrometer and Laser System

This chapter describes the spectrometer and the laser system. Specific experimental details are given in the subsequent chapters where the results are presented and discussed. The design and setup of the spectrometer was one part of this thesis. Because it was also planned to use the VMIS for pump-probe experiments with ultrashort XUV pulses, it had to fulfill some special requirements. XUV pulses cannot be transmitted through air and the reflection on surfaces leads to intensity losses. Therefore, XUV pump-probe experiments are often complex. It is thus a great advantage if the connected spectrometer can be easily adapted to the output of the XUV setup. Besides velocity map imaging of electrons and ions it should also be possible to measure ion time-of-flight spectra with the spectrometer. Additionally, we wanted to be able to adjust the temperature and density of the sample gas in the interaction volume.

2.1 The Spectrometer

A simplified depiction of the spectrometer is given in figure 2.1. The configuration of the electrostatic lenses was identical to the setup introduced by Eppink and Parker [31]. Cold molecules and atoms were formed by supersonic beam expansion. Therefore, either a pulsed valve or a leak valve was used. The gas jet entered the electrostatic lens system through a small hole in the first plate of the lens system. To reduce the gas load in the flight tube the vacuum chamber was separated by a plate into two sections. Each section was pumped individually by a turbomolecular pump. On a common axis with the valve and the lens system a skimmer was mounted on top of the plate. The temperature and the density of the gas could be reduced by increasing the distance between the valve and the focus where the molecules or atoms were



Figure 2.1: Simplified depiction of the VMIS. Details are given in the text.

ionized by an intense laser beam. Through the static electric field of the lens system either the electrons or the ions were accelerated towards the detector, depending on the sign of the voltage applied to the lenses. The arrival of an ion or an electron at the detector triggered an avalanche of electrons which finally hit a phosphor screen. The light emitted from the screen at the position of the event was collected by a camera mounted outside the vacuum chamber. Additionally, one could read out the electronic response of the detector and record it with an oscilloscope. In this way it was possible to measure ion time-of-flight spectra. In the following subsections detailed information about the main parts of the spectrometer will be given.

2.1.1 Vacuum Chamber

The final design of the vacuum chamber is shown in figure 2.2. The custommade chamber was 80 cm high and had an inner diameter of 20 cm. To achieve ultra-high vacuum (UHV) all flanges were ConFlat (CF) flanges which use copper rings as gaskets. The chamber was vertically mounted on a metal frame (see figure 2.4). The height of the spectrometer including the metal frame was ~ 200 cm. Without the electronic devices the spectrometer occupied an area of one square meter. All components which were inside the vacuum chamber were either connected to the top or bottom flange (NW200CF). Only the mirror mount was fixed on an additional tube (NW100CF, 13 cm tube length) which could be connected to the flange opposite to the laser input flange (NW100CF). With the mirror mount inside the vacuum chamber it was possible to use mirrors with focal lengths between 75 mm and 200 mm. Mirrors with



Figure 2.2: Different views of the spectrometer. The spectrometer was vertically mounted on a metal frame. All elements which were inside the chamber were connected with the top or bottom flange except for the mirror mount.

a longer focal length were mounted outside the chamber. In this case the tube was replaced with a window. A detailed image of the tube with mirror mount is given in figure 2.3. A zero-length reducer (NW100CF, NW35CF) together with a window (NW35CF) was connected to the laser input flange. Usually sapphire windows with a clear aperture of > 2 cm and a thickness of 2 mm or 2.5 mm were used. Optical elements which had to be placed close to the VMIS were mounted on an extension board (40 cm x 40 cm) which was attached directly to the chamber. The vacuum in the chamber was maintained by two turbomolecular pumps (Pfeiffer TPH 450H). The pumping speed was 450 1/min each. For the pre-vacuum an oil-free scroll pump (Varian TriScroll 300) with a pumping speed of 210 l/min was used. Without gas load the pressure in the spectrometer reached 10^{-8} mbar. The pressure of the prevacuum was between $3 \cdot 10^{-2}$ mbar and $5 \cdot 10^{-2}$ mbar. The pressure inside the chamber was first measured with two full range gauges (Pfeiffer PKR 251 in combination with the control unit Pfeiffer TPG 256A). These cold cathode gauges use magnets and although the magnets and the flight tube were



Figure 2.3: Tube (NW100CF) with mirror mount for mirrors with a diameter of one inch. Mirrors with a focal length between 75 mm and 200 mm could be mounted inside the vacuum chamber.

shielded with permalloy we could observe small aberrations of the velocity map images due to the magnetic field. Therefore, the two gauges were replaced by hot filament gauges (Kurt J. Lesker KJLC 354) without magnets. The pre-vacuum was measured directly behind the two turbo pumps and at the differentially pumped linear motion feedthrough with three Pirani gauges (Pfeiffer TPR 280). The gauge control unit (Pfeiffer TPG 256A) was also connected to the measurement computer to monitor the pressure inside the vacuum chamber during the measurements.

2.1.2 Top Flange Assembly

The complete top flange assembly is shown in the figures 2.5(a)-(d). The lower part of the manipulator (blue component in the figures 2.5(a) and (b), Thermionics Northwest Inc., EC-B275C-T275T-1.39-2) was directly connected to the flange. The upper part of the manipulator could be moved along the x, y and z axis. A double-sided flange (NW35CF) with a welded tube (green part in figure 2.5(a) and (b)) was connected to this part of the manipulator. The tube went through the welded below and ended ~ 7 cm below the main flange. All mechanical parts including the valve, the base plate with skimmer (Beam Dynamics Model A, 1 mm orifice) and the electrostatic lens system were connected to this tube. In this way the center of the lens system could be easily adjusted to the focus of the beam. The electrostatic lens system was fixed on the lower side of the base plate. A detailed description of the lens system will be given in the next section. The base plate had a diameter of 180 mm and in the center a hole with a diameter of 30 mm. If the skimmer was used this hole was covered by the skimmer holder. Two UHV compatible actuators (Newport Ultra-High Vacuum Picomotor Actuator 8301-UHV and 8302-UHV) were used to adjust the position of the skimmer and to move it in and out (see figure 2.5(c) and (d)). The base plate separated the chamber in two parts. To reduce diffusion of the gas through the gap between the cham-



Figure 2.4: Picture of the VMIS with the control unit and sample gas supply system.

ber wall and the base plate a separation tube (olive green component in figure 2.5(c) and (d)) sat loose on the brim of the base plate. The tube had an outer diameter of 196 mm and was 55 mm in height. With the separation tube a pressure ratio in the order of 100:1 between the compartment of the valve and that of the lens system could be maintained without losing the ability of freely positioning the lens system. Three rods connected the base plate with the end of the tube which was in turn connected to the manipulator. The valve system was mounted on a sliding assembly which was guided by the three rods. Either a leak valve (Lenox Laser, 10μ m orifice) or a pulsed valve (Even-Lavie valve, 1 kHz repetition rate, 150 μm orifice) were connected to the sliding assembly. With a differentially pumped linear motion feedthrough (Allectra 613-RLD200-DP-C40, depicted as red rod and black flange in the figures 2.5(a) and (b)) the z position of the sliding assembly was adjusted from outside. Two 40 kV and two 10 kV high-voltage (HV) feedthroughs were welded in the top flange for the connection of the electrostatic lenses. The flange had also three NW35CF ports which were used to connect additional electrical and gas feedthroughs.



Figure 2.5: (a)-(d) Different views of the top flange assembly. The electrostatic lens system, the skimmer and the valve were moved together with the xyz manipulator. The distance between the valve and the skimmer was adjusted with an additional manipulator. Two UHV compatible actuators were used to position the skimmer. If the skimmer was not used it was pushed away from the center by the help of the actuators (c).

2.1.3 Electrostatic Lens System

A dimensioned sectional drawing of the lens system and the flight tube is shown in figure 2.6. The electrostatic lens system consisted of the repeller, extractor and ground plate. The diameter of the plates was 76 mm. The skimmed gas pulse entered the lens system through a small hole (4 mm diameter) in the center of the repeller plate. To reduce field inhomogeneities due to the hole the repeller plate were cone shaped. The distance between the repeller and extractor plate was 17.8 mm. The extractor plate had a concentric hole with a diameter of 20 mm. The thickness of the plate was 1 mm. The dimensions of the ground plate were identical to the extractor plate. The two plates were separated by a distance of 30 mm. The distance between the point where the gas was ionized and the detector was ~ 308 mm depending on the exact position of the lens system. The flight tube was shielded by two permalloy tubes. The wall thickness of the tubes was 2 mm. The inner diameter of the smaller tube was 80 mm whereas the larger permalloy tube had an inner diameter of 104 mm. The active area of the detector had a diameter of 75 mm. For the sake of clarity the spacers placed between the electrodes are not shown in figure 2.6. A different view of the complete electrode assembly including the



Figure 2.6: Dimensioned sectional drawing of the lens system and the flight tube. All dimensions in the drawing are given in millimeters.



Figure 2.7: 3D view of the electrostatic lens system assembly. The spacers in green were made from polyether ether ketone (PEEK). The electrode stack was kept together by three screws which passed through the spacers.

spacers is given in figure 2.7. The spacers (green parts in figure 2.7) were made from polyether ether ketone (PEEK). The electrode stack was kept together by three screws inside the spacers. The ground plate was electrically connected through these screws to the chamber keeping the electrical potential of the plate at zero. The repeller and extractor plates were connected with kapton isolated wires to the high voltage feedthroughs which were welded in the top flange. When a positive voltage was applied to the repeller and extractor plate the ions which were generated in the laser focus were accelerated towards the detector whereas for negative voltages only the electrons left the lens system in the direction of the detector. By adjusting the voltage ratio between the two plates one could change the imaging properties of the lens system. If the two voltages were identical one obtained an image of the spatial charge distribution in the focus (spatial imaging mode) on the detector. However, if the ratio between the extractor and repeller voltage was 0.81 one obtained a momentum distribution image (velocity map imaging mode). The electron trajectories for this case are depicted in figure 2.8(a). The trajectories were calculated using SIMION 8.0. The electrons with energies of $0 \, \text{eV}$ (black traces), 2 eV (red traces), 4 eV (green traces) and 6 eV (blue traces) were released in the focus. The voltages of the repeller and extractor plate were set to -5 kV and -4.05 kV, respectively. For all electrons the initial velocity vector pointed in positive z direction whereas the z position was varied $(z = -2, \ldots, 2)$ mm). Although the starting position was different, all electrons with the same energy were focused onto the same spot on the detector. A figure of merit for the quality of the imaging property is the ratio $\Delta E/E$ where ΔE corresponds to the full width at half maximum of the spot on which electrons with energy E are imaged. In figure 2.8(b) $\Delta E/E$ as a function of the energy is shown. The red line indicates the measured resolution which was calculated based on the spectrum shown in figure 2.11(b). The spectrum was obtained from xenon ionized by a 400-nm pulse. The measured resolution for an energy of 2 eV was only 0.26. However, the width of the rings in figure 2.11(b) was mainly defined by the spectral width of the 400-nm laser pulse and the geometry of the laser focus and not by the resolution of the VMIS. For comparison, the result obtained from SIMION simulations were also plotted in figure 2.8(b) for electrons with an energy distribution width of 0.35 eV (blue line) and 0.1 eV(green line). For the two calculations the repeller plate was kept at -5.00 kVand the extractor plate at -4.05 kV (identical to the experimental conditions). The electrons were released within a sphere with radius 0.5 mm on the axis of the lens system between the repeller and extractor plate. The obtained resolution for an energy distribution of 0.35 eV (blue line) was close to the experimental result. For an energy distribution of 0.1 eV the resolution was $\Delta E/E = 0.06$ at E = 2 eV which shows that the imaging properties of the VMIS were sufficient. For a repeller voltage of -5 kV electrons with a maximal kinetic energy of 40 eV were focused on the detector. Usually -10 kV were applied which means that electrons with energies up to 80 eV were detected. Electrical breakdowns were observed for voltages above -15 kV. Due to safety reasons voltages higher than -20 kV were not applied. For the experiments two Spellman RHSR10PN60/BPS/FG/220 (±10 kV) high-voltage (HV) power supplies were used. The resolution of the VMIS in the time-of-flight mode is given in figure 2.8(c). It shows the width of the TOF signal $\Delta m/q$ for a given mass-to-charge ratio m/q. For $m/q = 77 \ \Delta m/q$ becomes one which means that two peaks which differ by m/q = 1 could be clearly resolved up to m/q = 77. For higher mass-to-charge ratio the peaks started to overlap. In the time-of-flight mode the resolution was limited by the response of the detector.





Figure 2.8: (a) Trajectories of electrons with an energy of 0 eV (black), 2 eV (red), 4 eV (green) and 6 eV (blue). The starting position varied between z = 2 mm and z = -2 mm. All electrons started with a momentum pointing parallel to the z axis. (b) $\Delta E/E$ as a function of the electron energy E. The red line represents the experimental result. The blue and green lines were calculated for an initial energy distribution of 0.35 eV and 0.1 eV, respectively. (c) Measured peak width of an ion time-of-flight spectrum as a function of the mass-to-charge ratio.

2.1.4 Bottom Flange Assembly

The permalloy tubes and the detector were mounted concentric on a zerolength reducer flange (NW200CF to NW100CF). On the opposite side a standard glass view port (NW100CF) with a view diameter of 90 mm was connected. Additionally four rods were attached to the flange. They were used to fix the camera mount. The distance between the camera mount and the flange was on the order of 20 cm. Three HV feedthroughs were directly welded into the zero-length reducer flange to connect the chevron microchannel plate detector (MCP) to the HV power supplies. The MCP detector was manufactured by Photonis. The diameter of the active area of the MCP detector was 75 mm. The pore size was 10 μ m, the center-to-center spacing 12 μ m and the bias angle 8° ± 1°. The thickness of the two MCP plates together was 1.2 mm. The maximum electron gain was 10⁷ at 2400 V. The detector assembly contained a P20 phosphor screen. For electron and ion imaging the phosphor screen was kept at +3300 V. To image electrons the input of the



Figure 2.9: Different views of the bottom flange assembly. The permalloy tubes and the microchannel plate detector were mounted on top of the flange. The camera mount was fixed with four rods to the outer side of the flange.

MCP assembly (front plate of the MCP) was connected to ground whereas a positive voltage between +1000 V and +2000 V was applied to the output (rear plate of the MCP). To image positive ions the output of the MCP was connected to ground and a negative voltage was applied to the input. However, to restrict the measurement to ions with a selected mass-to-charge ratio it was necessary to switch the input voltage such that the MCP was only active at the arrival time of the ions. A home build fast HV switch was used for this purpose. This device was able to switch the output voltage between two input voltage levels. The response of the output is shown in figure 2.10 for an input trigger signal with pulse lengths of 200 ns (black line), 100 ns (green line), 75 ns (blue line) and 50 ns (red line). For the measurement 700 V and 1500 V were applied to the two HV inputs. It was not necessary to switch the MCP input between 0 V and 1500 V because the MCP was not active if the input voltage was below 1000 V. The rise time of the HV switch output voltage was 100 ns. For trigger pulses shorter than 75 ns the output voltage did not exceed 1000 V which means that the MCP staved inactive. For the measurement of ions the HV switch was essential. However, the switch was also used to measure photoelectrons in order to reduce the background signal of secondary electrons. For the experiments three HV power supplies were used (Stanford Research Systems PS 350, ± 5 kV). One was connected to the phosphor screen the others were used for the HV switch. A digital delay generator (Stanford Research Systems DG645) was used for the distribution of the laser trigger signal. The HV switch and valve driver were connected to this device. Images of the phosphor screen were acquired with a chargecoupled device (CCD) camera (PCO Sensicam, 1280x1024 pixel resolution, 12 bit dynamic range, quantum efficiency up to 60%) in combination with a fixed focal length objective (Thorlabs MVL16M23, 16 mm focal length, f/1.4 aperture). The time-of-flight signal was tapped from the MCP input. A home-built



Figure 2.10: Output signal of the HV switch for input trigger pulses with pulse lengths of 200 ns (black line), 100 ns (green line), 75 ns (blue line) and 50 ns (red line). For the measurement 700 V and 1500 V were applied to the two HV inputs of the switch.

amplifier with an amplification of 33 and a band width of 410 MHz was used to amplify the AC signal which was then recorded by the oscilloscope (LeCroy WaveJet 354A, digital oscilloscope, 500 MHz band width, 2 GS/s). The band width of the amplifier and the oscilloscope were sufficient to resolve peaks with a full width at half maximum (FWHM) of ~ 2 ns. However, the FWHM of a single peak in the TOF spectrum was ~ 30 ns. The reason for that was the high capacity (~ 50 pF) of the MCP itself. Together with the amplifier the MCP corresponded to a RC-element with a band width of only ~ 30 MHz. This was the reason for the limited mass resolution (see figure 2.8(c)).

2.1.5 Image Processing

The two-dimensional (2D) image obtained from the VMIS represents a projection of the three-dimensional (3D) photoelectron momentum distribution spectrum. For linear polarization the 3D photoelectron spectrum has a cylindrical symmetry along the laser polarization axis. Therefore, the 3D distribution is fully described by $f(p_r, p_z)$ where p_z and p_r correspond to the momentum parallel and perpendicular to the polarization axis, respectively. The 2D distribution on the detector $g(p_x, p_z)$ is related with the 3D distribution by an Abel integral [32], i.e.

$$g(p_{\rm x}, p_{\rm z}) = 2 \int_{|p_{\rm x}|}^{\infty} \frac{p_{\rm r} f(p_{\rm r}, p_{\rm z})}{\sqrt{p_{\rm r}^2 - p_{\rm x}^2}} dp_{\rm r} \equiv A \left\{ f(p_{\rm r}, p_{\rm z}) \right\}.$$
 (2.1)

To obtain $f(p_r, p_z)$ from $g(p_x, p_z)$ the inverse of equation 2.1 has to be solved. However, this is a non-trivial task and therefore an iterative inversion method was used where only the functional A appears. The method is closely related to the procedure developed by M. Vrakking [33]. The procedure starts with



Figure 2.11: (a) Electron image obtained from xenon ionized by a 400-nm pulse. The laser peak intensity was $(3 \pm 1) \cdot 10^{13}$ W/cm². (b) Abel-inversion of the image shown in (a) obtained with the iterative inversion method explained in the text.

the Ansatz given in equation 2.2. Then equation 2.3 is solved iteratively until the difference between the measured projection $g(p_x, p_z)$ and the calculated projection $A\{f(p_r, p_z)\}$ is small. The parameter c in equation 2.3 corresponds to the correction amplitude.

$$f_0(p_{\rm r}, p_{\rm z}) = g(p_{\rm x}, p_{\rm z})$$
 (2.2)

$$f_i(p_r, p_z) = f_{i-1}(p_r, p_z) + c \left(g(p_x, p_z) - A \left\{f_{i-1}(p_r, p_z)\right\}\right)$$
(2.3)

An example of the inversion is given in figure 2.11. The 2D spectrum (raw image) $g(p_x, p_z)$ obtained from xenon multiphoton-ionized by a 400-nm laser pulse is shown in figure 2.11(a) and the retrieved 3D spectrum is given in figure 2.11(b). This iterative inversion procedure leads to the accumulation of noise along the symmetry axis of the spectrum.

2.2 The Laser System

The laser used for the experiments was a Legend Elite Duo USX 1K HE laser system from Coherent. The system contained a Coherent Micra-5 Titanium:sapphire laser oscillator system which produced mode-locked pulses with bandwidths of 100 nm at a center wavelength of 800 nm. The repetition rate was 80 MHz. The energy per pulse was on the order of 6 nJ. The output of the Micra-5 passed first the stretcher before it entered the regenerative amplifier which was pumped by a Coherent Evolution-30 diode-pumped, intra-cavity doubled, Q-switched Nd:YLF laser with a repetition rate of 1 kHz at 527 nm. The pulse energy of the Coherent Evolution-30 exceeded 20 mJ. After the regenerative amplifier the pulses had an energy of 3.3 mJ at a



Figure 2.12: (a) Spectrum of the laser output. (b) Pulse shape retrieved from a FROG measurement (blue line). The full width at half maximum of the Gaussian fit (red line) is 38 fs.

repetition rate of 1 kHz. The pulses were further amplified in a single-path amplifier stage which was pumped by a Coherent Evolution HE laser system which was similar to the Coherent Evolution-30 laser system except that the pulse energy was 38 mJ. After the single-pass amplifier stage pulse energies of 11 mJ were measured. After passing the compressor the pulses had an energy of 8 mJ and a pulse length of 38 femtoseconds. A typical spectrum of the laser output is shown in figure 2.12(a). The pulse shape which was retrieved from a frequency-resolved optical-gating (FROG) measurement is shown in figure 2.12(b). Additionally, an optical parametric amplifier (Light Conversion HE-TOPAS-C) was used for some experiments. With the optical parametric amplifier (OPA) it was possible to shift the center wavelength of the laser output to a wavelength between 1160 nm and 2580 nm. The conversion efficiency into signal or idler beams was between 5% and 25% depending on the output wavelength. For a reliable operation of the OPA a pulse energy of 6.5 mJ at the input was required.

Chapter 3

Electronic and Rotational Wave Packets in Nitric Oxide

The observation of electronic coherence in molecules was one of the main goals of this thesis. In this chapter an experiment is presented where an electron wave packet was examined by means of angle-resolved photoelectron spectroscopy. The chapter starts with a short introduction summarizing results obtained by high-harmonic spectroscopy. In the subsequent sections the specific experimental details will be explained followed by the presentation and discussion of the results. The chapter closes with a summary of the conclusions.

3.1 Introduction

Different previous experiments have shown that momentum-resolved photoelectron spectroscopy is a suitable tool to gain insights into electronic or nuclear structure of atoms or molecules [24–26, 34]. In the angle- and energyresolved photoelectron spectra the high-energy electrons have rescattered from the parent cation. Their angular distribution is directly related to the elastic differential electron scattering cross section of the target ion [8, 35]. Furthermore, also holographic patterns were observed. They were assigned to sub-laser-cycle time scale electron dynamics [27]. On the basis of this knowledge we have investigated an electron wave packet in nitric oxide. This was first observed by means of high-harmonic spectroscopy [13] where an electronic wave packet was prepared by a first pulse through stimulated Raman scattering. The subsequent probe pulse generated high-order harmonics which were analyzed with a spectrometer. The signal, integrated over the harmonic 9 to 23 as function of the pump-probe delay (figure 3.1(a)), showed a modulation with a period of $T = 275 \pm 3$ fs. This was in agreement with the energy level splitting of the two low-lying electronic states ${}^{2}\Pi_{1/2}$ and ${}^{2}\Pi_{3/2}$ of NO which are separated by ~ 120 cm⁻¹. In the limit of a low total angular momentum



Figure 3.1: (a) High-harmonic intensity integrated over the harmonic orders 9 to 23 as function of the pump-probe delay. The signal between 1 and 2 ps modulated with a period of $T = 275 \pm 3$ fs. (b) Temporal evolution of the electron density of the wave packet for the two spin states $\Sigma = \pm 1/2$. Figure adapted from [13].

J = L + S + R, where L stands for the total orbital angular momentum, S the total electron spin and R the angular momentum of the rotating nuclei, the wave packet

$$\left|\Psi^{+}(t)\right\rangle = \frac{1}{\sqrt{2}} \left(\left|^{2}\Pi_{1/2}\right\rangle + \left|^{2}\Pi_{3/2}\right\rangle e^{-i\Delta Et/\hbar}\right)$$
(3.1)

$$= \frac{1}{\sqrt{2}} \left(\left(\left| \pi^{+} \beta \right\rangle + \left| \pi^{-} \alpha \right\rangle \right) + \left(\left| \pi^{+} \alpha \right\rangle + \left| \pi^{-} \beta \right\rangle \right) e^{-i\Delta Et/\hbar} \right)$$
(3.2)

can be expressed as a coherent superposition of the ${}^{2}\Pi_{1/2}$ and ${}^{2}\Pi_{3/2}$ states. For brevity only the wave function with positive parity is considered. For the state with negative parity one would obtain a similar result. Equation 3.2 can be factorized into the spin parts α and β and one obtains

$$|\Psi^{+}(t)\rangle = \frac{1}{\sqrt{2}} \left(|\alpha\rangle \left(|\pi^{-}\rangle + |\pi^{+}\rangle e^{-i\Delta Et/\hbar} \right) + |\beta\rangle \left(|\pi^{+}\rangle + |\pi^{-}\rangle e^{-i\Delta Et/\hbar} \right) \right)$$
(3.3)

where $|\pi^{\pm}\rangle = |\pi_{\rm x}\rangle \pm i |\pi_{\rm y}\rangle$. The spatial wave functions $|\pi_{\rm x}\rangle$ and $|\pi_{\rm y}\rangle$ represent the real-valued molecular orbitals which lie in the xy or yz plane, respectively. One can show that the two spin parts of equation 3.3 correspond to two counter-rotating currents that rotate around the molecular axis. This is illustrated in figure 3.1(b) where the time evolution of the electron density $|\Psi^+(t)|^2$ is shown. Whether and how this wave packet influences the photoelectron momentum distribution was subject of this experiment and will be discussed after the section about the experimental details.



Figure 3.2: Sketch of the optical setup which was used for the two-pulse experiments. The abbreviations stand for: half-wave plate (WP), beam splitter (BS), mirror (M), translation stage (TS), lens (L), SF11 window (SF), velocity-map imaging spectrometer (VMIS).

3.2 Experimental Details

The setup, built for the two pulse experiments, is depicted in figure 3.2. The output of the laser with a center wavelength of 800 nm and a beam waist of 4.2 mm was split by a 50:50 beam splitter (BS1) into a pump and a probe beam. To increase the efficiency of the Raman transition, the pump pulse was stretched in time by a 3 mm thick SF11 window (SF). Further, the initial beam waist of the pump beam was reduced with a telescope (L1, L2) by a factor of 1.25 in order to increase the size of the focus of the pump beam inside the VMIS with respect to the size of the probe beam. With a second 50:50 beam splitter (BS2) the pump beam was then recombined with the probe beam. The time delay between the two pulses was adjusted by changing the path length of the probe pulse. Therefore, two mirrors (M5 and M6) were mounted on a linear translation stage (TS; controller: Newport ESP 100; translation stage: Newport UTM100PP.1 with a resolution of 100 nm). Finally, the laser was focused with a thin lens (f = 400 mm) into the VMIS. Typical intensities and pulse lengths of the pump and probe beams were $(1.2 \pm 0.2) \cdot 10^{14} \text{ W/cm}^2$ and 145 ± 2 fs, respectively $(2.3 \pm 0.1) \cdot 10^{14}$ W/cm² and 35 ± 2 fs. A crosscorrelation scan of both pulses is shown in figure 3.3(a). For the experiment a mixture of 1% NO in helium was prepared and injected into the VMIS with



Figure 3.3: (a) The blue line shows the normalized total photoelectron yield of a cross-correlation scan of the pump and probe pulses. The enveloping Gaussian function has a full-width at half maximum of 105 fs. (b) Ion time-of-flight measurement of the He/NO/Xe mixture. Fragments or multiply-charged parent ions of NO were not observed at the given intensities whereas very little Xe²⁺ ions were detected (small peak $m/q \approx 66$) besides the Xe⁺ signal.

an Even-Lavie valve (orifice $\phi 150 \ \mu m$). A skimmer (1 mm orifice) was used to increase the cooling efficiency of the gas jet. The distance between the nozzle and the skimmer was 5 cm. For the ion TOF measurement a small amount of xenon (less than 1%) was added to the gas mixture to use the Xe⁺ ion signal as an internal reference. Figure 3.3(b) shows a typical ion TOF spectrum. For the given intensities neither multiply-charged parent ions nor charged fragments of NO were observed. In case of xenon very little Xe²⁺ ions were detected in addition to the Xe⁺ ions.

3.3 Results

3.3.1 Ion Time-of-flight Measurement

Figure 3.4(a) shows the ion yield of NO^+ as a function of the pump-probe delay. A modulation of the signal cannot be recognized at first glance. As a comparison, the ion yield of Xe⁺, measured at the same time as the NO⁺ yield, is given in figure 3.4(b). In contrast to NO the pump pulse does not excite an electron wave packet in xenon. Therefore, the Xe⁺ signal directly reflected the fluctuations resulting from the highly nonlinear laser-induced strong-field ionization and gas-jet instabilities which, together, were on the order of 15% to 20%. By using the xenon signal as an internal reference to normalize the NO⁺-yield, the fluctuations could be reduced dramatically. This was done in order to obtain figure 3.4(c) where the ratio between the NO⁺ and the Xe⁺



Figure 3.4: For the ion time-of-flight measurements a gas mixture with 1% NO and <1% xenon in helium was used. The ion yield of NO⁺ and Xe⁺ for different pump-probe delays is shown in (a) and (b), respectively. The ratio of the two yields is given in (c).

signal

$$r = \frac{n_{\rm NO^+}}{n_{\rm Xe^+}},\tag{3.4}$$

where $n_{\rm NO^+}$ ($n_{\rm Xe^+}$) stands for the normalized NO⁺ (Xe⁺) yield, is depicted. The ratio r shows a modulation with a period of 277±3 fs whereas the modulation amplitude decreases for increasing pump-probe delays. Further, dips at 5, 10 and 15 picoseconds can be identified. From the ion time-of-flight spectrum (figure 3.3(b) it was known that for the given intensity only NO⁺ ions were produced. For that reason the integrated NO⁺ yield was directly related with the ionization rate of NO. The modulation of the yield and thus of the ionization rate was a clear indication that a wave packet was indeed excited by the pump pulse. More information was obtained from the power spectrum of the ratio r which is given in figure 3.5(a). In the spectrum a dominant peak at 120.5 cm⁻¹ with an amplitude of 1.6% is visible. The amplitude of the other peaks are at least three times lower and from figure 3.5(a) it is difficult to evaluate whether they can be assigned to a transition or whether they are



Figure 3.5: (a) Fourier-transformed power spectrum of the ratio r. (b) Interpolated spectrum of (a) with calculated peak positions. The interpolation was introduced by zero padding of the time-domain measurement.

just artefacts. Therefore, the spectrum was interpolated by zero-padding. The result is shown in figure 3.5(b) together with the labeled positions of rotational and electronic-rotational transitions. The positions of these labels were calculated by solving the Schrödinger equation for a Hamiltonian including the rotational motion as well as the spin-orbit interaction [13]. The eigenstates of this Hamiltonian are labeled F_1 and F_2 with the eigenenergies

$$E_J^{F_1} = B\left(J - \frac{1}{2}\right)\left(J + \frac{3}{2}\right) - \sqrt{B^2\left(J + \frac{1}{2}\right)^2 + \frac{A(A - 4B)}{4}} + \frac{A - 2B}{2} \quad (3.5)$$

and

$$E_J^{F_2} = B\left(J - \frac{1}{2}\right)\left(J + \frac{3}{2}\right) + \sqrt{B^2\left(J + \frac{1}{2}\right)^2 + \frac{A(A - 4B)}{4}} + \frac{A - 2B}{2} \quad (3.6)$$

where J represents the total angular momentum quantum number, $A = 123.13 \text{ cm}^{-1}$ the spin-orbit coupling constant and $B = 1.6961 \text{ cm}^{-1}$ the ground-state rotational constant [13]. Note that for low J numbers F_1 is dominated by the ${}^{2}\Pi_{1/2}$ state and F_2 by the ${}^{2}\Pi_{3/2}$ state. From the eigenenergies



Figure 3.6: Signal analysis in the time domain. (a) Spectrum of the measured ratio r (blue) and of the filter functions W_1 (red), W_2 (green) and W_3 (black). The processed signal is given in (b)-(d) after applying the filters W_1 , W_2 or W_3 .

one obtains the transition energies

$$\Delta E_{J'',\Delta J}^{\rm rot} = E_{J''+\Delta J}^{\rm F_1} - E_{J''}^{\rm F_1} \tag{3.7}$$

for pure rotational transitions or

$$\Delta E_{J'',\Delta J}^{\rm el} = E_{J''+\Delta J}^{\rm F_2} - E_{J''}^{\rm F_1} \tag{3.8}$$

for mixed, electronic and rotational transitions. Using equation 3.8 the peak at 120.5 cm⁻¹ could be assigned to a transition between the F_1 and the F_2 state for $\Delta J_{\rm el} = 0$. This was the proof that the pump-pulse created electronic coherence between the ${}^{2}\Pi_{1/2}$ ground state and the ${}^{2}\Pi_{3/2}$ excited state. But also pure rotational coherence was observed. The corresponding peaks appear in the spectrum around 40 cm⁻¹ for $\Delta J_{\rm rot} = 2$ and around 80 cm⁻¹ for $\Delta J_{\rm rot} = 4$. Even mixed rotational-electronic coherences for $\Delta J_{\rm el} = -1$ and $\Delta J_{\rm el} = 1$ occurred and led to peaks close to the peak at 120.5 cm⁻¹. Without an interpolation of the spectrum it would have been difficult to assign the small peaks to certain transitions. But also the analysis in the time domain showed that a rotational as well as an electronic wave packet was created by the pump pulse. Therefore, the signal given in figure 3.4(c) was processed by applying three different filter functions. The filter functions are depicted in figure 3.6(a). By applying filter W_1 (red line) the function given in figure



Figure 3.7: (a) Normalized total electron yield versus pump-probe delay. The exact delays of the measured spectra were: $\Delta t_{S_1} = 1.56$ ps, $\Delta t_{S_2} = 1.60$ ps, $\Delta t_{S_3} = 1.64$ ps, $\Delta t_{S_4} = 1.68$ and $\Delta t_{S_5} = 1.72$ ps. (b) Raw spectrum S_1 measured at 1.56 ps. The spectrum is not Abel inverted and represents a projection of the real momentum distribution.

3.6(b) was obtained. It shows clear revivals at 5, 10 and 15 ps which is characteristic for rotational coherence induced by impulsive laser alignment [36, 37]. Using filter W_2 (green line) one obtains the signal traces depicted in figure 3.6(c). From the spectral analysis it was known that frequencies within the transmission range of this filter correspond to rotational-electronic transitions. The revival of the signal around 9 ps in figure 3.4(c) and figure 3.6(c) was thus attributed to the mixed rotational-electronic wave packet [13]. Finally, figure 3.6(d) shows the dephasing of the electronic wave packet which becomes visible if W_3 (black line) is applied. This filter removes everything except for the frequencies which correspond to the $\Delta J_{\rm el} = 0$ transitions. Dephasing occurs because the energy level splitting between two adjacent rotational levels increases with the quantum number J. By selecting the proper time interval it is thus possible to restrict the observation to a wave packet which is dominated by the electronic or rotational coherence. In the next two sections the angular resolved electron momentum distributions characterizing the two different types of dynamics are presented.

3.3.2 Observation of the Electronic Coherence

The angle-resolved photoelectron momentum distributions were measured under the same conditions as the ion time-of-flight measurements. From the time domain analysis of the normalized NO^+ signal (see figure 3.6(b)-(d)) it was known that the optimal delay to observe the electronic coherence was between 1 and 2 ps. In this time interval the electronic coherence is still large and the molecular axis distribution varies very little. A temporal overlap of the



Figure 3.8: Normalized difference $D_5(\mathbf{p})$ calculated from the raw spectra (a) and Abel inverted spectra (b) of S_1 and S_5 .

pump and probe pulse could also be excluded (see figure 3.3). To obtain a maximal signal-to-noise ratio the electron spectra were recorded at only five different delays within a half-cycle of the electronic coherence. The total electron yield of these spectra is shown in figure 3.7(a). To simplify the further discussion the spectra are labeled with S_n where n = 1 - 5. As an example figure 3.7(b) shows the raw spectrum S_1 . The delay at which the spectrum S_1 and S_5 were measured was chosen such that for S_1 the electron yield was minimal and for S_5 maximal. The data acquisition took in total 24 hours during which each spectrum was repeatedly measured. The total integration time of a single spectrum was in the end close to 4 hours. The polarization vectors of the pump and probe beams were both parallel to p_z . The modulation depth of the total electron yield was 2% which was slightly less than what was expected from the NO⁺ ion yield measurement (modulation depth of ~ 3%). The total modulation of the signal was further compared with the modulation of the electron yield as a function of the final momentum p. Therefore, the normalized difference

$$D_5(\mathbf{p}) = 2\frac{S_5(\mathbf{p}) - S_1(\mathbf{p})}{S_5(\mathbf{p}) + S_1(\mathbf{p})}$$
(3.9)

between $S_1(\mathbf{p})$ and $S_5(\mathbf{p})$ was calculated for the unprocessed spectra as well as for the Abel inverted spectra. The result is depicted in figure 3.8(a) and 3.8(b), respectively. For the normalized difference we find that $D_5(\mathbf{p}) \ge 0$. Further, a strong dependence of the difference on \mathbf{p} was observed. In figure 3.8(a) the maximal normalized difference is ~ 4.7% for electrons with a final momentum close to $p_x = 0$ and $p_z = \pm 1$ a.u.. For $|p_z| > 1.4$ a.u. the differences are $D_5(\mathbf{p}) \leq 1\%$. Parallel to the main structure along p_z one can also observe side lobes. These structures are amplified in the normalized difference image of the inverted spectra (figure 3.8(b)). To obtain an optimal inversion of the initial spectra the constant background (due to camera dark counts and stray light) was removed. Furthermore, the spectra were symmetrized. These corrections enhanced the differences compared to figure 3.8(a). In the normalized difference image of the inverted spectra the limit of the transversal momentum $|p_x| \approx 1.3$ a.u. is clearly visible.

So far only the spectra measured at the minimum and maximum of the total electron yield function were compared and it remains to be verified whether the pattern changes its shape as a function of the pump-probe delay. Therefore, the normalized difference

$$D_n(\mathbf{p}) = 2 \frac{S_n(\mathbf{p}) - S_1(\mathbf{p})}{S_n(\mathbf{p}) + S_1(\mathbf{p})}$$
(3.10)

between spectra measured at different delays were compared. In the figures 3.9(a)-(d) $D_n(\mathbf{p})$ is shown for n = 2 - 5. One can see that the pattern only changes in amplitude but not in shape. We have also performed measurements over different and longer pump-probe delay ranges. All of them led to the same conclusions. In summary, strong modulations could only be observed within a certain momentum range whereby the maximal modulation amplitude was larger than the modulation amplitude of the total electron yield.

Similar spike-like structures, known as photoelectron holography pattern, had been observed in other experiments [27, 28, 38, 39] and were attributed to the interference of scattered and unscattered photoelectrons. There are several indications that the observed pattern was the result of interfering electron trajectories. But before these are discussed, a short introduction to photoelectron holography will be given starting with the time evolution of a one-electron wave function $\Psi(t)$ in presence of a laser-induced interaction potential $V_{\rm L}$ and a Coulomb potential $V_{\rm C}$. The exact wave function, starting with a bound initial state $\Psi(0)$, can be written as [27]

$$\begin{split} |\Psi(t)\rangle &= -\int_{0}^{t} \mathrm{d}t_{0} \int_{t_{0}}^{t} \mathrm{d}t_{r} U_{\mathrm{V}}(t,t_{\mathrm{r}}) V_{\mathrm{C}}(t_{\mathrm{r}}) U(t_{\mathrm{r}},t_{0}) V_{\mathrm{L}}(t_{0}) U_{0}(t_{0},0) \left|\Psi(0)\right\rangle \\ &- i \int_{0}^{t} \mathrm{d}t_{0} U_{\mathrm{V}}(t,t_{0}) V_{\mathrm{L}}(t_{0}) U_{0}(t_{0},0) \left|\Psi(0)\right\rangle \\ &+ U_{0}(t,0) \left|\Psi(0)\right\rangle. \end{split}$$
(3.11)

At the beginning the electron is bound and the time evolution is given by the field-free propagator U_0 . The first term in equation 3.11 describes the time evolution of the rescattered photoelectron. At time t_0 the interaction with the field $V_{\rm L}(t_0)$ induces a transition to the continuum. Propagation of the continuum electron between the time t_0 and $t_{\rm r}$ under the action of the


Figure 3.9: (a) - (d) Normalized difference $D_n(\mathbf{p})$ for n = 2 - 5 calculated from the Abel inverted spectra.

full propagator $U(t_{\rm r}, t_0)$ follows, where at $t_{\rm r}$ the electron is scattered by the Coulomb potential $V_{\rm C}(t_{\rm r})$. At time t it finally reaches the detector. Between the time $t_{\rm r}$ and t the propagation is described by $U_{\rm V}(t, t_{\rm r})$ which only includes the potential of the laser field. The second term of equation 3.11 represents the unscattered photoelectron. Again, the electron is bound until ionization occurs at t_0 through the laser field $V_{\rm L}(t_0)$, followed by the propagation to the detector under the action of $U_{\rm V}(t, t_0)$. The last term of equation 3.11 describes the time evolution of the residual bound-state wave function. In brief, the wave function of the free electron can be written as the sum of a signal (scattered) wave function $\Psi_{\rm sig}$ and a reference (unscattered) wave function $\Psi_{\rm ref}$

$$\Psi = \Psi_{\rm sig} + \Psi_{\rm ref}.\tag{3.12}$$

The interference between Ψ_{sig} and Ψ_{ref} leads to a holographic pattern in the photoelectron spectrum. In reference [27] the interference pattern was analyzed starting with equation 3.11 and using the strong-field and saddle-point approximations. In the following, a simplified picture based on the classical recollision three-step model, developed by Bian et al. [29], will be presented. Again, one starts at time t_0 where the electron reaches the continuum through tunneling ionization at a distance $z(t_0) = -I_{\text{P}}/E_0$ from the core. For the

subsequent propagation in the laser field $\boldsymbol{E}(t) = \hat{\boldsymbol{z}} E_0 \cos(\omega t)$ the influence of the Coulomb potential is neglected and the electron trajectories are calculated based on Newton's equation of motion (in atomic units)

$$\ddot{z}(t) = -E_0 \cos(\omega t). \tag{3.13}$$

For the position of the electron at a later time t it follows [40]

$$z(t) = z(t_0) + \frac{E_0}{\omega^2} \left(\cos(\omega t) - \cos(\omega t_0) \right) + \left(\frac{E_0}{\omega} \sin(\omega t_0) + \dot{z}(t_0) \right) \left(t - t_0 \right).$$
(3.14)

The next assumption includes that the initial velocity parallel to the field is $v_{z, sig}(t_0) = v_{z, ref} = 0$ for the scattered (signal) and unscattered (reference) electron. Additionally, the initial velocity of the scattered electron perpendicular to the electric field has to be $v_{x, sig}(t_0) = 0$. Otherwise the electron will not return to the parent ion [5]. The time of the first return t_r is thus related to the ionization time t_0 by

$$\cos(\omega t_{\rm r}) - \cos(\omega t_0) + \omega \sin(\omega t_0)(t_{\rm r} - t_0) - \gamma^2/2 = 0.$$
 (3.15)

where $\gamma = \sqrt{2I_{\rm p}}\omega/E_0$ stands for the Keldysh parameter. Between the time t_0 and $t_{\rm r}$ the velocity is given by

$$v_{\rm z}(t,t_0) = -\frac{E_0}{\omega} (\sin(\omega t) - \sin(\omega t_0)).$$
 (3.16)

At the moment when the signal electron returns to the parent ion it is elastically scattered in the direction θ and one obtains for the final momentum at the detector

$$p_{\rm z, sig}(t_{\rm r}, t_0) = \frac{E_0}{\omega} \sin(\omega t_{\rm r}) + \cos(\theta) v_{\rm z}(t_{\rm r}, t_0)$$
(3.17)

parallel and

$$p_{\rm x, \, sig}(t_{\rm r}, t_0) = \sin(\theta) v_{\rm z}(t_{\rm r}, t_0)$$
 (3.18)

perpendicular to the field where multiple scattering of the electron by the target was neglected and the vector potential A(t) is assumed to be zero at the end of the pulse. Interference between the scattered signal electron and the reference electron occurs only if both electrons have the same momentum directly after the scattering event. Therefore, the relation

$$v_{\rm z, \, ref}(t_{\rm r}, t_0') = \cos(\theta) v_{\rm z}(t_{\rm r}, t_0),$$
 (3.19)

where t'_0 stands for the ionization time of the reference electron, must be valid. We further assume that the initial momentum distribution of $v_{\rm x, \, ref}$ of the reference electron after tunneling ionization is larger compared to $v_{\rm x, \, sig}$ so that

$$v_{\rm x, \, ref} = v_{\rm x, \, sig} = \sin(\theta) v_{\rm z, \, sig}(t_{\rm r}, t_0) \tag{3.20}$$

is always true for all θ and t_0 . The phase difference between the signal and reference electron is then given by

$$\Delta \Phi = \int_{t_0}^{t_r} \frac{v_z^2(\tau, t_0)}{2} d\tau - \int_{t'_0}^{t_r} \frac{v_z^2(\tau, t'_0)}{2} d\tau - \frac{v_{x, ref}^2(t_r - t'_0)}{2} - \frac{I_p(t_0 - t'_0)}{\omega}.$$
 (3.21)

In this equation t_0 and θ are the independent variables. To obtain a phase difference as a function of the final momentum additional restriction for t'_0 has to be introduced because different ionization times are associated with the same final momentum. The restrictions are illustrated in the upper panel of the figures 3.10(a)-(d). In the first case t_0 and t'_0 are within the same quartercycle and only the forward scattered signal electrons will interfere with the reference electrons. This results in a holographic pattern depicted in the lower panel of figure 3.10(a) where $\cos(\Delta \Phi)$ is plotted. For the second case the signal electron is also forward-scattered but the reference electron is generated within the next quarter-cycle. This gives than a ring pattern centered at zero momentum which is shown in the lower panel of figure 3.10(b). In the third case, the signal electron needs to be backscattered that interference with the reference electron generated within the third quarter-cycle can occur. One obtains the pattern given in the lower panel of figure 3.10(c). The last case where the signal electron is also backscattered and the reference electron is generated in the fourth quarter-cycle leads then to a wave pattern shown in the lower panel of figure 3.10(d). For the calculation of the holographic patterns laser parameters as given in section 3.2 for the probe pulse were used. Out of these four holographic patterns the one given in figure 3.10(a) is very similar to the pattern of the normalized difference $D_5(\mathbf{p})$. For comparison reasons the maxima and minima of the calculated holographic pattern is shown on top of the measured spectrum in figure 3.11. Both patterns have a wide lobe close to $p_{\rm x} = 0$ and narrow side-lobes but the position of the maxima and minima do not match. For the calculated pattern the distance between the extremal values are slightly larger. Both patterns end at $p_z \approx 1.4$ a.u.. This momentum corresponds to a kinetic energy of $2U_{\rm p}$ where

$$U_{\rm p} = \frac{I}{4\omega^2} \tag{3.22}$$

stands for the ponderomotive energy in atomic units of a free electron in a laser field with intensity I and frequency ω . An electron which does not scatter at the parent ion cannot hit the detector with more kinetic energy in average than $2U_{\rm p}$ and thus interference between a scattered and unscattered electron can only occur below this limit. In figure 3.11 this limit is indicated by the blue horizontal line.

In equation 3.20 the assumption was made that the initial momentum distribution of the reference electron perpendicular to the tunneling direction



Figure 3.10: (a)-(d) In the upper panel the ionization time of the signal electron t_0 and the reference electron t'_0 are illustrated. In the lower panel the corresponding holographic pattern $\cos(\Delta\Phi)$ calculated for the same laser pulse parameters as given in section 3.2 are shown. The figure is adapted for NO from reference [29]. However, until now we were not able to reproduce the structure along $p_x = 0$ a.u. as observed in the holographic pattern (b)-(c) therein.

covers the whole range of the transversal momentum $v_{\rm x, sig}$ of the signal electron. Therefore, the holographic pattern shown in figure 3.10(a) goes from $p_{\rm x} = -1.4$ a.u. to $p_{\rm x} = 1.4$ a.u. for $p_{\rm z} = 0$ a.u.. But in the measured spectrum the pattern already ends at $p_{\rm x} \approx \pm 0.5$ a.u. although electrons with a lateral momentum up to $p_{\rm x} = \pm 1.4$ a.u. were detected. This is another evidence that the observed pattern is caused by the interference of different electron trajectories. To explain this, the transversal velocity distribution of the reference wave packet after tunneling has to be taken into account. Within the tunneling approximation of strong-field ionization it is given by [41]

$$\Psi(p_{\perp}) = \Psi(0) \exp\left(-\frac{p_{\perp}^2 \tau_0}{2}\right) \tag{3.23}$$

where $\tau_0 = \sqrt{2I_p}/E_0$ is the "tunneling time". The wave packet has a Gaussian dependence on the transversal momentum p_{\perp} . The $1/e^2$ half width of the exponential term in equation 3.23 is $w = 2/\sqrt{\tau_0}$. If the electric field amplitude E_0 in the tunneling time is replaced by the instantaneous field at the ionization



Figure 3.11: Normalized difference $D_5(\mathbf{p})$ together with the holographic pattern from figure 3.10(a). The black line shows $w(t'_0)$ and the blue line indicates the limit corresponding to the maximal kinetic energy of the direct electrons of $2U_{\rm p}$.

time t'_0 of the reference electron one obtains [42]

$$w(t'_0) = 2 \left(\frac{\sqrt{2I_p}}{E_0 \cos(\omega t'_0)}\right)^{-\frac{1}{2}}.$$
(3.24)

In figure 3.11 the width $w(t'_0)$, assuming an intensity of $2.3 \cdot 10^{14} \text{ W/cm}^2$, is indicated as solid black line and encloses the region of strong modulation. It shows the maximal transversal momentum of an electron which has not scattered at the parent ion. Thus, outside of this boundary interference cannot be observed because there are only signal electrons. In the normalized difference image a ring pattern is visible. This ring structure corresponds to the above threshold ionization pattern whereas the distance between the maxima is equal to the photon energy. The holographic ring pattern shown in figure 3.10(b) was not observed in the measured spectra. In contrast to the ATI pattern, the position of the maxima of the holographic ring pattern strongly depends on the electric field E_0 . This is depicted in figure 3.12 where the holographic pattern was calculated for two different laser intensities. For positive values



Figure 3.12: Intensity dependence of the holographic pattern shown in figure 3.10(b). The field strength for $p_x > 0$ is 10% smaller than for $p_x < 0$

of p_x the field strength E_0 is 10% lower than for negative values of p_x . The shift of the extrema is clearly visible. Due to the Gaussian intensity profile of the laser beam the measured momentum distribution is always intensity averaged. Intensity averaging would thus lead to an extinction of the holographic ring pattern and could explain why it was not observed in the final spectra. Also the patterns shown in figure 3.10(c) and (d) could be strongly attenuated by intensity averaging. Additionally, they involve backward scattering of the signal electron which is in general much less probable than forward scattering at the considered energies. In case of the first holographic pattern intensity averaging does not lead to complete extinction because of its longitudinal structure.

The fact that the intense modulation of the photoelectron signal was limited to the momentum range of the direct electrons and the striking similarity with the calculated holographic pattern led to the conclusion that it was indeed interference between different electron trajectories which was observed. In this case the question remains why the holographic pattern was found to modulate with respect to the pump-probe delay. One can see that within the $2U_p$ limit the modulation amplitude increases with the kinetic energy of the electrons. This is remarkable because electrons with high kinetic energy are ionized at times close to the zero-crossing of the electric field where the ionization rate is small. This is visualized in figure 3.13(a) where the normalized electric field $E(t_0)/E_0$ is shown as a function of the final electron momentum. Although it is known from the ion yield measurements that the ionization rate modulates with respect to the pump probe delay, it cannot explain the increasing modulation amplitude as a function of the electron momentum in the holographic pattern. In contrast to the electric field amplitude, the time $t_{\rm r} - t_0$ between ionization and scattering is approximately inversely proportional to the final kinetic energy of the electron. This is depicted in figure 3.13(b). Due to the



Figure 3.13: (a) Normalized electric field amplitude at the ionization time t_0 of the signal electron. (b) Delay between the ionization time t_0 and the return time t_r of the signal electron.

dispersion of the photoelectron wave packet in the continuum, the probability that the electron scatters upon return becomes smaller the more time it spent in the continuum. This would explain the trend of the modulation as a function of the kinetic energy and indicates that the modulation amplitude strongly depends on the amplitude of the signal electron wave function. However, this effect does not explain the modulation itself.

The amplitude of the signal electron wave function further depends on the initial lateral momentum distribution of the electron after tunneling and the scattering cross section of the parent ion. According to the quantitative rescattering theory (QRS) the scattering cross section can be extracted from the momentum distribution of the high-energy electrons $(E_{\rm kin} > 2U_{\rm p})$ [40, 43]. As already mentioned, the modulation amplitude of these electrons was much weaker than the modulation of the holographic pattern. The phase of the modulation was the same but in contrast to the low-energy electrons, the high-energy electrons did not show a momentum dependent modulation amplitude. Therefore, one can conclude that the DCS of the parent ion was not affected by the electron wave packet and did not depend on the pump-probe delay. This in turn is only possible if the high-energy electrons, which were scattered in the time-independent potential of the NO⁺ molecule, were initially the electrons of the wave packet.

Because the DCS could be excluded as the origin of the strong modulation of the holographic pattern, only a delay-dependent transversal momentum distribution of the electron after tunneling could explain the strong modulation of the photoelectron spectra. To analyze this, the lateral momentum distribution after tunneling was calculated as a function of time for the electron wave packet defined in equation 3.3.



Figure 3.14: Partial Fourier transformation analysis of the electron wave packet. (a) In the background the temporal evolution of the electron density is plotted and in the front the electron density at z_0 in the xy plane is shown. (b) Momentum distribution of the electron wave packet evaluated at z_0 for the times given in the first column. (c) Relative momentum distribution $A(p_{\rm r}, t)$ (see equation 3.31) calculated from the distribution given in (b).

Murray et al. [44–46] developed an algorithm to calculate the ionization rate based on a partial Fourier transformation. In this theory the ionization rate is given by

$$\Gamma \propto \int \mathrm{d}x \mathrm{d}y \left| \Psi(x, y, z_0) * g(\rho) \right|^2, \qquad (3.25)$$

i.e. it is proportional to the integral of the convolution of the bound wave

function $\Psi(x, y, z)$ at the point $z = z_0$ and the tunneling filter

$$g(\rho) = (1/\tau) \exp(-\rho^2/2\tau)$$
 (3.26)

where $\rho^2 = x^2 + y^2$. We assume that the lateral momentum distribution after tunneling is thus related to the lateral momentum distribution at the position z_0 of the initial wave function which is given by

$$\Phi(p_{\rm x}, p_{\rm y}, z_0) = \left| \frac{1}{2\pi} \int \int \Psi(x, y, z_0) \mathrm{e}^{ixp_{\rm x} + iyp_{\rm y}} \mathrm{d}x \mathrm{d}y \, G\left(p_{\rm x}^2 + p_{\rm y}^2\right) \right|^2.$$
(3.27)

with

$$G\left(p_{\rm x}^2 + p_{\rm y}^2\right) \equiv G(p_{\perp}) = {\rm e}^{-\frac{p_{\perp}^2 \tau}{2}},$$
 (3.28)

the Fourier transformed tunneling filter $g(\rho)$. In this experiment $|\Psi(x, y, z_0)|^2$ was time-dependent and equation 3.27 becomes

$$\Phi(p_{\rm x}, p_{\rm y}, z_0, t) = \left| \frac{1}{2\pi} \int \int \Psi(x, y, z_0, t) \mathrm{e}^{ixp_{\rm x} + iyp_{\rm y}} \mathrm{d}x \mathrm{d}y \, G\left(p_{\rm x}^2 + p_{\rm y}^2\right) \right|^2.$$
(3.29)

Together with the definition of the wave function $\Psi^+(t)$ (see equation 3.3). one can determine the time-dependent lateral momentum distribution for one spin component. Because the Raman transition rate strongly depends on the alignment of the molecule one can simplify the problem and restrict the calculations to the case where the molecular axis stands perpendicular to the polarization vector (z). Furthermore, z_0 was fixed at a distance of -1.83 Å from the molecular axis (for F = 0.08151 a.u. the tunnel exit point was at -2.2 Å). The result, evaluated at four different times between t = 0 and t = T/2 where T corresponds to the period of the electronic wave packet, is summarized in the figures 3.14(a)-(c). Figure 3.14(a) shows the temporal evolution of the electron density in three dimensions. At time t = 0 the wave packet was defined as $\Psi(x, y, z, t = 0) = 2 |\pi_x\rangle$. In the same figure the electron density in the xy plane at z_0 is depicted. The corresponding momentum distribution of the wave function in this plane $\Phi(p_x, p_y, z_0, t)$ is given in figure 3.14(b). Taking into account all possible orientations of the molecule in the xy plane one obtains the averaged momentum distribution

$$\Phi'(p_{\rm r}, z_0, t) = \frac{\oint_{p_{\rm r}} \Phi(p_{\rm x}, p_{\rm y}, z_0, t) ds}{\oint_{p_{\rm r}} ds}$$
(3.30)

where $p_{\rm r} = \sqrt{p_{\rm y}^2 + p_{\rm x}^2}$ corresponds to the total momentum. Further, the relative, averaged momentum distribution

$$A(p_{\rm r},t) = \frac{\Phi'(p_{\rm r},z_0,t)}{\Phi'(p_{\rm r}=0,z_0,t=T/2)}$$
(3.31)



Figure 3.15: (a) Time evolution of $A(p_r = 0, t)$. (b) Normalized ionization rate calculated using the relation given in equation 3.25.

is defined as a function of the total momentum $p_{\rm r}$ and time t evaluated at $z_0 = -1.83$ Å. This function is shown in figure 3.14(c). The time evolution of $A(p_{\rm r},t)$ indicates an increasing ionization rate between t=0 and t=T/2and for t = T/2, $A(p_r, t)$ becomes Gaussian-shaped. In fact, at t = T/2 the $1/e^2$ half width of the lateral momentum distribution is close to $w = 2/\sqrt{\tau}$. According to the semi-classical theory the time evolution of $A(p_r = 0, t)$ is of particular importance because only electrons with an initial momentum $p_{\rm r} = 0$ can rescatter from the parent ion. $A(p_r = 0, t)$, depicted in figure 3.15(a), is zero for t = 0 and one for t = T/2. In the limit of this simple model it follows that the holographic pattern should be minimal or even vanishes for t = 0 and become maximal for t = T/2. Additionally, the relative ionization rate, which was calculated using the relation given in equation 3.25, is also much lower for t = 0 than for t = T/2. This is shown in figure 3.15(b). Considering the modulation of $A(p_r = 0, t)$ and of the ionization rate we arrive at the conclusion that a modulation of the holographic pattern as a function of the pump-probe delay could be attributed to the time-dependent lateral momentum distribution of the electron after tunneling.

3.3.3 Observation of the Rotational Coherence

From the spectral analysis of the ion yield measurement it was known that the dips in the ion yield trace (figure 3.4(a) and (c)) close to 5, 10 and 15 ps were the result of rotational coherence induced by the pump pulse through a Raman transition. The time between the dips corresponds to half of the rotational revival time $T_{\rm rev} = 1/2B = 9.83$ ps of the NO molecule where B is the rotational constant. At these delays the axis distribution changes significantly. Approaching the time of the first half-revival, the axis distribution becomes oblate-shaped. This is depicted in figure 3.16(a) where the polariza-



Figure 3.16: Axis distributions at the rotational revival. The axis distribution of the coherent rotational wave packet in NO is first delocalized in the xy plane (a) and ~ 200 fs later localized along the z axis (b) assuming a pump pulse which is polarized along the z axis.

tion axis points along the z axis. About ~ 200 fs later the axis distribution becomes aligned along the z axis (see figure 3.16(b)). Because the ionization rate of a molecule is in general orientation dependent, the ion yield should be different for both distributions. For NO the orientation dependent normalized ionization rate is given in figure 3.21(b). For $\theta = 0^{\circ}$ the molecule is ionized at the oxygen atom. At $\theta = 100^{\circ}$ the ionization rate reaches a minimum. Thus, one expects in average a lower ionization rate for the oblate-shaped axis distribution than for the dumbbell-shaped distribution. This is exactly what was observed in the ion yield signal shown in figure 3.4(c) as well as in the total electron yield given in figure 3.17. The total electron yield was measured for the first half-revival at ~ 5 ps and was obtained by integrating the momentum resolved photoelectron spectra S_n where n = 1 - 15. The spectra were recorded between delays of 4.86 ps and 5.1 ps. The integration time of a single spectrum was 40 minutes. At 4.91 ps the axis distribution was delocalized in the xy plane where at 5.1 ps the axis distribution was localized along the polarization axis. The difference of the total electron yield between the minimum and the maximum was 2.3%. To study the effect of the rotational coherence on the photoelectron signal in more detail, it was again useful to calculate the normalized difference

$$D_{m,n}(\mathbf{p}) = 2\frac{S_m(\mathbf{p}) - S_n(\mathbf{p})}{S_m(\mathbf{p}) + S_n(\mathbf{p})}$$
(3.32)

between two spectra, S_m and S_n , measured at different delays. The results of the normalized differences $D_{m,4}$ with m = 1, 8, 10, 15 are shown in the figures 3.18(a)-(d) whereas in the figure 3.18(e) and 3.18(f) the normalized difference $D_{11,8}$ and $D_{15,11}$ are given. As in figure 3.11 the solid line on top of the images indicates the limit of the lateral momentum after tunneling. Within this



Figure 3.17: Normalized total electron yield measured at the first rotational half-revival. The total electron yield was obtained by integrating the photoelectron spectra.

range the pattern of the normalized difference $D_{1,4}$ is similar to the holographic pattern of figure 3.11 whereas $D_{8,4}$ shows several significant differences. The pattern observed in $D_{8,4}$ is even more pronounced in $D_{10,4}$ and $D_{15,4}$ and it is also visible in $D_{11,8}$ but not in $D_{15,11}$. The latter is again similar to $D_{1,4}$. Hence, we could conclude that the difference between spectra measured at the beginning or at the end of the rotational half-revival were mainly caused by the electronic coherence whereas the differences between spectra measured at 4.91 ps and 5.1 ps were the result of electronic and the rotational coherence. In reference [47] Bian et al. presented calculated photoelectron momentum distributions of oriented HeH²⁺ molecules. They could identify all holographic patterns which were predicted by the semiclassical model (see fig. 3.10) for the case where the molecular axis was parallel to the polarization vector. They could also show that the backward rescattering holography becomes less pronounced when the orientation angle was increased and even vanishes for angles larger than 60° . In contrast, the forward rescattering holography was observable for all orientations. A similar pattern as seen in the figures 3.18(a)-(e) has not been predicted. Of course, these images only show the differences between two spectra and a direct comparison with a single photoelectron spectrum is not appropriate. But one can argue that large differences are caused by interference and therefore reflect the holographic pattern. To the knowledge of the authors a theory to describe the effect of a mixed electronic and rotational wave packet on the photoelectron spectrum has not yet been developed and a full numerical solution of the time-dependent Schrödinger equation would have been beyond the scope of this thesis. Therefore, a further more quantitative discussion about the low-energy electrons was not possible.

But in the normalized difference $D_{15,4}$ also a pattern in the region of the high-energy electrons is visible. This indicates that the elastic scattering DCS



Figure 3.18: Normalized difference $D_{m,n}(\mathbf{p})$ of spectra measured at the first rotational half-revival close to 5 ps. (a) - (d) $D_{m,n}(\mathbf{p})$ for n = 4 and m = 1, 8, 10, 15. (e) $D_{11,8}(\mathbf{p})$ (f) $D_{15,11}(\mathbf{p})$. The maximal momentum of a direct electron is indicated as solid black line. Electrons outside of this boundary were scattered at the parent ion.

had changed between S_4 and S_{15} . To prove that, calculated elastic differential scattering cross sections were compared with the experimental result.

The numerical calculations were done with the program $Quantemol^{\textcircled{B}}$. It can calculate the elastic scattering DCS for randomly oriented and for aligned molecules. Using the latter option it was possible to calculate a DCS for a partially aligned sample. The output of the program included the DCS in the xz plane for the selected orientations and scattering energies. In the program the orientation of the molecule is defined in terms of three Euler angles.



Figure 3.19: Definition of the angles which appear in the calculated DCS $\sigma_{xz}(E, \alpha, \phi, \theta)$. The momentum vector of the incident electron beam was antiparallel to the z axis. The output of the program provides the DCS in the zx plane. The definition of the angles is unusual but it was chosen to avoid confusion with the definition in Quantemol.

For a linear molecule two angles are sufficient and therefore the Euler angles are replaced by θ and ϕ for the following discussion. The calculated DCS $\sigma_{xz}(E, \alpha, \phi, \theta)$ thus depend on the kinetic energy of the scattered electron E, the scattering angle α and the orientation of the molecule. The definition of the angles is depicted in figure 3.19. The momentum vector of the incident electron beam is anti-parallel to the z axis and a scattering angle $\alpha = 0^{\circ}$ means that the electron is back scattered. The averaged DCS $\bar{\sigma}(\alpha, E)$ is then defined as

$$\bar{\sigma}(\alpha, E) = \frac{\sum_{i=1}^{m} \sum_{j=1}^{n} f(\theta_j) \sigma_{\text{xz}}(\alpha, E, \phi_i, \theta_j) \sin(\theta_j)}{\sum_{i=1}^{m} \sum_{j=1}^{n} f(\theta_j) \sin(\theta_j)}$$
(3.33)

with $\phi_i = (i-1)\Delta\phi$ and $\theta_j = (j-1)\Delta\theta$. The step size $\Delta\phi = 2\pi/m$ and $\Delta\theta = \pi/(n-1)$ depend on the number of different calculated orientations where in general m = 36 and n = 37. The weighting factor $f(\theta) = \Gamma_n(\theta)A(\theta)$ includes the normalized orientation-dependent ionization rate $\Gamma_n(\theta)$ and the alignment distribution $A(\theta)$. Note that the averaged DCS $\bar{\sigma}(\alpha, E)$ is symmetric with respect to a rotation around the z axis. For the case where $f(\theta) = 1$ the average DCS should be identical with the DCS calculated by the program for a randomly oriented sample. Figure 3.20 shows the two results where the averaged DCS is given in (a) and the output for a randomly oriented sample is given in (b) (Quantemol; basis set: cc-pVTZ; method: Hartree-Fock; R-matrix radius: 10 a.u.; NO bond length: 1.154 Å). The two results are similar which shows that the error due to the averaging of a finite number of orientations is small. To obtain $\bar{\sigma}(\alpha, E)$ for a partially aligned NO⁺ sample a moderate alignment of $\langle \cos^2 \theta \rangle = 0.5$ was assumed. This corresponds to an axis distribution $A^z(\theta) = \left(1 + a/\sqrt{\cos^2 \theta + \epsilon^2 \sin^2 \theta}\right)/n$ with $\epsilon = 1.93$, a = -2.40 and



Figure 3.20: Elastic scattering DCS calculated for NO⁺ using Quantemol. (a) Averaged DCS $\bar{\sigma}(\alpha, E)$ for $f(\theta) = 1$, m = 36 and n = 37. (b) Direct output of the program for a randomly oriented sample. A scattering angle $\alpha = 0^{\circ}$ designates back scattering.

n = -0.98 [48]. For the case where the axis distribution is delocalized in the xy plane one can define $A^{xy}(\theta) = A^z(\theta - 90^\circ)/n$ with n = 1.74. $A^z(\theta)$ and $A^{xy}(\theta)$ are depicted in figure 3.21(a) as red and blue line, respectively. Further, an anisotropic ionization rate $\Gamma_n(\theta)$ as shown in figure 3.21(b) was taken into account. $\Gamma_n(\theta)$ was calculated for NO using the weak-field asymptotic theory [49, 50] for an electric field strength of F = 0.0815 a.u.. The averaged DCS for $f^z(\theta) = \Gamma_n(\theta)A^z(\theta)$ and $f^{xy}(\theta) = \Gamma_n(\theta)A^{xy}(\theta)$ is shown in figure 3.22(a) and 3.22(b) (Quantemol; basis set: cc-pVTZ; method: Hartree-Fock; R-matrix radius: 10 a.u.; NO bond length: 1.154 Å), respectively. One can see that the forward scattering amplitude at $\alpha = 180^\circ$ is in both cases larger than the backward scattering amplitude. For both axis distributions the total elastic scattering cross section drops drastically between a scattering energy of 0 and 15 eV. In figure 3.23 the normalized difference

$$D_{\text{DCS}}(\alpha, E) = \frac{2(\bar{\sigma}^{z}(\alpha, E) - \bar{\sigma}^{xy}(\alpha, E))}{\bar{\sigma}^{z}(\alpha, E) + \bar{\sigma}^{xy}(\alpha, E)}$$
(3.34)

is shown whereas $\bar{\sigma}^{z}(\alpha, E)$ represents the average DCS for $f^{z}(\theta) = \Gamma_{n}(\theta)A^{z}(\theta)$ and $\bar{\sigma}^{xy}(\alpha, E)$ for $f^{xy}(\theta) = \Gamma_{n}(\theta)A^{xy}(\theta)$.

In a photoelectron momentum distribution spectrum electrons which return to the parent ion with a momentum $p_{\rm r}$ and scatter elastically are located on a circle with radius $p_{\rm r}$ (see figure 3.24). The center of this circle is shifted from the origin by $p_{\rm s}$ along the polarization axis. The variable $p_{\rm s}$ represents the momentum which the electron additionally acquires in the laser field after it was scattered in the potential of the parent ion.



Figure 3.21: (a) Alignment distribution $A^{z}(\theta)$ (red) and $A^{xy}(\theta)$ (blue). The distributions correspond to an alignment of $\langle \cos^{2} \theta \rangle = 0.5$. (b) Normalized ionization rate $\Gamma_{n}(\theta)$ of NO. For $\theta = 0^{\circ}$ the molecule is ionized at the oxygen atom.



Figure 3.22: Averaged elastic scattering DCS for aligned $\bar{\sigma}^{z}(\alpha, E)$ (a) and antialigned $\bar{\sigma}^{xy}(\alpha, E)$ (b) axis distributions of NO⁺ molecules. For both cases the orientation dependent ionization rate was taken into account.



Figure 3.23: Normalized difference $D_{\text{DCS}}(\alpha, E)$ of the calculated DCSs $\bar{\sigma}^{z}(\alpha, E)$ and $\bar{\sigma}^{xy}(\alpha, E)$.



Figure 3.24: (a) Experimental photoelectron momentum distribution of the spectrum S_4 . The circle represents the position where a scattered photoelectron with scattering momentum $p_{\rm r}$ appears in the spectrum. An angle $\alpha = 0^{\circ}$ represents an electron that was back rescattered. The circle is shifted from the origin by $p_{\rm s}$, the momentum which the electron additionally acquires after it scattered off the parent ion. (b) Electron yield of the spectrum S_4 (blue) and S_{15} (red) along the red circle shown in (a). The scattering momentum $p_{\rm r}$ was 1 a.u.

According to the QRS theory the momentum distribution along this circle is mainly dependent on the elastic scattering DCS of the parent ion. It is thus possible to transform the calculated difference $D_{\rm DCS}(\alpha, E)$ to $D_{\rm DCS}(\boldsymbol{p})$, where p stands for the final electron momentum measured at the detector, provided that the ratio p_r/p_s is known. Within the QRS theory the ratio between p_r and $p_{\rm s}$ can be calculated using the classical equation of motion (equation 3.13). In figure 3.25(b) the ratio $p_{\rm r}/p_{\rm s}$ is plotted as a function of the return time $\omega t_{\rm r}$. At $\omega t_{\rm r} = 180^{\circ}$ the ratio $p_{\rm r}/p_{\rm s}$ is not defined because $p_{\rm s} = 0$. The color of the line indicates the final kinetic energy $E_{\rm kin}^{\rm max}$ of the electron after it was back rescattered, i. e. for a scattering angle $\alpha = 0^{\circ}$. For a return time close to $\omega t_{\rm r}=262^\circ$ the electron reaches a kinetic energy up to $E_{\rm kin}^{\rm max}=10\,U_{\rm p}.$ Together with equation 3.15 one can show that an electron which returns at this time was ionized at $\omega t_0 = 17^{\circ}$. Electrons with an ionization time $\omega t_0 < 17^{\circ}$ will return at $\omega t_{\rm r}>262^\circ$ and reach a final kinetic energy of $E_{\rm kin}^{\rm max}<10U_{\rm p}.$ But from figure 3.25(b) one can see that for each time $\omega t_r > 262^\circ$ there is a second trajectory with a return time $\omega t_{\rm r}\,<\,262^\circ$ and the same final energy $E_{\rm kin}^{\rm max}$ but with a different p_r/p_s ratio. The two different trajectories are often referred to as long and short trajectories. The transformation from $D_{\text{DCS}}(\alpha, E)$ to $D_{\text{DCS}}(\mathbf{p})$ is thus only uniquely defined for either the "long" or the "short" trajectories. However, the short trajectories are suppressed due to the lower ionization rate. The relative ionization rate as function of the returning time is given in figure 3.25(a). The rate was calculated based on the Yudin-Ivanov ionization model



Figure 3.25: (a) Relative ionization rate as a function of the return time [51]. (b) p_r/p_s ratio as a function of the return time. The color of the line corresponds to a certain final kinetic energy for the case where the photoelectron was back rescattered by the parent ion.

for atoms [51]. The result of the transformed difference $D_{\text{DCS}}(\mathbf{p})$ is shown in figure 3.26(a) for the short and in figure 3.26(b) for the long trajectories. For the transformation a laser peak intensity of $2.2 \cdot 10^{14} \,\text{W/cm}^2$ was assumed with $z(t_0) = -I_{\text{P}}/E_0$ and $v_x(t_0) = v_z(t_0) = 0$. Specific features of the experimental result given in figure 3.26(d) are labeled with the letters A-F to compare them with the transformed differences $D_{\text{DCS}}(\mathbf{p})$. The positions of these labels are the same in all spectra. However, figure 3.26(d) does not represent $D_{15,4}$ (see figure 3.18(d)). Instead, the normalized difference

$$D_{S_{\rm h},\,S_{\rm l}} = 2\frac{S_{\rm h} - S_{\rm l}}{S_{\rm h} + S_{\rm l}} \tag{3.35}$$

between the averaged spectrum $S_{\rm l} = 1/9 \sum_{n=1}^{9} S_n$ and $S_{\rm h} = 1/6 \sum_{n=10}^{15} S_n$ is shown. $D_{S_{\rm h},S_{\rm l}}$ is almost identical to $D_{15,4}$ but has a higher signal-to-noise ratio. For the pattern E, which is prominent in the spectrum 3.26(a) for short trajectories, one cannot identify corresponding structures in the experimental spectrum. But unfortunately at these positions the electron yield is already very low. Because the Abel inversion increases the noise level in the spectrum, the normalized difference was also calculated for the raw data. The result is shown in figure 3.26(c). But a better agreement of the spectrum 3.26(a) with the experimental data was also not observed. However, due to the focal volume effect [52] a laser peak intensity of $2.2 \cdot 10^{14} \,\mathrm{W/cm^2}$ (which was calculated from the initial beam parameters and was in agreement with the limit of the holographic pattern) which was assumed for the transformation from $D_{\rm DCS}(\alpha, E)$ to $D_{\rm DCS}(\mathbf{p})$ might be too high. Therefore, the normalized difference $D_{\rm DCS}(\mathbf{p})$ was also calculated for an intensity of $1.2 \cdot 10^{14} \,\mathrm{W/cm^2}$.



Figure 3.26: (a) Normalized difference $D_{\text{DCS}}(\boldsymbol{p})$ calculated for short trajectories for a laser peak intensity of $2.2 \cdot 10^{14} \text{ W/cm}^2$. (b) Same as in (a) calculated for long trajectories. (c) Normalized difference $D_{S_{\rm h},S_{\rm l}}$ of the raw spectra. (d) Normalized difference $D_{S_{\rm h},S_{\rm l}}$ of the Abel inverted spectra. (e) Same as (a) for an intensity of $1.2 \cdot 10^{14} \text{ W/cm}^2$. (f) Same as (b) for an intensity of $1.2 \cdot 10^{14} \text{ W/cm}^2$. Some specific features are labeled with letters. The positions of the letters are identical in all spectra. The black circles on top of the spectra indicate the detection range.



Figure 3.27: (a) Normalized difference $D_{S_{\rm h}, S_{\rm l}}$ as a function of scattering angle α and scattering momentum $p_{\rm r}$ assuming long electron trajectories. (b) Same as figure 3.23.

The result for the short and long trajectories are given in figure 3.26(e) and 3.26(f), respectively. One can observe a clear shift of the features in the normalized difference calculated for short trajectories whereas the normalized difference calculated for long trajectories only slightly changes. The agreement of the calculated difference for short trajectories with the experimental result becomes even worse. However, the calculated normalized difference for the long trajectories (figure 3.26(b)) has similarities with the experimental result. For a better comparison both results are shown in figure 3.27(a) and (b) as a function of the scattering angle α and scattering momentum p_r . The experimental and calculated normalized difference is positive at $\alpha = 0^{\circ}$ and $\alpha = 100^{\circ}$ and negative for scattering angles $\alpha \approx 50^{\circ}$. For increasing scattering momentum the local minimum shifts to larger scattering angles in both spectra. However, the position of the minimum in the calculated and experimental spectra does not exactly coincide. Nevertheless, this clearly shows that the pattern observed in the high-energy region is caused by the change of the elastic differential scattering cross section at the revival of the nuclear coherence.

3.4 Conclusion

In summary, we could observe the motion of an electronic wave packet imprinted on the momentum distribution of photoelectrons. Via a Raman transition a coherent superposition of the ${}^{2}\Pi_{1/2}$ and ${}^{2}\Pi_{3/2}$ states of nitric oxide was prepared. At the same time a rotational wave packet was excited by the pump pulse. By measuring the yield of the parent ion as a function of the pump-probe delay we could identify pump-probe delays where the ionization rate was mainly modified by one wave packet. Therefore, it was possible to attribute the different changes in the photoelectron spectra to the different types of wave-packet motion.

For delays where the wave packet was mainly defined by the electronic coherence we could observe a strong modulation of the direct electron yield as a function of the pump-probe delay. In contrast to the rescattered photoelectrons, the modulation amplitude did also depend on the final electron momentum. The pattern of this modulation was very similar to a holographic pattern known from other experiments. Using detailed simulations, we could attribute this modulation to the motion of the electronic wave packet.

At delays close to an alignment revival the structure of the rescattered photoelectrons changed. Using the program Quantemol we have calculated elastic scattering DCS for NO^+ and compared the result with the pattern observed in the rescattered photoelectrons. The calculated result was in partial agreement with the experimental data assuming that the long electron trajectories were dominating over the short trajectories.

Chapter 4

Isotope Effects in Strong-Field Ionization Rates

Within this chapter ion time-of-flight (TOF) measurements are presented. Besides the electron and ion momentum distribution measurements these experiments represent another attempt to gain insight into molecular dynamics on the femtosecond time scale. Compared to the imaging mode, the TOF mode has the advantage that the yield of all ions generated within a single laser shot can be measured simultaneously. This enables the investigation of ionization or fragmentation processes occurring when a molecule is exposed to an intense laser field. This experiment was motivated by the question whether there is an isotope effect in strong-field ionization.

4.1 Introduction

The main goal of these experiments was to compare the ionization rate of molecules with the ionization rate of their corresponding isotopologues. Tolstikhin *et al.* showed in reference [53] that the ionization rate of H_2 and D_2 should be different. The prediction is based on the weak-field asymptotic theory (WFAT) which is explained in reference [49]. This theory includes the nuclear motion into the calculation of the tunneling ionization rate. The calculation starts with the Schrödinger equation of a diatomic molecule with a single active electron in a static, electric field. Applying the Born-Oppenheimer approximation the electronic and nuclear motion can be separated. By using the WFAT, the authors solved the equation for the electronic motion and derive the tunneling ionization rate for fields $F \ll F_{\rm c}$, where $F_{\rm c}$ represents the boundary between tunneling and over-the-barrier ionization. From the equation of the nuclear motion together with the result for the electronic motion they finally derived the ionization rate which depends on the vibrational and rotational state of the molecule. The result predicted an ionization-rate ratio between ${\rm H}_2$ and ${\rm D}_2$ which is larger than one. Although the theory is based on

the assumption of a static electric field, it remains valid for laser fields with a frequency that is low compared to the motion of the electron.

In this chapter measurements and results are presented where isotope effects on the ionization and fragmentation processes were investigated. First, a detailed description of the experimental setup, the measurement procedure and laser peak intensity calibration is given. Finally, the results of $\rm H_2/D_2$ and $\rm CH_4/CD_4$ are presented and discussed.

4.2 Experimental Details

4.2.1 Optical Setup

Figures 4.1(a)-(c) show the optical setup. For the ionization rate measurements the VMIS was operated in the time-of-flight mode. The ion yield of two different molecules and their fully deuterated isotopologues were measured for different laser intensities. During the measurement session the laser output was shared with another independent measurement which included an optical parametric amplifier (OPA). Because the OPA conversion efficiency strongly depends on the length of the incident pulse, the compressor of the laser system was always optimized with respect to the OPA output and not with respect to the TOF signal. For the H_2/D_2 and CH_4/CD_4 measurements the laser output (figure 4.1(a)) was directly guided to optical setup (figure 4.1(c)). However, for some measurements the dispersion of the laser was additionally compensated with chirped mirrors (figure 4.1(b)). Details about the measured pulse lengths will be given in the next section. To adjust the intensity a motorized half wave plate (WP 1, Newport SR50PP stepper motor together with the Newport ESP 100 controller) was used in combination with two thin-film polarizers (TFPK 1 and 2). The beam was focused by a silver coated spherical mirror (SM) with a focal length f = 250 mm. During the measurement the laser intensity was directly recorded by a fast photodiode (PD 3, Thorlabs DET 10 A/M) and a calibrated power meter (PD 2, Thorlabs S302C in combination with the control unit Thorlabs PM100D). To monitor intensity and pulse length fluctuations of the laser the second-harmonic signal generated in a BBO crystal was recorded by a third photodiode (PD 1, Thorlabs DET 10 A/M). The TOF ion signal was recorded together with the signal of PD 1 and PD 3 with an oscilloscope (LeCroy Wavejet 354A). During the experiment the valve backing pressure was monitored with a pressure gauge (IFM PN2024). The analog output of the IFM PN2024 gauge and the output of the calibrated power meter were digitized by an analog-to-digital converter (IOtech ADC 488/8 SA). The pressure inside the chamber was monitored by two full range gauges (Pfeiffer PKR 251 controlled by MaxiGauge TPG 256A). A standard computer running MatLab and LabView was used to control the stepper motor and to read out and save all measured parameters.



Figure 4.1: Optical setup used for ionization rate measurements. For the H_2 and CH_4 experiments the laser output (a) was directly guided to the setup (c). For some measurements chirped mirrors were used to compensate the dispersion of the pulse (b). The abbreviations are: optical parametric amplifier (OPA), beam splitter (BS), chirped mirror (CM), wedged window (WW), BBO crystal (BBO), dichroic mirror (DM), photodiode (PD), wave plate (WP), thin-film polarizer (TFPK), velocity map imaging spectrometer (VMIS) and spherical mirror (SM).

4.2.2 Laser Pulse Characterization

The laser was characterized using the frequency-resolved optical gating (FROG) method [54, 55]. The initial pulse was split into two replicas with a variable delay. The two pulses were then spatially overlapped in a β -barium borate (BBO) crystal. This crystal is a nonlinear optical medium and emits light with twice the frequency of the input beam. This process is called secondharmonic-generation (SHG) and is proportional to the squared intensity. Because the overlapping beams are crossed at a small angle inside the crystal, a third beam bisecting the two outcoming fundamental beams appeared after the BBO when the two pulses overlapped in time. The spectrum of this beam was then recorded for different delays. To extract the complete envelope of the pulse from the measured spectra the program FROG 3.03 from Femtosoft Technologies was used. It applies several different algorithms to reconstruct the electric field as a function of time from the measured spectra. The position at which the SHG FROG was measured is indicated in figure 4.1(c) of the optical setup. For reasons mentioned above the FROG traces were measured after the output of the OPA was maximized and pulse lengths of 57 ± 2 femtoseconds were measured.

4.2.3 Detection Efficiency and Gas Density Calibration

In general, the measured ion yield is a function of the ionization rate, the temporal and spatial shape of the laser pulse, the detection efficiency and the sample density in the laser focus. To extract the absolute ionization rate from the ion yield, it is essential that all the parameters are known. This would require a lot of characterization measurements, especially to obtain the absolute detection efficiency of the multi-channel plate detector. Because we were only interested in relative ionization rates, the absolute values did not have to be known and only a few parameters needed to be known.

First one has to ensure that the spatial and temporal shape of the laser pulse does not change within the time it takes to measure both molecules. This turned out to be difficult. Although we observed a good stability of the spatial mode of the laser, the temporal shape and the peak intensity of the pulse changed on a time scale of hours. Therefore, we installed a photodiode which continuously measured the second-harmonic signal as explained in section 4.2.1. Furthermore, the measurements were repeated several times within an hour. In this way differences due to power and pulse length fluctuations of the laser were addressed and minimized.

A second important point is the relative detection efficiency of the ions. The detection efficiency of an MCP detector is a function that depends on many parameters like the atomic number, velocity and charge of the ion as well as several parameters which reflect the geometry of the MCP [56]. Brehm et al. [57] have measured total detection efficiencies for protons and deuterons with kinetic energies between 0.5 and 5 keV. For all ions the detection efficiency increases between 0.5 and 3 keV and stays constant between 3 and 5 keV. Only a small ion mass effect was observed in these measurements. The mean values of the absolute detection efficiency for kinetic energies between 3-5 keV are for H_2^+ , $(43 \pm 1)\%$; D_2^+ , $(40 \pm 1)\%$; H^+ , $(40 \pm 5)\%$ and D^+ , $(41 \pm 5)\%$ [57]. Besides this, Peko et al. present in [58] a similar experiment for kinetic energies between 30 eV and 1 keV. Within this range they could observe an isotope effect but it decreases with increasing energy. In our case the kinetic energy of the ions was 2 keV. Based on these two papers we conclude that ion yield difference due to the detection efficiency of H_2^+ , D_2^+ , H^+ and D^+ can be neglected.

The third parameter, the gas density in the focus of the laser, strongly depends on the mass because the pump rate of the turbomolecular pump and the leak rate of the valve are both a function of the mass of the molecule. For example, the pumping speed for helium of the HiPaceTM 400, a comparable turbomolecular pump to the one used in the experiment, is about 10% higher than for hydrogen. The leak rate of the sample gas through the nozzle can be estimated assuming a choked flow. Under this condition the flow rate difference between hydrogen and helium (or deuterium) is 41%. Also the expansion of the gas after the valve depends on the mass. All effects together lead to a

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different spatial density distribution of the sample gas in the focus of the laser and a different background pressure in the chamber. During the experiment the background pressure was measured with a Pfeiffer PKR 251 full range gauge. This device measures the pressure via electron impact ionization. To obtain the absolute pressure a species-dependent correction factor is needed which was not known for deuterium. Using the pressure signal to calibrate the gas density is thus inaccurate.

Another attempt to calibrate the density was made by measuring the thirdorder harmonic generation (THG). The THG signal intensity for diluted gases is proportional to the density and the third-order nonlinear susceptibility $\chi^{(3)}$. For H₂ and D₂ the microscopic second hyperpolarizability tensor γ , which is the microscopic expression for $\chi^{(3)}$, is very similar. In reference [59] the ratio $\langle \gamma_{\rm H_2} \rangle / \langle \gamma_{\rm D_2} \rangle$ is 1.002 ± 0.001 measured at a wavelength of 1064 nm and 1.013 ± 0.003 for 1319 nm. $\langle \gamma \rangle$ stands for the isotropically averaged hyperpolarizability. Based on this result we assume that the ratio is also very close to one for a wavelength of 800 nm. Thus, the third-harmonic signal can be used to calibrate the gas density. Therefore, the laser was focused with a spherical mirror with f = 100 mm in the center of the gas jet formed by a pulsed Even-Lavie valve with a nozzle diameter of 150 μ m and a repetition rate of 1 kHz. With a dichroic mirror and a prism the THG signal was separated from the fundamental wavelength and detected by a photomultiplier tube. Because of third-harmonic generation in the air and the optical elements through which the laser was transmitted, the background signal was quite large. It could be improved to a certain extent by reducing the optical elements in the path and by reducing the focal length of the spherical mirror. But it was not possible to entirely eliminate the background. To reach a signal to background ratio of about 20% with a laser peak intensity of $\sim 10^{15}$ W/cm², it was necessary to increase the opening time of the pulsed valve and to operate it beyond the specified conditions. The distance between the nozzle and the focus was only 10 mm. The THG signal of hydrogen and deuterium was then measured under the same conditions. The experiment was repeated for different backing pressures between 6 and 10 bar. As expected, the THG signal ratio of the two molecules was independent of the backing pressure. A ratio of 1.35 ± 0.10 was found. It follows that for the same backing pressure the density in the focus was 1.35 times higher for H_2 than for D_2 . During the THG measurements the pressure in the VMIS was around 0.01 mbar. Under this condition it was not possible to use the MCP detector. Besides that, the valve was in contact with the repeller plate. Due to these two reasons it was not possible to perform ion yield measurements under the same conditions as the THG measurements. The opening time of the valve and the distance between the nozzle and focus of the laser beam had to be adapted for the TOF measurements. Although it was not clear whether the density ratio was affected by these changes several attempts were made to compare the ion yield of hydrogen and deuterium

assuming a density ratio of 1.35. Unfortunately, the results were not reproducible from one measurement to another.

To improve the reproducibility the pulsed valve was replaced by a leak valve from Lenox Laser with a nozzle diameter of 10 μ m. Additionally, 1% xenon was added to the sample gas to use the xenon ion signal as an internal reference. If the concentration of xenon is low, segregation processes in the gas jet should be negligible and one can assume that the concentration of xenon in the gas jet is the same as in the initial mixture. Therefore, one can used the xenon ion signal to calibrate the gas density in the focal volume. Because the density calibration based on the THG measurement did not lead to the desired result. the xenon reference was the only calibration method which could be applied without rebuilding the VMIS. For the H_2/D_2 and CH_4/CD_4 experiments 1% xenon was added to the pure sample gas. The concentration of xenon could be determined with a precision of 4%. This was limited by the accuracy of the sample-independent pressure gauges IFM PN2009 (from -1 to 1 bar with an accuracy of ± 2 mbar) and IFM PN2024 (from -1 to 10 bar with an accuracy of ± 22 mbar) which were used to prepare the mixtures. Besides that, the xenon ion signal can also be used to calibrate the laser peak intensity (see section 4.3).

4.2.4 Measurement Procedure

The measurement procedure was the same for all measurements presented in the result sections. At the beginning the dispersion of the laser was adjusted such that the output of the OPA was maximal. As mentioned above, the OPA output was used for a second, independent experiment. The first bottle containing the gas mixture was connected to the system and 2 bar backing pressure was applied to the leak valve. The motorized half-wave plate was set to the angle which corresponded to the highest intensity. Starting from this value 9 other angles were defined. The last one corresponded to the lowest possible intensity at which an ion signal was measurable with the MCP detector set to the highest possible gain. For each intensity the gain parameter of the MCP was adjusted such that the ion signal was within the detection range of the oscilloscope. The selected intensities and corresponding MCP gain parameters were then kept constant for all following measurements. At each half-wave plate position 2560 TOF spectra were recorded and averaged. In parallel the signal of both photodiodes, the calibrated power meter, the backing pressure of the valve and the pressure in the VMIS were recorded. This procedure was repeated three times to address long-term laser fluctuations. After finishing, the gas system and the leak valve were evacuated and rinsed two times with the gas mixture of the second sample. The new sample was then measured for the same half-wave plate positions and MCP voltages. The whole procedure was repeated several times within a day.



Figure 4.2: The solid line shows the calculated ion signal from xenon ionized by an 11 fs laser pulse with a center wavelength of 1800 nm. The beam is focused by a spherical mirror with f = 250 mm. The red points are measured data taken from reference [60].

4.3 Numerical Calculation of the Xenon Ionization Rate

To calibrate the laser intensity the measured Xe⁺ ion yield was compared with the calculated ionization rate based on the Yudin-Ivanov ionization model [51]. The spatial as well as the temporal shape of the pulse were taken into account. The calculation was also compared with the result published in reference [60] where the same method was used to calibrate the intensity. In figure 4.2 the solid line shows our calculated results whereas the red points represent the measured yield taken from reference [60]. The calculated results are based on the experimental conditions given in reference [60]. Both data sets overlap perfectly. In reference [61] the total ion signal for a Gaussian radial intensity profile with a peak intensity I_0 and an intensity I_0/e at radius R is given by

$$S = \alpha \pi R^2 c l \int_0^{I_0} \frac{1 - e^{-\int_{-\infty}^{\infty} W(I_r f(t)) dt}}{I_r} dI_r$$
(4.1)

where W(I) is the intensity-dependent ionization rate, I_r the laser peak intensity at radius r, f(t) the temporal envelope of the pulse, α the detection efficiency and c the concentration of the neutral species. The parameter l corresponds to the length of the cylinder from which the ion signal is collected. Within this cylinder R is constant (parallel beam irradiation). This approximation is only valid if the collection volume is much smaller than the Rayleigh length of the Gaussian beam. In figure 4.3(a) S is plotted for different pulse durations as a function of I_0 . One can see that the ion yield becomes a linear function with respect to $\ln(I_0)$ for intensities $> 10^{14}$ W/cm². Above this value one can assume that

$$\int_{-\infty}^{\infty} W(I_0 f(t)) \mathrm{d}t \gg 1 \tag{4.2}$$

and the function for the ion yield becomes [61]

$$S = \alpha \pi R^2 c l(\ln(I_0) - \ln(I_{\text{sat}})).$$
(4.3)

 $I_{\rm sat}$ is called the saturation intensity and is simply the intensity at which the linear regression intersects the x axis. The slope of the linear regression can be expressed as $\alpha \pi R^2 cl$ and only depends on beam parameters and the gas concentration. It is thus possible to factor out the gas density and the detection efficiency. Therefore, one could obtain the absolute ionization rates from a single measurement. But this approach is only valid for a parallel Gaussian beam. For a strongly focused beam R and I_0 are no longer constant within the detection volume and equation 4.3 is no longer valid. The intensity dependent ion yield for different spatial beam profiles is depicted in figure 4.3(b). The blue line represents the yield for a parallel Gaussian beam and the red one the yield function for a strongly focused beam. It is obvious that the red line does not converge to a linear function for high intensities. For both cases a homogeneous gas density within the integration volume was assumed. If one also takes the gas density profile of the gas jet into account, one obtains the yield function represented by the green line. This function comes very close to the measured function and is used to retrieve the correct laser peak intensities from the measured xenon yield. As parameters for the calculation an initial beam waist of 4.2 mm and a focal length of 250 mm were used. The pulse length was determined by the FROG measurement and was set to 60 femtoseconds. For the gas jet a Gaussian density distribution with a full width at half maximum of 2 mm was assumed. Further, the ratio between the maximal density in the center of the gas jet to the background density was set to 99:1. Because the assumption of a parallel beam did not hold for this experiment, it was not possible to use the same method given in [61, 62] to measure the absolute ionization rate. In these references a time-offlight mass spectrometer with a 0.5 mm slit aperture was used. The Rayleigh length of 3 mm was large enough that the beam could be described as a parallel Gaussian within the detection volume. However, we did not intend to modify our experiment in this way because it would have limited us to yield measurements. Angular resolved momentum measurements would not have been possible with a slit in the interaction region.

4.4 H₂ and D₂ Results

In an intense laser field molecules are not only ionized, they also tend to dissociative ionization. For example H_2^+ can dissociate to a hydrogen atom and a proton or it is further ionized leading to two protons. It is thus not possible to directly extract the total ionization rate of H_2 by just adding the yields of the H^+ and H_2^+ ions (the neutral hydrogen atom cannot be



Figure 4.3: (a) Calculated ion yield of xenon for a parallel Gaussian beam. The saturation intensity I_{sat} increases for decreasing pulse lengths. (b) Ion yield as function of the laser peak intensity for a parallel (blue), a focused Gaussian beam (red) and a Gaussian beam focused into a gas jet (green).

detected with the VMIS). It is therefore necessary to measure the yield of each channel independently. As the final kinetic energy of the ions depends on the fragmentation mechanism several separated peaks should appear in the TOF signal close to the time where H^+ is expected and it should be possible to associate each of them to a certain dissociation channel. With this information it would be possible to obtain the total ionization rate. However, the resolution of our VMIS operated in the TOF mode was not good enough to clearly resolve these peaks. Therefore, the angle-resolved momentum distribution spectra of the H^+ ions were measured for different laser peak intensities to take advantage of the high resolution of the VMIS in the imaging mode. But before these images are presented, a short overview of the different possible dissociation mechanisms of H_2^+ will be given.

4.4.1 Dissociation Mechanism in H₂

A graphical summary of all fragmentation processes is shown in figure 4.4 which is taken from Rudenko *et al.* [63]. It includes the potential energy curve of the ground state of H_2 (black), the ground and first excited state of H_2^+ (red and green) and the potential curve of two protons (pink). Because all ionization or excitation processes are much faster than the nuclear motion, they follow the Frank-Condon principle and are thus indicated as vertical arrows. The most important processes are [63–65]:

• Sequential ionization (SI): H_2 is initially in the vibrational ground state with an equilibrium distance of $R_e = 1.4$ a.u.. Because the equilibrium



Figure 4.4: Potential energy curve of the ground state of H_2 and the two lowest electronic states of H_2^{+} . For the latter dressed states with one up to three photons are given. The vertical arrows indicate the different fragmentation channels. The abbreviations stand for: sequential ionization (SI), non-sequential double ionization (NSDI), sequential double ionization (SDI) and charge resonance enhanced ionization (CREI). The figure is taken from reference [63].

distance in H_2^+ is larger, a multiphoton ionization of the ground state of H_2 will lead to the formation of a traveling wave packet in the $1s\sigma_g$ state of the H_2^+ ion. The wave packet is formed by a coherent superposition of different vibrational levels.

• Bond-softening (**BS**): After ionization the residual H_2^+ ion can dissociate into a proton and a hydrogen atom through absorption of one or two photons. This is possible because the $1s\sigma_g$ state couples with the $2p\sigma_u$ state in the presence of an oscillating electromagnetic field. At a certain internuclear distance the energy difference between the $1s\sigma_g$ and $2p\sigma_u$ state is equal to the energy of a single photon and the transition becomes resonant. Because the amplitude of the wave function of the first vibrational states is almost zero at this distance only levels with $v \geq 5$ are coupled efficiently to the $2p\sigma_u$ state. The lower states can only dissociate via a three-photon transition. But since the three-photon absorption is followed by the emission of a photon, the result is a net two-photon process. In the limit of the dipole coupling a direct two photon transition is forbidden.

This fact can also be explained using field-dressed states. Dressed states are the solution of the Schördinger equation for a molecule (or atom) in a quantized electromagnetic field. They are written as a product of the molecular states and the photon-number states (Fock states). In this case the $1s\sigma_g$ state becomes $|1s\sigma_g, n\rangle$ and the $2p\sigma_u$ state $|2p\sigma_u, n\rangle$ where n stands for the number of photons associated with these states. In figure 4.4 some selected dressed states are plotted as thin black lines. Close to the $1s\sigma_g$ state one finds the $|1s\sigma_g, n-2\rangle$ state and close to the $2p\sigma_u$ state the states $|2p\sigma_u, n-1\rangle$ and $|2p\sigma_u, n-3\rangle$. Some of these states cross each other but due to the strong coupling between the $1s\sigma_g$ and the $2p\sigma_u$ state these crossings are avoided. This leads to the adiabatic curves depicted as light and dark blue lines. For small laser field intensities the wave packet will follow the light blue curve which corresponds to a 1-photon absorption. One can see that the gap between the $|1s\sigma_g, n\rangle$ curve (red) and the adiabatic curve (light blue) is small and the wave packet is still trapped. Only states with $v \geq 5$ are no longer bound and

packet is still trapped. Only states with $v \ge 5$ are no longer bound and can dissociate. For increasing intensities the 3-photon crossing becomes dominant and the adiabatic potential curve changes to the shape indicated by the dark blue curve. Now, also states with v < 5 are no longer bound leading to rapid dissociation of the H_2^+ ion. As the internuclear separation reaches R = 5 a.u. a second avoided crossing between the $|1s\sigma_g, n - 2\rangle$ and $|2p\sigma_u, n - 3\rangle$ forces the wave packet to follow the potential curve of the $|1s\sigma_g, n - 2\rangle$ state. This is the reason why a photon is emitted.

- Non-sequential double ionization (**NSDI**): After tunnel ionization of the H₂ molecules the electrons are in the continuum and are driven by the oscillating electric field. During this oscillation some electrons scatter elastically or inelastically off their parent ion (only for linear polarized light). The latter process can cause the excitation or even the ionization of the parent ion, which then leads to dissociation or Coulomb explosion of the molecule, respectively.
- Sequential double ionization (**SDI**): The H₂⁺ ions in the ground or excited state can again absorb several photons (independent from the first ionization step) and reach the repulsive state.
- Charge-resonance enhanced ionization (**CREI**): For a certain bond length SDI is strongly enhanced as a result of the interaction of the $1s\sigma_g$ and $2p\sigma_u$ states. In the limit of a static electric field this effect can be described in terms of localized electronic wave functions. In figure 4.5(a) the Coulomb potential experienced by the electron in H₂⁺ is plotted for different bond lengths for the field-free case. In 4.5(b)-(d) the same potential curves are given including the effect of the electric field. For a small internuclear distance the electron is delocalized between the two



Figure 4.5: Electronic potential energy functions of H_2^+ for different bond lengths for the field free case (a) and in a static electric field (b) - (d). Above a certain bond length the electron is localized at one proton. The figure is taken from [65].

protons. To reach the continuum it has to tunnel through the external potential barrier. For an intermediate bond length the electron is localized at one of the two protons. In the case where it is localized at the left proton, it only has to tunnel through the internal barrier to reach a continuum state. Because the internal barrier is smaller than the external, the ionization rate is increased in this situation above the corresponding atomic ionization rate. A further stretch of the bond leads to a raise of the internal barrier and the ionization rate decreases again towards the atomic value.

Each of these processes lead to $\rm H^+$ ions with a specific kinetic energy. From previous experiments it was known that hydrogen ions with a kinetic energy between 0 and ~1 eV are the result of the bond softening processes whereas kinetic energies between ~1 and ~5 eV arise from the CREI process [64, 66]. These two are the most dominant processes which lead to the fragmentation of the $\rm H_2^+$ ions. In addition, the NSDI channel is much less probable and leads to fragment energies up to ~9 eV [63]. Further processes



Figure 4.6: (a)-(c) Angle-resolved momentum distribution spectra of H^+ ions for different laser peak intensities. The laser was linearly polarized along the p_x axis. The noise close to $p_z = 0$ is an artifact of the Abel inversion of the raw data.

like bond-hardening, below-threshold dissociation, above-threshold dissociation and zero-photon dissociation are not discussed here. They all lead to fragments with lower kinetic energies compared to the Coulomb explosion channels. Details can be found in the review article by Posthumus *et al.* [64]. Also the neutral dissociation of H_2 can be neglected. So far this process has never been observed.

4.4.2 Momentum Distribution Spectra of H⁺ and D⁺ Ions

The angle-resolved momentum distribution spectra of H⁺ fragments for different laser peak intensities are presented in figures 4.6(a)-(c). The polarization axis was parallel to p_x . The slight distortion around the horizontal center line is an artifact of the Abel inversion of the raw spectra. The distribution around the p_x axis is very narrow and implies that dissociation mainly occurs if the molecular axis is parallel to the electric field vector. This is mainly caused by the fact that dissociation and enhanced ionization are much faster if the molecule stands parallel to the electric field [66]. A second reason is the ionization asymmetry of H₂ itself which is in the order of 1.32 (ratio between the ionization rate parallel and perpendicular to the molecular axis) [67]. Both effects lead to a very strong selection of molecules which are initially aligned along the polarization axis. The angular distribution depends further on the laser-induced reorientation of the molecule. But this effect was not part of the study and will not be discussed in detail here. More information can be found in [64, 68, 69].

From the figures 4.6(a)-(c) one can calculate the yield as a function of the total kinetic energy of the fragment. This is depicted in figure 4.7. Besides the data



Figure 4.7: Energy spectra for linearly polarized light for different laser peak intensities. The solid lines represent the H^+ data and the dashed line the D^+ data. These spectra are calculated using the angular resolved momentum distribution spectra. The legend indicates the laser peak intensity.

for H⁺ (solid lines) also the results for D⁺ (dashed lines) are presented. Both functions are quite similar. One can clearly identify two peaks centered at $\sim 0.5 \text{ eV}$ and $\sim 2 \text{ eV}$. These are the result of the dissociation of the molecule through BS and CREI, respectively [66]. On the low-energy side of the BS peak a shoulder is visible which becomes less pronounced for higher intensities. This shoulder is the result of the 1ω BS dissociation whereas the main yield comes from the 2ω BS dissociation. For intensities above 10^{14} W/cm² the 2ω BS channel is widely open and allows a dissociation of all vibrational states. Therefore, the shape and position of the BS peak reflect the initial population distribution over the vibrational levels of H_2^+ (D_2^+). This distribution can be predicted by calculating the Franck-Condon factors. For the transition from the vibrational ground state in H_2 to the $1s\sigma_g$ state in H_2^+ these factors, as function of the final vibrational state v', have a maximum at v' = 2 [70]. The dissociation through 2ω BS of the $1s\sigma_g$ state with v' = 2 leads then to a fragment energy of ~ 0.5 eV which coincides with the center of the BS peak [70].

BS and CREI are competing processes and for high intensities CREI becomes dominant. Therefore, the BS yield decreases with increasing intensity. In contrast to the BS yield the CREI yield not only increases with intensity, but also the mean kinetic energy of the fragments shifts noticeably to higher energies (in [71] an intensity dependent shift of the BS peak in the range of 0.1 eV towards lower energies was observed). This is expected because CREI leads to Coulomb explosion of the molecule. The final kinetic energy of the fragment is thus the sum of the asymptotic dissociation energy and the Coulomb repulsion energy [70]. Because the latter is a function proportional to 1/R, where R stands for the internuclear distance, the final kinetic energy of the fragments is directly related with the bond length at which the CREI


Figure 4.8: Same as figure 4.6 but for circular polarization. The laser peak intensity is given in each frame.



Figure 4.9: Same as figure 4.7 but for circular polarization.

transition occurs. For increasing intensity CREI becomes significant at smaller internuclear distances and gives thus rise to fragments with higher kinetic energies. The weak modulation of the CREI yield peak is an artifact of the Abel inversion.

BS and CREI occur also if the fragmentation process is induced by a circular polarized laser pulse. In figure 4.8, which shows the angle-resolved momentum distribution for circular polarization, four peaks also appear. From the kinetic energy distribution given in figure 4.9 one can see that the mean energy of these peaks is the same as for linear polarization.

The spectra for linear and circular polarization only differ much for fragment energies above 5 eV. The two cases are compared in figure 4.10. Above a kinetic energy of 5 eV the fragment yield for circular polarization is already close to zero. The remaining signal fluctuation is mainly caused by the iterative Abel inversion code which was used to transform the raw data. For linear polarization the signal does not drop that fast and fragment energies up to 9



Figure 4.10: Kinetic energy distribution spectra of H^+ fragments for circular (blue) and linear (red) polarized light. The laser peak intensity was $2.5 \cdot 10^{14} W/cm^2$.

eV were detected. Such high fragment energies can only occur if the neutral hydrogen molecule is totally ionized within a very short time. It is known that these fragments are the result of recollision-ionization or recollision-excitation followed by field ionization of the molecules [63, 72]. It turned out that the latter process dominates in hydrogen molecules [63]. Both processes cannot occur for circularly polarized light because the electrons are not driven back to the parent ion.

If the kinetic energy spectra of H^+ and D^+ which were measured under the same conditions are compared, one recognizes that the ratio of the BS and CREI yield is different for both molecules and that the CREI peak of D^+ ions is shifted to higher kinetic energies compared to the corresponding H^+ data. This is the result of the different nuclear dynamics of the two isotopologues. Due to the mass difference, the time evolution of the nuclear wave packet is slower in D_2^+ than in H_2^+ . Within the same time the wave packet in H_2^+ reaches a larger R compared to D_2^+ , resulting in Coulomb explosion fragments with less kinetic energy [70]. On the other hand, the wave packet in H_2^+ reaches the critical distance, where the enhanced ionization is maximal, faster and a higher fraction of H_2^+ dissociates through CREI compared to D_2^+ . This fact explains the result shown in figure 4.11(a). It shows the CREI yield n_{CREI}^{X+} with respect to the total H^+ or D^+ ion yield n_{tot}^{X+} , respectively for different laser peak intensities, i.e.

$$f_{\rm CE}^{\rm X_2} = \frac{n_{\rm CREI}^{\rm X^+}}{n_{\rm tot}^{\rm X^+}}.$$
 (4.4)

The blue markers correspond to the ratio $f_{CE}^{D_2}$ measured for D⁺ ions and the red markers to the ratio $f_{CE}^{H_2}$ for H⁺ ions. Each marker type represents an

independent set of measurements. The solid lines in the figure are polynomial fits which were used to determine the ratio between the H⁺ and D⁺ data sets. This ratio $r_{\rm CE} = f_{\rm CE}^{\rm H_2} / f_{\rm CE}^{\rm D_2}$ is shown in figure 4.11(b). At $2 \cdot 10^{14} \rm W/cm^2$ the ratio is 1.4 and decreases towards one for high intensities. This means that the CREI rate is larger in H_2^+ than in D_2^+ for low intensities and the rates become equal at high intensities. This result can be explained by the fact that the pulse duration is quite long with respect to the period of the nuclear wave packets. At high intensities, the molecules are already ionized within the leading edge of the pulse and the H_2^+ as well as the D_2^+ wave packets have enough time to reach the critical distance before the intensity drops below the threshold intensity of CREI. For low intensities where ionization occurs closer to the maximum of the pulse, the time window in which CREI can occur is short with respect to the time scale of the nuclear dynamic. More H_2^+ ions dissociate via \hat{CREI} compared to D_2^+ as the wave packet in H_2^+ reaches larger R within the time window. Similar measurements have already been published in [65, 66, 73, 74] but in none of them the CREI rate of H_2^+ and D_2^+ were directly compared.

Using this result it was possible to calculate the initial number of dissociating H_2^+ and D_2^+ molecules from the total H^+ , respectively D^+ yield. Together with the TOF spectra where the parent ions and the dissociation fragments are measured at the same time, one can calculate the initial number of molecules which were ionized by the pulse and thus obtain the ionization rate independent from the subsequent dissociation of the molecules.

The Coulomb explosion fractions $f_{CE}^{X_2}$ given in figure 4.11 are plotted against the laser peak intensity. This gives the impression that the values were measured for these particular intensities. But as explained in section 4.3, one has to take the focal volume effect into account. Therefore, the presented results are intensity averaged. Besides that it is also known that the Coulomb explosion fraction depends on the pulse duration [65]. Therefore, the obtained result is only valid for the specified spatial and temporal shape of the pulse. It is thus crucial that the ion TOF spectra and the angular resolved momentum distribution spectra of ions are measured under the same experimental conditions.

4.4.3 Intensity Calibration

Before the results of the ion TOF measurements are presented, it will be explained how the xenon ion signal and the SHG signal were included in the data analysis.

Section 4.3 describes how the xenon ionization yield for a focused Gaussian beam is calculated for different laser peak intensities including volume averaging effects as well as the density of the gas jet. By fitting the measured xenon yield to the calculated function it is thus possible to calibrate the signal of the



Figure 4.11: (a) Coulomb explosion fraction $f_{CE}^{X_2}$ for linearly polarized light as a function of the laser peak intensity where red markers stand for H⁺ results and the blue markers for the D⁺ results. The solid lines represent polynomial fits. The ratio r_{CE} between the two fits is given in (b).

photodiode PD 2 (see figure 4.1) and one obtains the laser peak intensity as a function of the photodiode signal. This calibration was done for each measurement individually. The result is given in figure 4.12 where the xenon yield of all measurements, indicated by different marker colors, are depicted. All of them overlap well with the theoretical yield (black solid line, corresponds to the green line in figure 4.3(b)) except for the points at low intensities where the ion signal can no longer be distinguished from the constant background. Calibrating the laser peak intensity with this method allowed us to compare measurements which were taken at different days under slightly different experimental conditions. This was important because it was almost impossible to maintain identical conditions for more than one day. But also the intensity and pulse length fluctuations of the laser which occurred on the time scale of hours were taken into account. As explained in the previous section 4.2, this problem was addressed by measuring the SHG response of the laser pulse at the same time as the ion signal.

Using the example of the normalized parent ion yield $n_{X_2^+}/n_{Xe^+}$ it will be explained how the SHG signal was included in the data analysis. $n_{X_2^+}$ and n_{Xe^+} stand for the parent ion yield of the sample molecule and the xenon ion yield which were measured at the same time. In the figures 4.13(a)-(e) the normalized yield is shown for H₂ (circles) and D₂ (triangles) of a single measurement session as function of the SHG signal and for different laser peak intensities. The SHG signal range was the same for all intensities because the SHG signal was recorded before the laser passes the optics to adjust the intensity (see figure 4.1). In the figure each marker color corresponds to an independent measurement. During the measurement session the laser pulse



Figure 4.12: Xe⁺ yield versus laser peak intensity. The solid line shows the calculated xenon yield for a focused Gaussian beam. The markers represent the measured yield whereas each color corresponds to a certain measurement.

properties were fluctuating leading to an increase of the SHG signal and normalized yield. The ratio between the H_2 and D_2 data set was then calculated as a function of the SHG signal to take these fluctuations into account. As a consequence some of the measurements had to be discarded because there were no corresponding measurements of the other isotopologue within the same SHG signal range. Measurements of the same molecule which share the same SHG signal value were simply averaged before they were included in the calculation. The result, given in figures 4.14(a)-(e), was finally used to determine the mean ratio (black line) and standard deviation (red lines) for each intensity individually. Therefore, all ratios which will be presented in the following sections are always calculated based on several data sets measured on the same day (measurement session). The measurements were then repeated on different days. In the figures of the following sections the ratios resulting from measurements of the same day are usually indicated with a specific marker color.

4.4.4 Fragmentation Rate

The analysis of the angle-resolved momentum distribution spectra of the H^+ or D^+ fragments in section 4.4.2 leads to the conclusion that the dissociation of the parent ion through CREI is faster for H_2^+ than for D_2^+ with respect to the dissociation through BS (see figure 4.11). An absolute measurement of the dissociation rate was not possible because the parent ion yield was unknown. But together with the TOF measurement this can be quantified. In figure 4.15(a) the ratio



Figure 4.13: (a) - (e) Normalized parent ion yield $\frac{n_{X_2^+}}{n_{Xe^+}}$ for H₂ (circles) and D₂ (triangles) as a function of the SHG signal measured for different laser peak intensities. The laser was linearly polarized. Each marker color corresponds to an independent measurement.

$$r_1 = \frac{r_{\rm frag}^{\rm H_2}}{r_{\rm frag}^{\rm L_2}} \tag{4.5}$$

is plotted for linear polarization where

$$r_{\rm frag}^{\rm X_2} = \frac{n_{\rm X^+}}{n_{\rm X_2^+}} \tag{4.6}$$

stands for the fragmentation ratio including the parent ion yield $n_{\rm X_2^{+}}$ and the fragment yield $n_{\rm X^+}$. Each marker color corresponds to a data set taken during a different measurement session. For each session the ratio was determined as explained in the previous section. The solid black line represents the mean value of all ratios. This line has a minimum between $1 \cdot 10^{14}$ W/cm² and $2 \cdot 10^{14}$ W/cm². Within this range the ratio is close to one. This means that



Figure 4.14: (a) - (e) Ratio between the normalized $n_{\rm H_2^+}/n_{\rm Xe^+}$ and $n_{\rm D_2^+}/n_{\rm Xe^+}$ yield given in figure 4.13 as function of the SHG signal for different laser peak intensities. The black line indicates the mean value and the red lines the standard deviation of all points within a single graph.

the fragmentation ratio is equal for both molecules where for higher and lower intensities more H^+ than D^+ ions are detected relative to the parent ion yield. In figure 4.15(b) a second ratio

$$r_2 = \frac{r_{\rm diss}^{\rm H_2}}{r_{\rm diss}^{\rm D_2}} \tag{4.7}$$

is given where

$$r_{\rm diss}^{\rm X_2} = \frac{n_{\rm diss}^{\rm X_2^+}}{n_{\rm stab}^{\rm X_2^+}}$$
(4.8)

represents the ratio between the number of parent ions which dissociate $n_{\text{diss}}^{X_2^+}$ and the number of parent ions which do not dissociate $n_{\text{stab}}^{X_2^+}$. $n_{\text{diss}}^{X_2^+}$ is calculated



Figure 4.15: Fragmentation ratio r_1 (a) and dissociation ratio r_2 (b) as a function of the laser peak intensity for linearly polarized light. Each marker color corresponds to an individual data set. The black line indicates the mean value of all data sets.

using the result of section 4.4.2, i.e.

$$n_{\rm diss}^{X_2^+} = (1 - 0.5 f_{\rm CE}^{X_2}) n_{\rm X^+}.$$
(4.9)

Compared to r_1 the ratio r_2 is close to one for intensities above $2 \cdot 10^{14}$ W/cm² but also increases with decreasing intensity. This shows that at low intensities H_2^+ dissociates faster than D_2^+ . At high intensities the dissociation rate is equal for both molecules because the first ionization step occurs at the rising edge of the pulse. Within the duration of the laser pulse the wave packets have enough time to either dissociate through BS or reach a position at which CREI becomes resonant. The increase of the ratio r_2 at low intensities shows again the strong relation between the dissociation rate and the nuclear dynamics but it is not an indication that H_2 ionizes faster than D_2 . The ratios r_1 and r_2 are independent of the ionization rate of the neutral molecules. Again, one should keep in mind that the presented results depend on the temporal and spatial shape of the laser pulse.

4.4.5 Total Ionization Rate

Finally, the ionization rate of hydrogen and deuterium are compared. The ratios presented in the figures 4.16(a)-(c) are calculated based on the same measurements which were used for the comparison of the fragmentation rates. Each marker color corresponds to an individual data set whereas the black line represents the mean value of all data sets. The red line shows the predicted ionization rate ratio calculated using the modified WFAT [49, 53]. Figure



Figure 4.16: Total ion yield ratio r_3 (a), r_4 (b) and r_5 (c) as a function of the laser peak intensity for linearly polarized light. The red line indicates the predicted ratio and the black line represents the mean value of all measurements.

4.16(a) shows the ratio

$$r_3 = \frac{n_{\rm diss}^{\rm H_2^+} + n_{\rm H_2^+}}{n_{\rm diss}^{\rm D_2^+} + n_{\rm D_2^+}}$$
(4.10)

where $n_{\text{diss}}^{X_2^+}$ corresponds to the number of dissociated molecules (equation 4.9) and $n_{X_2^+}$, the yield of the parent ions. The ratio r_3 is close to 2.5, far above the theoretical value. This ratio does not include a correction due to the different gas densities in the focal volume. A direct correction of the ratio r_3 based on the pressure measured with pressure gauge p_{X_2} leads to the pressure corrected ratio

$$r_4 = r_3 * \frac{p_{\mathrm{D}_2}}{p_{\mathrm{H}_2}}.\tag{4.11}$$

This ratio is shown in figure 4.16(b). For high intensities r_4 is close to the theoretical value but it does not show the strong increase for low intensities. As already mentioned, the density correction based on the pressure gauge signal is not fully reliable insofar as the pressure gauge measures the density by means of electron impact ionization. But this measurement is also species

dependent which leads to a constant offset of the ratio r_4 . As explained in section 4.2.3 we therefore use the xenon signal to calibrate the particle density. Figure 4.16(c) shows the ratio

$$r_5 = r_3 * \frac{n_{\rm Xe^+}^{\rm D_2} c_{\rm Xe^+}^{\rm H_2}}{n_{\rm Xe^+}^{\rm H_2} c_{\rm Xe^+}^{\rm D_2}}$$
(4.12)

where $n_{Xe^+}^{X_2}$ represents the Xe⁺ ion yield and $c_{Xe^+}^{X_2}$ the concentration of xenon in the sample gas. Although a slight increase of the mean value for low intensities can be observed, the ratio r_5 does not decrease towards one for high intensities. From this we conclude that the density calibration with xenon may not lead to the correct result. Also other attempts has been made to calibrate the density (see section 4.2.3), but the xenon method has delivered the most trustworthy and reproducible results. One should also keep in mind that the presented results include data measured on seven different days where the two molecules were measured multiple times each day. But finally, it turned out that the large differences in the leak rate, the expansion of the gas jet and the pumping efficiency between hydrogen and deuterium made it impossible to retrieve a sufficiently accurate density correction. However, the dramatic increase of the ionization rate predicted by the theory has not been conclusively identified.

4.5 CH_4 and CD_4 Results

Methane is one of the simplest hydrocarbon molecules but its interaction with an intense femtosecond laser field is far from being fully understood. As mentioned in the beginning of this chapter we were mainly interested in measuring the ionization rate of the neutral methane and the fully deuterated isotopologue to compare it with the result of the WFAT. Like hydrogen, CH_4^+ (CD_4^+) can also dissociate and one observes several different products. But to compare the ionization rate, the initial amount of the singly charged parent ion needs to be known as well as all fragmentation channels. This makes it difficult to obtain the initial ionization rate from an ion TOF measurement of CH_4^+ (CD_4^+).

In figure 4.17(a) a typical ion TOF spectrum for a laser peak intensity of $3.2 \cdot 10^{14}$ W/cm² and linear polarization is shown. The polarization vector was parallel to the TOF axis. At $m/q \approx 66$ and $m/q \approx 130$ the Xe²⁺ and Xe⁺ ions appear, respectively. As in the hydrogen experiments, the xenon signal was used to calibrate the laser peak intensity and the gas density in the focal volume. The figures 4.17(b) and 4.17(c) show the same spectrum for different axis ranges. For the given intensity one can mainly observe X⁺ and CX⁺_n (n = 0 - 4) fragments. Besides that also a tiny amount of X₂⁺ and doubly charged CX²⁺_n (n = 0, 2, 4) fragments are observed. The ion yield of the singly



Figure 4.17: (a) Ion time-of-flight spectrum of CH_4 (red) and CD_4 (blue) for a laser peak intensity of $3.2 \cdot 10^{14}$ W/cm². (b) Same spectrum as in (a) with focus on the methane fragments. (c) Same as (a) with focus on the doubly charged methane fragments. (d) Ion signal relative to the ion yield of Xe⁺ versus laser peak intensity. The circles represent the fragments of CH_4 and the triangles the fragments of CD_4 . The colors stand for: CX_4^+ (red), CX_3^+ (green), CX_2^+ (blue), CX^+ (magenta), C^+ (gray), X⁺ (cyan). The black curve indicates the expected X⁺ yield assuming that the only fragmentation process would have been Coulomb explosion.

charged fragments relative to the Xe⁺ yield as a function of the laser peak intensity is given in figure 4.17(d). The circles represent the relative yields for the CH_4 sample and the triangles for the CD_4 sample whereas each color corresponds to a specific fragment. The black lines represent the expected H^+ or D^+ yield, respectively with Coulomb explosion assumed to be the only dissociation channel, i.e.

$$n_{\rm X^+,ce} = n_{\rm CX_2^+} + 2n_{\rm CX_2^+} + 3n_{\rm CX^+} + 4n_{\rm C^+}.$$
(4.13)

The fact that doubly charged fragments can be observed shows that Coulomb explosion has to be considered. For high intensities the expected and the measured proton yield are almost the same. Therefore, one can assume that for high intensities Coulomb explosion is the dominant reaction channel which



Figure 4.18: Ion yield ratios r_n (n = 6 - 9) versus laser peak intensity. Each marker color corresponds to a single measurement. The black line with the error bar shows the mean value and standard deviation of all measurements. The red line indicates the predicted ratio.

leads to the production of H^+ or D^+ ions (and probably also to H_2^+) whereas for low intensities the dissociation of singly charged ions dominates. Because the dissociation of singly charged ions does not affect the total amount of observed ions, one could simply add up the yield of all fragments to obtain the initial CH_4^+ (CD_4^+) yield. But as soon as doubly charged molecules are produced, they can Coulomb explode and the total amount of ions does no longer correspond to the initial amount of ionized molecules. Because the relative rate of the two different reaction channels was unknown it was thus not possible to obtain the exact parent ion yield. By using the previous assumption about the dominant reaction channel one can estimate the initial ion yield. Therefore, at low intensities where dissociation dominates one should take all fragments into account whereas at high intensities only the fragments which include a carbon atom should be considered. This was done in order to compare the initial parent ion yield of CH_4 and CD_4 which is depicted in the figures 4.18(a)-(d). Each marker color corresponds to an independent measurement and the black line with error bars shows the mean value and

the standard deviation of all measurements. The red line indicates the value predicted by the WFAT theory. Thereby, figure 4.18(a) shows the yield ratio

$$r_{6} = \frac{n_{\text{tot}}^{\text{CH}_{4}}}{n_{\text{tot}}^{\text{CD}_{4}}} \frac{p_{\text{CH}_{4}}^{\text{CD}_{4}}}{p_{\text{CH}_{4}}^{\text{CH}_{4}}}$$
(4.14)

where $n_{\text{tot}}^{\text{CX}_4}$ stands for the total yield of all fragments including protons and deuterons, respectively. Further, the ratio is normalized by the pressure p^{CX_4} which was measured by the pressure gauge. If only the carbon containing fragments are taken into account one obtains the result depicted in figure 4.18(c) where the ratio

$$r_8 = \frac{n_{\text{totC}}^{\text{CH}_4}}{n_{\text{totC}}^{\text{CD}_4}} \frac{p^{\text{CD}_4}}{p^{\text{CH}_4}}$$
(4.15)

is shown with $n_{\text{totC}}^{\text{CX}_4}$, the total yield of the carbon containing charged fragments. In figure 4.18(a) the mean ratio and the calculated ratio are similar for low intensities whereas for high intensities the mean ratio depicted in figure 4.18(c) is in good agreement with the theoretical value. But due to the large standard deviation of the mean ratio this measurement cannot be used to prove or reject the WFAT theory which predicts a different ionization rate for CH₄ and CD₄. And as already discussed also the density correction based on the pressure gauge signal is problematic. One can use again the xenon signal to calibrate the density, although we showed in the previous chapter that also this method does not give the correct density. But at least one obtains a smaller standard deviation of the mean ratio because signal fluctuations due to laser instabilities are reduced. The corresponding result for the ratio r_6 is given in figure 4.18(b) where the ratio

$$r_{7} = \frac{n_{\text{tot}}^{\text{CH}_{4}}}{n_{\text{tot}}^{\text{CD}_{4}}} \frac{n_{\text{Xe}^{+}}^{\text{CD}_{4}}}{n_{\text{Xe}^{+}}^{\text{CH}_{4}}} \frac{c_{\text{Xe}}^{\text{CH}_{4}}}{c_{\text{Xe}}^{\text{CD}_{4}}}$$
(4.16)

is shown. It includes the Xe⁺ yield measured for the CH₄ sample $n_{Xe^+}^{CH_4}$ as well as for the CD₄ sample $n_{Xe^+}^{CD_4}$. Because the xenon concentration can vary for the two different samples also the concentrations $c_{Xe}^{CH_4}$ and $c_{Xe}^{CD_4}$ have to be taken into account. The equivalent to the ratio r_8 is the ratio

$$r_{9} = \frac{n_{\text{totC}}^{\text{CH}_{4}}}{n_{\text{totC}}^{\text{CD}_{4}}} \frac{n_{\text{Xe}^{+}}^{\text{CD}_{4}}}{n_{\text{Xe}^{+}}^{\text{CH}_{4}}} \frac{n_{\text{Xe}^{+}}^{\text{CH}_{4}}}{n_{\text{Xe}^{+}}^{\text{CD}_{4}}}$$
(4.17)

which is identical to ratio r_7 except that only the carbon containing fragments were taken into account. The ratio r_9 is depicted in figure 4.18(d). For high intensities the mean value of the ratio r_9 is close to the predicted value whereas for low intensities the mean value of the ratio r_7 is slightly above the theoretical result. If both results are considered together one could conclude that there is a trend that CH_4 tends to ionize faster for low intensities compared to CD_4 . But due to the uncertainties in the density calibration and the lack of exact knowledge of all possible reaction channels and their rate it is possible that the observed trend is only an artifact.

Additional interesting information can be found in ratios where the parent ion yield is taken as internal reference. The resulting ratios are independent of any density effects and therefore more reliable than the ratios of the total ion yield. In figure 4.19(a)-(d) the ratios

$$r_{j} = \frac{n_{\rm CH_{4}}^{\rm CH_{4}}}{n_{\rm CH_{4}}^{\rm CH_{4}}} \left(\frac{n_{\rm CD_{4}}^{\rm CD_{4}}}{n_{\rm CD_{4}}^{\rm CD_{4}}} \right)^{-1}$$
(4.18)

for j = 10 - 13 and k = 3 - 0 are depicted. Figure 4.19(e) shows the ratio

$$r_{14} = \frac{n_{\rm H^+}^{\rm CH_4}}{n_{\rm CH_4^+}^{\rm CH_4}} \left(\frac{n_{\rm D^+}^{\rm CD_4}}{n_{\rm CD_4^+}^{\rm CD_4}}\right)^{-1}.$$
(4.19)

The different marker colors represent again the different measurements and the black line the mean value of those. One can immediately see that the yield of the carbon containing fragments with respect to the parent ion yield is always smaller for CH_4 than for CD_4 whereas the relative proton yield is larger compared to the relative yield of deuterons. In general one would expect that the dissociation of CH_4^+ is faster than CD_4^+ due to the larger mass of the deuterons. Assuming that the fragmentation of CH_n^+ is a stepwise process [75] one can focus on the dissociation of CH_4^+ . In principle there are two different reaction channels for CH_4^+ :

$$\operatorname{CH}_4^+ \to \operatorname{CH}_3^+ + \operatorname{H},$$
 (4.20a)

$$\operatorname{CH}_4^+ \to \operatorname{CH}_3 + \operatorname{H}^+.$$
 (4.20b)

In reference [76] Wang *et al.* showed that $CH_4^+ \rightarrow CH_3 + H^+$ is the preferred dissociation channel. This prediction is based on the so called field-assisted dissociation model (FAD). Within this model only the bond which lies along the polarization axis is considered. The positions of the other atoms are fixed. Due to the laser field the potential energy surface is distorted which leads to the dissociation of the CH_4^+ ion along the parallel CH-bond. The model predicts that the dissociation is faster if the polarization vector points from the C to the H atom. But this prediction appears to be inconsistent with the experimental



Figure 4.19: (a)-(d) Ion yield ratios r_n (n=10-14). The marker color corresponds to an individual measurement. The black line with error bars indicates the mean value and standard deviation of all measurements. See text for more details.

results. In figure 4.17(d) one can see that the CH_3^+ yield is larger than the H^+ yield for intensities below $3 \cdot 10^{14} \text{ W/cm}^2$ and thus the reaction $\text{CH}_4^+ \rightarrow \text{CH}_3^+ + \text{H}$ has to be the dominant channel. This is also what is predicted by the quasi-equilibrium theory (QET) [77]. Within this model the dissociation rate is calculated based on the statistical energy distribution among different states of the molecule. However, the two theories are not mutually exclusive. In fact, Strohaber *at al.* [75] could show experimentally that for intensities below $1.3 \cdot 10^{14} \text{ W/cm}^2$ both processes take place where reaction 4.20a dominates over reaction 4.20b whereas for higher intensity Coulomb explosion also plays a role. In contrast to FAD the dissociation described by QET does only depend on the energy transferred from the laser pulse to the molecule whereas the dissociation itself can also occur a long time after the pulse (FAD must occur while the electric field is non-zero). Hence, one can conclude that the nuclear dynamic affect the FAD rate more than the QET rate, provided that

the dissociation time through FAD is comparable with the laser pulse length (see reference [78] for pulse length effects on the dissociation of methane). Because the nuclear dynamics are faster in CH_4^+ than in CD_4^+ one expects that a higher fraction of CH_4^+ molecules dissociates through FAD compare to CD_4^+ . This could explain the larger relative yield of H⁺ and the smaller relative yield of CH_3^+ compared to the deuterated fragments. To prove this assumption a detailed quantum mechanical calculation would be necessary. But such a calculation is beyond the scope of this thesis.

4.6 Conclusion

In conclusion a difference in the dissociation rate through BS and CREI between hydrogen and deuterium in a ~ 60 femtosecond laser pulse was observed. The difference is a clear indication for the strong relation between the nuclear dynamics and the dissociation probability of a molecule in an intense femtosecond laser pulse. According to the modified WFAT not only the dissociation rate but also the ionization rate should depend on the nuclear dynamics. In case of hydrogen and deuterium the theory predicts an ionization rate ratio which is on the order of 3 for an intensity of $1.4 \cdot 10^{13}$ W/cm². With increasing intensities this ratio decreases to one. But within the accuracy of the experimental result this trend was not observed. Due to the lack of a reliable method to measure the gas density in the focal volume it was not possible to evaluate the absolute ratio of the rates with sufficient precision. Several methods have been tested where, among other things, the THG response of the sample or the xenon ion signal was used to calibrate the density. But none of them was found to be sufficiently accurate.

In contrast to the H_2/D_2 measurements the measured ionization ratio between CH_4 and CD_4 decreases with increasing intensity. But it was not possible to uniquely associate this trend with the ionization rate. However, we could also observe differences in the dissociation rate of CH_4 and CD_4 . The ratio of the H^+ and CH_4^+ yields was higher compared to the corresponding ratio of the isotopologue for the complete measured intensity range. However, the ratio of the CH_3^+ and CH_4^+ yields in the same measurement was smaller. The difference could be the result of the field-assisted dissociation of CH_4^+ to $CH_3^+H^+$ and CD_4^+ to $CD_3^+D^+$, respectively which is faster for CH_4 compared to CD_4 .

Chapter 5

Photoelectron Diffraction from H_2 , D_2 , CH_4 and CD_4

In this chapter angle-resolved momentum distribution spectra of photoelectrons from strong-field ionization of H_2 , D_2 , CH_4 and CD_4 will be presented. The spectra were measured for laser pulses with center wavelengths of 800 nm and 1800 nm. The spectra of the corresponding isotopologues should differ due to the different nuclear dynamics between ionization and rescattering. Also the results of ab-initio calculations of the elastic scattering cross section are presented. In this context a short introduction to the R-matrix program Quantemol will be given.

5.1 Introduction

In chapter 3 experimental results are presented which clearly show a change of the angular distribution of the high-energy photoelectrons for pump-probe delays at which the axis distribution of the NO molecules changes significantly. It is argued that the change of the momentum distribution is related to the alignment dependence of the elastic-scattering differential cross section (DCS). This explanation is based on the quantitative rescattering theory (QRS) [21, 23, 40] developed by C. D. Lin and coworkers. They showed that the highenergy photoelectron momentum distribution $D(p, \theta)$ can be expressed as

$$D(p,\theta) = W(p_{\rm r})\sigma(p_{\rm r},\theta_{\rm r})$$
(5.1)

where $\sigma(p_{\rm r}, \theta_{\rm r})$ is the DCS of the parent ion as a function of the scattering momentum $p_{\rm r}$, the scattering angle $\theta_{\rm r}$ and $W(p_{\rm r})$, the momentum distribution of the returning electron. The momentum p and angle θ are the laboratoryframe momentum polar coordinates of the electron. Shortly after the QRS theory was published M. Okunishi *at al.* [20] presented experimental photoelectron momentum distribution spectra for rare gas atoms where they showed



Figure 5.1: (a) Calculated nuclear motion of H_2^+ (blue solid line) and D_2^+ (blue dashed line) triggered by photoionization. The red lines indicate the motion reconstructed from high-harmonic spectra. The figure is taken from reference [7]. (b) Jahn-Teller distortion of CH_4^+ . In methane photoionization also triggers an ultra-fast motion of the protons because of the very different equilibrium geometry of CH_4 and CH_4^+ .

that the DCS can indeed be extracted from the experimental data. Similar results are also presented in references [22, 79]. Meanwhile, this method, often referred to as laser-induced electron diffraction (LIED), has been applied to molecules [24, 25, 34, 35, 80]. In contrast to conventional electron diffraction, LIED has in principle the capability of femto- or even subfemtosecond time resolution [26]. We wanted to exploit the temporal resolution of LIED to image fast nuclear dynamics in molecules. Baker et al. [7] measured the nuclear dynamics in H₂ and D₂ by means of high-harmonic spectroscopy. Because the equilibrium distances of H_2 and H_2^+ are different the ionization triggers a fast motion of the nuclei. This is depicted in figure 5.1(a) which is taken from reference [7]. The blue solid line shows the calculated nuclear motion of H_2^+ and the blue dashed line the motion for D_2^+ . The red lines indicate the motion reconstructed from the experimental data. In a laser pulse with center wavelength of 800 nm the time it takes for an electron to return to the parent ion is ~ 1.8 fs. One can see from figure 5.1(a) that the internuclear distance of H_2^+ increases faster within 1.8 fs compared to D_2^+ . Therefore, one expects that the scattering of the returning electron has to be different for the two molecules. We tried to observe this by measuring the momentum distribution of the high-energy electrons for H_2 and D_2 under identical conditions. A fast nuclear rearrangement after ionization is also expected for $\mathrm{CH}_4.$ Due to the Jahn-Teller effect the equilibrium geometry of CH_4^+ is very different from the equilibrium geometry of the neutral CH_4 molecule. The two structures are depicted in figure 5.1(b). We also tried to observe these dynamics by comparing the photoelectron spectra obtained from CH_4 and CD_4 .

5.2 Experimental Details

For this experiment the VMIS was operated in the electron imaging mode. A fraction of the laser output with a center wavelength of 800 nm and a pulse length of 40 ± 5 fs was focused into the center of the VMIS with a spherical mirror (f = 100 mm, mounted inside the VMIS). Additionally, the laser intensity and pulse length fluctuations were recorded. This was done using the identical setup as described in section 4.2.1. A sketch of the setup is given in figure 4.1. The only difference was that for this experiment the intensity was adjusted with an iris placed in front of the VMIS. The measurements were also repeated using the output of an optical parametric amplifier (OPA, LightConversion HE-TOPAS-C) which was tuned to generated pulses with a center wavelength of 1800 nm. For measurements with the OPA no other optical elements were used except for silver mirrors. The intensity was adjusted with an iris. To monitor the intensity a special photodiode (Thorlabs DET10D, wavelength range 1200 - 2600 nm) was placed behind the last mirror. The light leaking through the mirror was enough to obtain a clear response of the photodiode. For all measurements a leak valve (Lenox Laser, orifice 10 μ m) was used (see section 2.1). All samples were measured pure. The voltage applied to the repeller and extractor was -10.00 kV and -8.24 kV, respectively. The integration time was between several hours and three days. In parallel, the signals of the photodiodes were recorded.

5.3 Calculation of Differential Cross Sections

During the discussion of the NO experiment (chapter 3) it was already mentioned that the program Quantemol was used to calculate the DCS. Before the results of the calculations are presented a short introduction to the program will be given. The focus will be on how a calculation is started and what the output file contains.

5.3.1 Using Quantemol

The program used for this work was Quantemol-N version 4.4b. The program calculates the differential scattering cross section of atoms and molecules based on the R-matrix method [81]. The idea behind the R-matrix method is to divide the space into two regions: an inner region where physics is complex and an outer region where the process can be described by simplified one-electron scattering equations. To solve the problem in the inner region Quantemol uses quantum chemistry methods and for the outer region an asymptotic electron-atom scattering algorithm. Quantemol has a graphical user interface which leads stepwise through all necessary inputs. The following inputs are requested:

- 1. Molecule definition: Molecular formula including charge (e.g. H_2^+ , Ne⁺ etc.).
- 2. Coordinate entry: Cartesian coordinates of each atom in angstrom. When placing the molecule consider that the calculations are done with respect to an electron beam pointing along the z axes form positive to negative z values. Additionally, one should know that for molecules with a specific orientation the DCS is only computed in the xz plane.
- 3. Symmetry definition: Select the symmetry group of the molecule. The following point groups can be selected: C₁, C_i, C_s, C₂, C_{2h}, C_{2v}, D₂, D_{2h}. Additionally, the non-redundant atoms need to be defined. The non-redundant atoms are those from which all other atoms can be generated by applying symmetry operations of the selected point group.
- 4. Electronic structure: Select the electronic structure including the charge of the molecule. If "optimize electronic configuration automatically" is selected, no further input is required. Else the electronic structure needs to be specified. Therefore, the number and symmetry of singly and doubly occupied orbitals has to be known.
- 5. Target Model: One can either choose Hartree Fock (HF) or configuration interaction (CI). Additionally one has to choose a basis set. There is also the possibility to use user-defined basis sets. The basis set has to be in the SUPERMOLECULE format. Additional basis sets can be downloaded from http://bse.pnl.gov/bse/portal.
- 6. Scattering parameters: In this step the scattering parameters are defined. This includes the electron scattering energies and the radius of the R-matrix sphere with respect to the center of mass in atomic units.
- 7. Electron attachment: For scattering calculations this input form can be skipped.
- 8. Advanced settings: To enable scattering cross-section calculations a tick has to be set for the option "Enable advanced options". Then one can choose "Calculate differential and momentum transfer cross sections". If this option is selected the program calculates the DCS averaged over all orientations. If the DCS of a defined orientation is needed, the option "Calculate Aligned molecule cross section" has to be selected. The orientation of the molecule is defined by the three Euler angles α , β and γ which correspond to a rotation of the molecule around the z axis, y axis and again z axis of the initial frame. In matrix representation the full rotation can be written as

$$R = R_z(\gamma)R_y(\beta)R_z(\alpha) \tag{5.2}$$

where R_z and R_y represent the rotation matrix

$$R_z(\alpha) = \begin{bmatrix} \cos(\alpha) & \sin(\alpha) & 0\\ -\sin(\alpha) & \cos(\alpha) & 0\\ 0 & 0 & 1 \end{bmatrix}$$
(5.3)

and

$$R_y(\alpha) = \begin{bmatrix} \cos(\alpha) & 0 & -\sin(\alpha) \\ 0 & 1 & 0 \\ \sin(\alpha) & 0 & \cos(\alpha) \end{bmatrix}.$$
 (5.4)

For each of the Euler angles a start, stop and step value have to be defined. All inputs are separated by commas. The final input is:

 $[\alpha_{start}, \, \alpha_{stop}, \, \alpha_{steps}, \, \beta_{start}, \, \beta_{stop}, \, \beta_{steps}, \, \gamma_{start}, \, \gamma_{stop}, \, \gamma_{steps}].$

If the input is for example: [0, 180, 2, 0, 180, 1, 0, 180, 1], Quantemol will only calculate the DCS for the following two orientations:

- (a) $\alpha = 0, \beta = 0, \gamma = 0$ and
- (b) $\alpha = 90, \beta = 0, \gamma = 0.$
- Review input parameters: In the last step one can check all inputs and save the input file. After saving has been completed one can start the calculation.

After the calculation is finished Quantemol saves all the output data in the subdirectory workspace/project automatically. In the project folder a file and folder is generated with the same name as given by the user for the input file. The content of the file includes all information which is displayed during the calculation. This file is useful if an error occurred during the calculation. If the program finishes without error the calculated DCS for a randomly oriented sample is found in the subdirectory "polyDCS_outputs". The DCS for aligned molecules is saved in the subdirectory "Aligned" whereas for each orientation a file is generated labeled by the corresponding Euler angles, i.e. " $\alpha_{-\beta}$ - γ .dat". In the output files for a randomly oriented sample 0° indicates forward scattering whereas in the output for the aligned molecules 0° means that the electron is backscattered.



Figure 5.2: Averaged DCS $\bar{\sigma}(\alpha, E)$ for H_2^+ as a function of the scattering angle α and scattering energy E. For $\alpha = 0^{\circ}$ the electron is backscattered. The distance between the two protons was set to 0.753 Å. The result represents an averaged DCS where the orientation-dependent ionization rate was taken into account (see text for details). The structures observed for scattering energies above 40 eV may be artifacts of the calculations.

5.3.2 Calculated DCS

The averaged DCS $\bar{\sigma}(\alpha, E)$ for $\mathrm{H_2}^+$ for an internuclear distance of 0.753 Å is given in figure 5.2. The averaged DCS $\bar{\sigma}(\alpha, E)$ was calculated using equation 3.33 where $\sigma_{\mathrm{xz}}(\alpha, E, \phi_i, \theta_j)$ represents the output of Quantemol for a given orientation of the molecule and $f(\theta) = \Gamma_{\mathrm{n}}(\theta)A(\theta)$. The definition of $\sigma_{\mathrm{xz}}(\alpha, E, \phi_i, \theta_j)$ and the angles α, ϕ and θ are given in section 3.3.3. Because the sample molecules were randomly oriented the weighting factor was just a function of the orientation-dependent ionization rate, i.e. $f(\theta) = \Gamma_{\mathrm{n}}(\theta)$. For $\Gamma_{\mathrm{n}}(\theta)$ the experimental result given in reference [67] was used. It is defined as $\Gamma_{\mathrm{n}}(\theta) = \sqrt{w_{\perp}^2 \sin^2(\theta) + w_{\parallel}^2 \cos^2(\theta)}$ with $w_{\parallel}/w_{\perp} = 1.32$. The calculations in Quantemol were done using cc-pVTZ as basis set and the HF method. The Rmatrix radius was set to 10 a.u.. The DCS $\sigma_{\mathrm{xz}}(\alpha, E, \phi_i, \theta_j)$ was then calculated for $\theta = 0^\circ$, 5°, 10°, ..., 90° and $\phi = 0^\circ$, 10°, 20°, ..., 360°.

According to the calculation of Baker *et al.* [7] (figure 5.1(a)) the internuclear distance R increases from 0.753 Å to 0.927 Å for H_2^+ and from 0.747 Å to 0.840 Å for D_2^+ within $\Delta t = t_r - t_0 = 1.8$ fs after the molecule was ionized. The delay Δt corresponds to the transit time of an electron removed from the molecules by an intense 800-nm laser field at $\omega t_0 = 14^\circ$. The electron will then return to the parent ion at $\omega t_r = 260^\circ$ [40]. Due to the different internuclear distances R of H_2^+ and D_2^+ at the time of the return the subsequent scattering process and hence the final momentum distribution spectrum should also be different. This difference can be estimated by comparing the DCS calculated for different R. Because R varies only little within 1.8 fs the result is very



Figure 5.3: Normalized difference $D_{\text{R}_1, \text{R}_2}(\alpha, E)$ calculated for $R_1 = 0.927$ Å (internuclear distance of H_2^+ at $\Delta t = 1.8$ fs) and $R_2 = 0.840$ Å (internuclear distance of D_2^+ at $\Delta t = 1.8$ fs).

similar to the result presented in figure 5.2 for R = 0.753 Å. To visualize the differences it is useful to calculate the normalized difference

$$D_{\mathrm{R}_1, \mathrm{R}_2}(\alpha, E) = \frac{2(\bar{\sigma}_{R_1}(\alpha, E) - \bar{\sigma}_{R_2}(\alpha, E))}{\bar{\sigma}_{R_1}(\alpha, E) + \bar{\sigma}_{R_2}(\alpha, E)}$$
(5.5)

where $\bar{\sigma}_{R_1}(\alpha, E)$ and $\bar{\sigma}_{R_2}(\alpha, E)$ represent the averaged DCS calculated for an internuclear distance of R_1 and R_2 , respectively. The obtained normalized difference $D_{R_1, R_2}(\alpha, E)$ for $R_1 = 0.927$ Å (internuclear distance of H_2^+ at $\Delta t = 1.8$ fs) and $R_2 = 0.840$ Å (internuclear distance of D_2^+ at $\Delta t = 1.8$ fs) is given in figure 5.3. The large differences above a scattering energy of 30 eV close to a scattering angle $\alpha = 100^\circ$ are artifacts. At these positions the DCS is close to zero (see figure 5.2) and small deviations in the calculation lead to large normalized differences. Also the oscillation of the normalized difference between negative and positive values is most probably due to the limited accuracy of the calculation. For scattering energies below 30 eV the result does not show oscillations. In this energy region the normalized difference is positive for all scattering angles. For a better view the result for $D_{R_1, R_2}(\alpha, E)$ is shown for some selected scattering energies E as a function of the scattering angle α in figure 5.4.

To the knowledge of the author the temporal evolution of the nuclear structure of CH_4 and CD_4 after ionization was not known in detail. It was thus not possible to calculate the normalized difference between the DCS of CH_4^+ and CD_4^+ 1.8 fs after ionization. Instead, one can compare the DCS for the cation with the structure of the neutral molecule (T_d symmetry) and the DCS obtained for the equilibrium structure of the cation (C_{2v} symmetry). Due to the Jahn-Teller distortion the two structures are completely different. For the



Figure 5.4: Same result as shown in figure 5.3 for some selected scattering energies.

tetrahedral cation a C-H bond length of 1.087 Å and HCH angle of 109.47° was assumed [82]. The angles and bond lengths for the equilibrium geometry of CH_4^+ are given in table 5.1. The values are taken from the NIST database [83] and represent the result of an ab-initio calculation (basis set: aug-cc-pVTZ, method: coupled cluster, CCSD(T)). The given angles and bond lengths of CH_4^+ are comparable to the experimental values of $CD_2H_2^+$ given in reference [84]. The calculated structure should thus be close to the real geometry of the methane cation.

C-H1, C-H2	C-H3, C-H4	\angle H1CH2	\angle H3CH4	\angle H2CH3
(Å)	(Å)	(°)	(°)	(°)
1.08	1.183	125.5	55.3	113.9

Table 5.1: Ab-initio structure for the ground state of CH_4^+ . The values are taken from the NIST database (basis set: aug-cc-pVTZ, method: coupled cluster, CCSD(T)) [83].

Because of its high symmetry, we approximate the ionization rate of methane as orientation independent and therefore directly use the Quantemol output for a randomly oriented sample. The results for the tetrahedral and equilibrium structure of CH_4^+ are given in figure 5.5(a) and (b), respectively. For the two calculations using the HF method the cc-pVDZ basis set was selected. The radius of the R-matrix was set to 10 a.u.. The normalized difference of the two results is shown in figure 5.6. This difference image only represents an upper limit of what can be expected from the experiment. Nevertheless, this result shows the strong effect of the structure on the DCS, especially for low scattering energies.



Figure 5.5: Calculated DCS for CH_4^+ with a tetrahedral structure (a) and for the CH_4^+ in the ground state (Jahn-Teller distorted geometry) (b).



Figure 5.6: Normalized difference of the result given in figure 5.5 for the tetrahedral and equilibrium structure of CH_4^+ .

5.4 Experimental Results

At first glance this experiment seemed straightforward. The optical setup was simple and the calculations predicted large effects. However, it turned out to be very challenging. The main problem was the long-term stability of the laser. To obtain a sufficient signal-to-noise ratio it was necessary to integrate the photoelectron signal for several hours. During this time the laser intensity and the pulse lengths were changing. Also pointing instabilities were observed. All these variations influence the momentum spectrum of the photoelectrons directly. Without any further information it was thus not possible to assign the observed differences to target specific features. To solve this problem we started recording the laser intensity in parallel and saved the photoelectron spectrum every second. For the further analysis only those spectra were used for which the corresponding intensity signal was within predefined limits. However, we still observed difference images which were not reproducible.



Figure 5.7: Number of measured spectra for a given mean energy of the photoelectrons. The blue line represents the H_2 data set and the red line the D_2 data set. Only the spectra with a mean energy within the energy range indicated by the dashed black lines were used for further analysis.

Therefore, we additionally recorded the intensity of the second-harmonic light which was generated with a small fraction (~ 1%) of the initial beam. Due to the non-linearity of the process, the second-harmonic signal was better suited to monitor intensity and pulse-length fluctuations. But also this method did not provide satisfactory results. Finally, we used the photoelectron spectrum itself to characterize the laser pulse. The spectra were continuously recorded (1 s integration time) and saved. For each spectrum the mean electron energy was calculated. In this way one obtains an energy distribution as shown in figure 5.7. The red line corresponds to the number of measured H₂ spectra as a function of the mean electron energy. The blue line represents the D₂ measurement. The total acquisition time of all spectra was close to eight hours. Due to the continuous change of the laser parameters the maximum of the two functions do not coincide and only the spectra with a mean energy between 3.80 eV and 4.03 eV could be used for the further analysis.

From the selected spectra the mean spectra were calculated. The result is shown in figure 5.8(a) for H₂ and in figure 5.8(b) for D₂, respectively. The center wavelength was 800 nm and the intensity $(9 \pm 1) \cdot 10^{13}$ W/cm². The normalized difference of the two spectra

$$D_{\rm H_2, \ D_2}(\boldsymbol{p}) = 2 \frac{S_{\rm H_2}(\boldsymbol{p}) - S_{\rm D_2}(\boldsymbol{p})}{S_{\rm H_2}(\boldsymbol{p}) + S_{\rm D_2}(\boldsymbol{p})}$$
(5.6)

where $S_{H_2}(\mathbf{p})$ and $S_{D_2}(\mathbf{p})$ represent the momentum-resolved spectrum for H_2 and D_2 , respectively, is given in figure 5.8(c). In the normalized difference image a clear periodic pattern is visible. It follows that the position of the ATI peaks in the H_2 and D_2 spectra are shifted with respect to each other. This is an indication that the laser intensity for the two spectra was not identical despite of the applied pre-selection. Nevertheless, this method led to the best results as compared to the pre-selection based on the intensity or second-



Figure 5.8: (a) Angle-resolved momentum distribution spectrum of the photoelectrons from H₂. (b) Same as (a) but for D₂. (c) Normalized difference of the H₂ and D₂ spectra. The center wavelength of the laser was 800 nm and the peak intensity was $(9 \pm 1) \cdot 10^{13}$ W/cm².

harmonic signal. However, for the rescattered (high-energy) photoelectrons the normalized difference becomes zero. As explained in section 3.3.3 these electrons are located on a circle with radius $p_{\rm r}$ in the momentum-resolved spectra whereas the center of the circle is shifted from the origin of the spectrum by $p_{\rm s}$. For the photoelectrons which reach the detector with energies close to 10 $U_{\rm p}$ the ratio between $p_{\rm r}$ and $p_{\rm s}$ is 1.26 [40]. The corresponding circle for $p_{\rm r} = 0.71$ a.u. is shown on top of the spectra in the figures 5.8(a)-(c). The scattering angle α (see figure 5.8(a)) is defined such that for $\alpha = 0^{\circ}$ the electron is backscattered from the parent ion. The electron yield as function of the scattering angle α for $p_r = 0.71$ a.u. is given in figure 5.9(a). The red solid line corresponds to the data obtained for H_2 and the black dashed line for D_2 . The normalized difference between the two yield functions is shown in figure 5.9(b) as red solid line. For scattering angles larger than 20° the difference is zero. The green line in figure 5.9(b) shows the differences obtained from the ab-initio calculations presented above (a scattering momentum of $p_{\rm r} = 0.71$ a.u. corresponds to a kinetic energy of 6.9 eV). The theoretical calculation



Figure 5.9: (a) Electron yield as a function of the scattering angle α for H₂ (red solid line) and D₂ (black dashed line). For $\alpha = 0^{\circ}$ the electron is backscattered. (b) Normalized difference of the yield functions given in (a) (red line) together with the calculated normalized difference (green line).

predicts a normalized difference of 0.3 which is almost constant with respect to the scattering angle. This is not in agreement with the experimental result. However, a constant offset is difficult to observe because one has to normalize the spectrum by the total electron yield. This is necessary because the total yield does also depend on the gas density in the focal volume which is different for H_2 and D_2 .

The measurements were repeated with pulses with a center wavelength of 1800 nm. In an 1800-nm laser field the high-energy electrons take 4.1 fs to return to the parent ion, more than twice as long as in 800-nm laser field. Therefore, one expects to observe larger differences between the photoelectron spectra. However, the normalized difference between the two spectra given in figure 5.10(c) does not show large differences (the differences close to $p_x = 0$ a.u. are caused by the Abel inversion). The complete measurement took 45 hours. Within this time spectra with a total integration time of 25 hours were recorded. The spectra were again sorted and selected based on the mean electron energy. For H₂ spectra with a total integration time of 76 minutes and for D₂ 38 minutes were used for the further analysis. The result for H₂ and D₂ are shown in the figures 5.10(a) and (b), respectively. The laser peak intensity was $(9 \pm 1) \cdot 10^{13}$ W/cm².

The spectra obtained from CH_4 and CD_4 ionized by 800-nm laser pulses are given in figure 5.11(a) and (b), respectively. The laser peak intensity was $(9 \pm 1) \cdot 10^{13}$ W/cm². The normalized difference between CH_4 and CD_4 , given in figure 5.11(c), also shows differences for electrons with low kinetic energy as observed for hydrogen. The shape of the pattern varies for different measurements. However, a distinct pattern in the high-energy region was not observed. For the rescattered electrons with scattering energy of $p_r = 0.71$ a.u (indicated as red solid circle in the spectra) the electron yield is extracted



Figure 5.10: (a) Angle-resolved momentum distribution spectra of the photoelectrons from H₂. (b) Same as (a) for D₂. (c) Normalized difference of the H₂ and D₂ spectra. The center wavelength of the laser was 1800 nm. The laser peak intensity was $(9 \pm 1) \cdot 10^{13}$ W/cm².

and shown in figure 5.12(a) for CH_4 (red solid line) and CD_4 (black dashed line). The normalized difference between the two functions is given in figure 5.12(b). The results obtained for laser pulses with a center wavelength of 1800 nm are shown in figure 5.13(a) and (b) for CH_4 and CD_4 , respectively. From the normalized difference image given in figure 5.13(c) one can see that the two spectra are nearly identical. However, the normalized difference becomes positive for high kinetic energies which was most probably due to different laser conditions. The assumption is based on the fact that the sensitivity of the sorting method was not sufficient.

For the two isotopologues we could observe differences in the low-energy region of the photoelectron spectra recorded with 800-nm laser pulses. From the NO experiment presented in chapter 3 we knew that the pattern in this energy region is very sensitive to the electronic and nuclear structure due to the inference of different electron trajectories. However, it was not possible to distinguish between differences which are caused by laser fluctuations and differences which are the result of a different electronic and nuclear structure of the targets.



Figure 5.11: (a) Angle-resolved momentum distribution spectra of the photoelectrons from CH₄. (b) Same as (a) for CD₄. (c) Normalized difference of the CH₄ and CD₄ spectra. The laser peak intensity was $(6 \pm 1) \cdot 10^{13}$ W/cm². The center wavelength of the laser was 800 nm.



Figure 5.12: (a) Electron yield as a function of the scattering angle α for CH₄ (red solid line) and CD₄ (black dashed line). For $\alpha = 0^{\circ}$ the electron is backscattered. (b) Normalized difference of the yield functions given in (a).



Figure 5.13: (a) Angle-resolved momentum distribution spectra of the photoelectrons from CH₄. (b) Same as (a) for CD₄. (c) Normalized difference of the CH₄ and CD₄ spectra. The center wavelength of the laser was 1800 nm. The laser peak intensity was $(9 \pm 1) \cdot 10^{13}$ W/cm².

But because the result obtained with an 1800-nm laser does not show any clean difference in the low-energy region we had to conclude that the differences caused by laser instabilities were dominating.

5.5 Conclusion

We have measured the photoelectron spectra for H_2 , D_2 , CH_4 and CD_4 strongfield ionized with laser pulses with center wavelengths of 800 nm and 1800 nm. The spectra of the corresponding isotopologues were then compared. We found that the differences strongly depend on the intensity of the laser pulse. To reduce this effect several different methods were applied. First the intensity was monitored with a photodiode. Based on this signal the spectra were sorted and compared. As a further improvement we recorded the secondharmonic signal which was generated from a small fraction of the ionizing pulse. Finally, the spectra were compared based on the mean electron energy which was obtained from the spectrum themselves. This method led to the best results but it did not completely remove the differences which were caused by small variations of the laser pulse properties. In the spectrum obtained for H_2 and D_2 with 800-nm laser pulses differences in the low-energy region of the photoelectrons were observed which were absent in the spectra measured with an 1800-nm laser pulse. Therefore, we conclude that differences are mainly caused by intensity fluctuations of the laser during the measurements. For the two wavelengths the strong differences for the rescattered electrons (high-energy photoelectrons) that were predicted by calculations were not observed. These conclusions also apply to CH_4 and CD_4 . However, these results are not a final proof that there are no differences between the spectra of the corresponding isotopologues. In the future, technical improvements of the laser system may increase the stability and eliminate the need for a preselection of the spectra and exclude intensity fluctuations as the source of the differences.

Chapter 6

Strong-Field Ionization of Methyl Halides with a Phase-Controlled Two-Color Laser Field

In this chapter an experiment is presented in which methyl halides (CH_3X) where X = F, Cl, Br, I) were investigated by means of angle-resolved momentum distribution spectroscopy of ions. Dissociative ionization and Coulomb explosion of the methyl halides were induced by an intense phase-controlled two-color laser field. At the beginning of this chapter a short introduction will be given, followed by the explanation of the method and the description of the optical setup. In the subsequent sections the results are presented and discussed. The chapter closes with the conclusion.

6.1 Introduction

The understanding of strong-field ionization of atoms and molecules is of great importance as it describes the initial step in phenomena like laser-induced electron diffraction, attosecond pulse generation or high-harmonic generation. Although Keldysh presented a theory about tunneling ionization already in the mid-1960s [6], it still remains difficult to describe this process with adequate precision especially for molecules. Tong *et al.* [85] adapted an atomic tunneling ionization theory to molecules known as molecular Ammosov-Delone-Krainov theory (MO-ADK, the atomic ADK theory itself is related to the theory of Perelomov, Popov, and Terent'ev, see reference [86] for a review of the early works). From the MO-ADK theory it follows that the angular dependence of the tunneling ionization rate is strongly related to the shape of the highest occupied molecular orbital (HOMO) [87]. Further, it predicts that the ionization rate is maximal if the electric field points in the opposite direction of the highest electron density of the HOMO, i.e. for an electron escaping in the direction of highest electron density. But for the OCS molecule Holmegaard etal. showed experimentally that this is not the case [88]. They found that the ionization rate was larger for an electron escaping from the oxygen end of the molecule, although the HOMO of OCS has a higher electron density on the S atom. Based on a different theory, a highly-simplified version of the strongfield approximation (SFA) which replaced the molecular orbital with an atomic orbital, the authors were able to explain the observation when the Stark shift of the HOMO up to second order in the electric field was included in the theory [89]. The Stark shift of the HOMO is a simple approximation for the differential Stark shifts of the neutral and cationic electronic ground states. The experiment presented by Holmegaard *et al.* was performed using circularly polarized light. However, Hansen et al. could show that for linearly polarized light the ionization rate has a maximum when the field vector is perpendicular to the molecular axis [90]. In this case even the Stark-shift-corrected MO-ADK theory failed to predict the experimental result. In the previously mentioned experiments [88, 90] the OCS molecules were initially aligned or oriented with a laser pulse. But it is also possible to obtain information about the angular dependence of the tunneling ionization rate from a randomly oriented sample, e.g., when the molecules are ionized by an asymmetric field. An asymmetric field can be obtained when two pulses with frequency ω and 2ω are superimposed with a fixed phase relation. Using this method Ohmura et al. [91] studied the ionization of OCS. They observed that the electrons were preferentially removed from the part of the HOMO with the highest electron density (from the sulfur atom of the OCS molecule). This is just the opposite result as for the case where the OCS molecules were ionized with a single frequency pulse [88]. Besides that, Ohmura *et al.* showed that their result is in agreement with the theoretical calculations based on the weak-field asymptotic theory (WFAT) [49]. In contrast to MO-ADK and SFA the WFAT already includes the Stark effect [91]. However, a theory which could explain the result of all experiments is, to the knowledge of the author, still missing. Therefore, it is essential that more experiments are realized based on which the strong-field-ionization theories can be further developed.

Using the phase-controlled two-color field method CO and NO were also investigated [92, 93]. The conclusion of these experiments was that the shape of the HOMO dominates in determining the asymmetry of the ionization. For both molecules the result was also in qualitative agreement with MO-ADK and Stark-shift corrected SFA calculations. In this chapter experimental results of the ionization asymmetry of the methyl halides (CH₃X, with X = F, Cl, Br, I) measured by the same method will be presented. A similar study has already been published by Ohmura *et al.* [94]. They have used a time-of-flight spectrometer whereas we have used a velocity-map-imaging spectrometer. This



Figure 6.1: (a)-(c) Two-color ($\omega/2\omega$) laser pulse for phase delays $\Delta \phi = 0, \pi/2$ and π .

enabled us to observe new effects in angle- and momentum-resolved spectra which could not be measured by Ohmura *et al.*. Moreover, we have systematically studied the role of the laser intensity on the observed fragmentation patterns.

6.2 Experimental Details

When two linearly polarized, symmetric electric fields with frequency ω and 2ω are superimposed with a fixed relative phase $\Delta\phi$ between the two fields, i.e.

$$E(t) = E_1(t)\cos(\omega t) + E_2(t)\cos(2\omega t + \Delta\phi), \qquad (6.1)$$

the resulting field E(t) is not necessarily symmetric. This is depicted in figure 6.1(a)-(c) for $\Delta \phi = 0$, $\pi/2$, and π . For $\Delta \phi = 0$ the maximal amplitude is larger for positive values than for negative values of E(t). For $\Delta \phi = \pi/2$ one obtains a symmetric pulse and for $\Delta \phi = \pi$ it is again asymmetric with an amplitude maximum pointing downwards.

When an intense asymmetric two-color pulse is focused on a randomly oriented sample, dissociative ionization and even Coulomb explosion of the molecules is induced. In general these fragmentation reactions are orientation dependent. Mainly because of the orientation dependence of the initial step, the strongfield ionization of the molecule. But also the rate of the subsequent processes like bond softening, non-sequential double ionization or charge-resonanceenhanced ionization (see chapter 4) show a certain angular dependence. Therefore, one obtains an asymmetric distribution of the fragments which is illustrated in figure 6.2. In the figure the asymmetric pulse with a large amplitude pointing upwards is focused into the center of the VMIS where randomly oriented CO molecules in a molecular beam are ionized. Because CO molecules ionize faster when the electric field points from the C to the O atom a larger



Figure 6.2: Illustration of the experimental setup. The asymmetric two-color pulse is focused in the VMIS where CO molecules are ionized. Upon ionization the molecules can dissociate. The resulting momentum distribution of the O^+ (C^+) fragments shows a clear up-down asymmetry.

fraction of O^+ appear with a momentum pointing in this direction. This was observed by Li *et al.* [92]. Initially, the phase delay between the ω and 2ω pulse is not known and needs to be calibrated. Li *et al.* solved this problem by measuring the asymmetric momentum distribution of photoelectrons from xenon and compared it with the result of a TDSE calculation. In this way they could calibrate the phase precisely and could show that the maximal distribution asymmetry of the O^+ ions of the CO molecules coincides with the maximal field asymmetry. Therefore, the O^+ ion signal can be used in our experiments to calibrate the relative phase $\Delta \phi$ of the two-color field.

The optical setup used to generate the two-color field is depicted in figure 6.3. A vertical polarized pulse with center wavelength of 800 nm, a pulse duration of 50 ± 10 fs and an energy of ~ 1.3 mJ first passed a β -barium-borate (BBO) crystal. The thickness of the crystal was 300 μ m. Due to second-harmonic generation (SHG) in the BBO one obtains an additional 400-nm pulse after the crystal which is horizontal polarized. To rotate the polarization of the 800-nm pulse a zeroth-order half-wave plate (at 800 nm) was used. After the half-wave plate both pulses were horizontal polarized. To adjust the intensity an iris was placed just in front of the VMIS. The two pulses entered the VMIS through a sapphire window (2.6 mm thickness). A spherical mirror, mounted inside the VMIS chamber, with a focal length of f=100 mm focused the beam backwards into the center of the supersonic gas jet. The gas jet was formed by a pulsed Even-Lavie valve (orifice 150 μ m, 1 kHz repetition rate). The target molecules were all diluted in helium to a concentration of < 1%. To compensate the dispersion of the BBO, the half-wave plate and the sapphire window, 2.6 mm calcite and two UV fused silica plates with a total thickness of 2.5 mm were placed in the optical beam path between the BBO and the


Figure 6.3: Optical setup used for the two-color experiments. See text for further details.

half-wave plate. One UV fused silica plate (1.5 mm thickness) was mounted on a motorized rotational stage (Newport PR50PP together with the controller Newport ESP 100). By tilting this plate, the relative phase $\Delta \phi$ between the ω and 2ω pulse was adjusted. The intensity of the 400-nm pulse was $(22\pm3)\%$ of the total intensity. If the dispersion of the initial laser pulse was optimized for second harmonic generation a conversion efficiency of 25% was reached. However, for the experiment the dispersion of the laser was optimized in terms of ion yield leading to a reduction of the conversion efficiency. The VMIS was operated in the ion-imaging mode. The polarization of the two-color laser pulse was parallel to the multi-channel plate detector (MCP). Usually, 4.00 kV and 3.14 kV were applied to the repeller and extractor plate, respectively. The MCP gain was switched such that only fragments with a specific massto-charge ratio were detected. The switching time was in the range of 100 ns to 300 ns. For each fragment 100 images were recorded each at a specific tilt angle of the 1.5 mm UV fused silica plate. The tilt angles ranged from 31° to 41° and were equally spaced. To obtain the momentum-distribution spectra the measured images were Abel inverted using an iterative inversion method. However, due to signal fluctuations and MCP sensitivity inhomogeneities the retrieved spectra can deviate from the real spectra. In some cases the inversion algorithm also gives negative numbers especially for momenta where the signal is close to zero or which are close to the symmetry axis of the spectrum. These momenta were localized by calculating the mean spectrum. Momenta with negative values in the mean spectra were then excluded from the further analysis. The spectra were further convoluted with a Gaussian filter to reduce the high-frequency noise caused by the inversion. The full width at half maximum of the filter function was 1% of the momentum detection range. During each measurement session the four methyl halides $(CH_3X;$ X = F, Cl, Br, I) were measured using different intensities. The iris diameter was between (1.6 ± 0.1) mm and (3.2 ± 0.1) mm which corresponds to pulse energies between ~ 60 $\mu\rm{J}$ and ~ 200 $\mu\rm{J}$, respectively. First, an ion time-of-flight spectrum was recorded to determine which fragments occur for the given intensities. From these data the timing for the MCP gain was derived. For all intensities the phase-dependent angle-resolved momentum distributions of $\rm{CH_3^+}$ fragments and halogen ions were measured. Additionally, also CO was measured to calibrate the relative phase of the two-color field.

6.3 Electronic and Geometric Structure of Methyl Halides

Table 6.1 gives the adiabatic ionization potential $I_{\rm p}$, the permanent electric dipole moment μ_0 , the rotational constant B_0 and the length of the C-X bond for the methyl halides. The ionization potential decreases from CH₃F to CH₃I. In the same order the C-X bond length increases. In an experiment where all molecules are measured under similar conditions the ionization rate will thus increase from CH₃F to CH₃I. This is no further problem because we were only interested in the angular distribution of the dissociation products and not in the absolute ion yield. The methyl halides have a rather large rotational constant. Hence, it is safe to assume that within a 50 femtosecond laser pulse dynamic alignment or orientation of the molecules can be neglected. Besides that, the permanent dipole of all methyl halides points from the halogen to the carbon atom [94] and the absolute values of the dipole are similar for all four molecules.

	$I_{\rm p}$	μ_0	B_0	$R_{\rm CX}$
	$(eV)^{(a)}$	$(D)^{(a)}$	$(MHz)^{(a)}$	$(Å)^{(b)}$
CH_3F	12.47	1.858	25536.12	1.383
CH_3 ^{35}Cl	11.22	1.8963	13292.95	1.785
CH_3 ⁷⁹ Br	10.541	1.8203	9568.19	1.934
$CH_{3}I$	9.538	1.6406	7501.31	2.136

Table 6.1: Adiabatic ionization potentials $I_{\rm p}$, electric dipole moment μ_0 , rotational constant B_0 and C-X bond length $R_{\rm CX}$ of the methyl halides. (a) values taken from reference [94]. (b) values taken from reference [83]. Table adapted from reference [94].

Most theories which are currently used to calculate the ionization rate are single-active electron theories which can only be applied to one orbital at a time - usually the HOMO. Contributions of the lower lying orbitals are neglected because they are much smaller. As starting point to understand the following experimental results it is thus helpful to study the structure of the highest-lying orbitals. These can be calculated using standard quantum chemistry programs such as Gaussian or GAMESS. In figure 6.4 the isocontours of the HOMO, HOMO-1 and HOMO-2 for all methyl halides are shown (GAMESS Version 11; method: restricted HF; basis sets: aug-ccpVQZ for CH₃F, CH₃Cl and CH_2Br ; Def2-QZVP for CH_2I). The color indicates the sign of the wave function. The HOMO and HOMO-2 are both doubly degenerate and are therefore additionally labeled with a and b. From the structure of the HOMO a and HOMO **b** one can see that for CH₃F the amplitude of the wave function is larger on the methyl side whereas for the other three molecules the largest amplitude is found on the halogen atom. According to the MO-ADK or SFA theory one would thus expect that the maximum of the angle-dependent ionization rate should point towards the methyl part for CH₃F and towards the halogen atom for CH₃Cl, CH₃Br and CH₃I. Further due to the existence of a nodal plane containing the C-X axis in the HOMO the ionization rate parallel to the C-X axis should be minimal for all molecules. This also applies for the HOMO-2 orbitals because they also have a nodal plane containing the molecular axis. But in contrast to the HOMO the wave function of the HOMO-2 is larger on the methyl side for all molecules. The HOMO-1 has no nodal plane parallel to the C-X axis and the asymmetry of the wave function is small. The angle-dependent ionization rate from the HOMO-1 should thus be similar for all methyl halides.

The angle-dependent ionization rate of the HOMO is shown in the figure 6.5(a)-(d). The angle θ is the polar angle between the electric field direction and the C-X axis. For $\theta = 0^{\circ}$ the electron is removed from the methyl side (in the direction opposite to the electric field). The black line corresponds to the rate calculated using the partial Fourier transform method (PFT) [45]. The calculations were done by D. Baykusheva for an intensity of 10^{14} W/cm². Because the PFT theory does not include the Stark effect the obtained rate was multiplied by the Stark-corrected tunnel ionization rate [95]

$$w(\mathbf{F}) = \frac{1}{2\kappa(\mathbf{F})^{\frac{2}{\kappa(\mathbf{F})}-1}} \left[\frac{2\kappa(\mathbf{F})^3}{F}\right]^{\frac{2}{\kappa(\mathbf{F})}-1} \exp\left[-\frac{2\kappa(\mathbf{F})^3}{3F}\right] \times \exp\left\{-6\left[\frac{2}{\kappa(\mathbf{F})^2}\right] \left[\frac{F}{\kappa(\mathbf{F})^3}\right]\right\},\tag{6.2}$$

where

$$\kappa(\boldsymbol{F}) = \sqrt{2I_{\rm p}^{\rm eff}(\boldsymbol{F})}.$$
(6.3)

Equation 6.2 does also include a correction term to account for over-the-barrier ionization [96]. The orientation dependence of $w(\mathbf{F})$ is introduced through the effective ionization potential including the Stark effect up to second order in the field [89]



Figure 6.4: Isocontours of the HOMO, HOMO-1 and HOMO-2 orbitals of the methyl halides. The color indicates the sign of the wave function. The HOMO and HOMO-2 orbitals are doubly degenerate and are labeled with a and b. The orbital wave functions were calculated using the quantum chemistry program GAMESS.

$$I_{\rm p}^{\rm eff}(\boldsymbol{F}) = I_{\rm p}(0) + \boldsymbol{\Delta}\boldsymbol{\mu} \cdot \boldsymbol{F} + \frac{1}{2}\boldsymbol{F}^{\rm T}\boldsymbol{\Delta}\boldsymbol{\alpha}\boldsymbol{F}, \qquad (6.4)$$

where

$$\Delta \mu = \mu^{\mathrm{M}} - \mu^{\mathrm{I}}, \ \Delta \alpha = \alpha^{\mathrm{M}} - \alpha^{\mathrm{I}}.$$
(6.5)

 $I_{\rm p}^{\rm eff}(\boldsymbol{F})$ depends on the electric field vector \boldsymbol{F} and thus on the orientation of the molecule with respect to the field. The parameter $\boldsymbol{\mu}^{\rm M}$ and $\boldsymbol{\mu}^{\rm I}$ represent the dipole moment of the molecule and of the unrelaxed cation, respectively. The parameter $\boldsymbol{\alpha}^{\rm M}$ and $\boldsymbol{\alpha}^{\rm I}$ are the corresponding polarizability tensors and $I_{\rm p}(0)$ the field-free ionization potential. In a first approximation the difference between the two dipole moments, i.e. $\boldsymbol{\Delta}\boldsymbol{\mu}$, corresponds to the dipole

of the HOMO. Hence, for CH_3F , for example, $\Delta\mu$ points along the CX axis in the direction of the halogen atom. From equation 6.4 one can see that the effective ionization potential $I_{\rm p}^{\rm eff}$ is increased when the field **F** points in the same direction as $\Delta \mu$ leading to a suppression of the tunneling ionization. But following the argumentation of the PFT theory one would expect an increase of the ionization rate for this direction because the electron is removed from the side of the HOMO with the largest amplitude. Depending on the field strength, the magnitude of $\Delta \mu$ and $\Delta \alpha$ the Stark effect can thus change the ionization preference, obtained from the PFT calculations alone, completely. However, as expected from the structure of the HOMO the calculated orientation-dependent ionization rates have a minimum at $\theta = 0^{\circ}$ and $\theta = 180^{\circ}$. But one should keep in mind that these results may be different from the real ionization rate due to several reasons. First, the Stark-effect is not directly included in the PFT theory and the way it is introduced may lead to an overestimation of the effect. Second, the mixing of the degenerated orbitals due to the interaction with the laser field is neglected. Third, multi-orbital effects were not considered. The values of μ and α used for the calculations are listed in table 6.2 where α_{\parallel} and α_{\perp} represent the polarizability of the HOMO parallel and perpendicular to the C-X bond. The dipole moment μ stands parallel to the C-X bond pointing from the methyl group to the halogen atom for $\mu > 0$.

	μ	$lpha_{\parallel}$	α_{\perp}
	(a.u.)	(a.u.)	(a.u.)
CH ₃ F	0.767	2.22	4.87
CH ₃ Cl	-0.103	3.66	7.47
$\mathrm{CH}_{3}\mathrm{Br}$	-0.122	3.70	2.84
CH ₃ I	-0.160	5.41	4.30

Table 6.2: Values for the dipole moment μ and polarizability α_{\parallel} and α_{\perp} of the HOMO used for the PFT calculations.

More accurate results were obtained from the WFAT theory. As already mentioned in the beginning, the WFAT treats the first-order Stark effect rigorously. Further, the mixing of the two degenerate orbitals in the laser field was also taken into account. The results for the new eigenfunctions Ψ^{A} and Ψ^{B} , which are orientation-dependent linear combinations of the field-free orbitals, are indicated in the figures 6.5(a)-(c) as blue and green solid lines, respectively. The WFAT calculations were done by O. Tolstikhin, T. Morishita, F. Jensen and L. Madsen [97]. The results for the different molecules can be compared based



Figure 6.5: (a)-(d) Calculated normalized ionization rate as a function of the angle θ for the methyl halide molecules CH₃X (X = F, Cl, Br, I). θ is defined as the angle between the direction in which the electron is removed and the C-X molecular axis. For $\theta = 0^{\circ}$ the electron is removed from the methyl side. The black lines indicate the ionization rate calculated based on the PFT method. The blue and green lines are the result of the WFAT theory for Ψ^{A} and Ψ^{B} , respectively.

on the head-to-tail ionization asymmetry, which can be defined as

$$a = \frac{\int_{0^{\circ}}^{90^{\circ}} \Gamma(\theta) \sin(\theta) d\theta - \int_{90^{\circ}}^{180^{\circ}} \Gamma(\theta) \sin(\theta) d\theta}{\int_{0^{\circ}}^{180^{\circ}} \Gamma(\theta) \sin(\theta) d\theta}$$
(6.6)

where $\Gamma(\theta)$ stands for the angle-dependent ionization rate. The results for the asymmetry *a* for the different models are given in table 6.3. From the WFAT one obtains a positive asymmetry for CH₃F for the two eigenfunctions. This means that CH₃F is preferentially ionized at the methyl group. For CH₃Cl, CH₃Br and for CH₃I it follows that these molecules are ionized preferentially at the halogen atom. In general one can conclude that for CH₃F the absolute asymmetry is predicted to be larger compared to CH₃Cl, CH₃Br and CH₃I. The results obtained from the PFT calculations are different. The asymmetry is negative for all molecules except for CH₃Cl. The largest asymmetry is obtained for CH₃Cl and CH₃I. The large discrepancy between the PFT and WFAT results may be due to the overestimation of the Stark effect in the

		WFAT	\mathbf{PFT}
CHE	$\Psi^{\rm A}$	0.69	0.81
01131	Ψ^{B}	0.58	-0.01
CH-Cl	$\Psi^{\rm A}$	-0.01	0.04
011301	Ψ^{B}	-0.45	0.94
CIL Dr	$\Psi^{\rm A}$	-0.20	0.99
CH3DI	Ψ^{B}	-0.46	-0.22
CH ₃ I	$\Psi^{\rm A}$	-0.39	0.06
	Ψ^{B}	-0.43	-0.90

Table 6.3: Calculated ionization asymmetry a for the methyl halides. The asymmetry a is calculated based on the results shown in the figure 6.5(a)-(d).

Stark-corrected PFT calculation. As explained above the Stark-effect can change the ionization preference completely and we will see that the PFT results indeed disagree with the experimental observations.

6.4 Results

6.4.1 Ion Time-Of-Flight Spectra of Methyl Halides

The figures 6.6 to 6.9 show the ion time-of-flight spectra for the methyl halides $(CH_3X, X = F, Cl, Br, I)$ measured for three different laser peak intensities: $(5 \pm 2) \cdot 10^{13} \text{ W/cm}^2$, $(1 \pm 0.4) \cdot 10^{14} \text{ W/cm}^2$ and $(1.6 \pm 0.6) \cdot 10^{14} \text{ W/cm}^2$. The blue solid lines show the same data as the red lines just magnified by a factor of 20. In the spectra of the CH_3F molecule the peak which corresponds to the parent ion appears at m/q = 34. The peaks at m/q = 31, 32, and 33 correspond to the fragments CH_xF^+ with x = 0 - 2. For the lowest intensity (figure 6.6(a)) the H⁺ yield is very small with respect to the CH_xF^+ fragments and one can conclude that the dominant reaction leading to these fragments was

$$\mathrm{CH}_{r}\mathrm{F}^{+} \to \mathrm{CH}_{r-1}\mathrm{F}^{+} + \mathrm{H}$$

$$(6.7)$$

where x = 1 - 3. This also implies that the dissociation occurs sequentially. For higher intensities the H⁺ yield becomes large and other dissociation channels leading to CH_xF^+ fragments, for example the Coulomb explosion of the doubly-charged parent ion, can no longer be excluded. CH_xCl^+ fragments with x = 0 - 2 were also observed for methyl chloride (figure 6.7). But because chlorine possesses two stable isotopes, ³⁵Cl and ³⁷Cl, two peaks corresponding to the singly charged parent ions appear at m/q = 50 and m/q = 52. Also



Figure 6.6: (a)-(c) Ion time-of-flight spectra of CH₃F ionized by a two-color field for different laser peak intensities (red line). The intensities were $(5 \pm 2) \cdot 10^{13}$ W/cm², $(1 \pm 0.4) \cdot 10^{14}$ W/cm² and $(1.6 \pm 0.6) \cdot 10^{14}$ W/cm². The spectrum magnified by a factor 20 is shown as blue line.

for methyl bromide two isotopologues exist. Therefore, the parent ion peaks appear at m/q = 94 and m/q = 96 (figure 6.8(a)) for the molecules including ⁷⁹Br and ⁸¹Br, respectively. On the left side of the peak at m/q = 94 one can observe a shoulder in the magnified spectrum of CH_3Br (blue line). This shoulder corresponds to the $C^{79}Br^+$ ion. Fragmentation of the methyl bromide ion similar to the reaction 6.7 can thus not be excluded. For methyl iodide only a single peak centered at m/q = 142 can be observed (figure 6.9). This peak corresponds to the parent ion but there was no sign that reactions resulting in CH_xI^+ fragments with x = 0 - 2 occurred. Indeed, also Liu *et al.* [98] did not observe these fragments.

Heavier ions which could have been identified as originating from clusters were not observed for any of the methyl halides. Particular attention was also paid to space-charge effects especially if samples with a low ionization potential were ionized with an intense laser pulse. Because space-charge effects affect the expansion of the ion cloud, it is important that this effect is minimized by choosing the concentration of the sample molecule carefully. In the ion TOF spectra space charge would lead to a broadening or even to a splitting of the



Figure 6.7: Same as figure 6.6 but for CH_3Cl .

peaks. But none of the spectra show any of these indications.

For CH_3I also the doubly-charged parent ion (m/q = 71) was observed whereas for CH_3F no evidence for this fragment was found. Either they are unstable or the detection sensitivity was too low. For CH_3Cl and CH_3Br the signals from the CH_nX^{2+} ions with n = 0 - 3 (peaks close to m/q = 24 for CH_3Cl and m/q = 47 for CH_3Br) were just at the detection limit. For CH_3Cl the doubly-charged parent ions were also observed by Sun *et al.* [99] and Tanaka *et al.* [100] (both experiments were done using a single frequency laser pulse but under similar conditions otherwise). The observation of doubly-charged parent ions indicates that there is a potential well on the corresponding potential energy surface which prevents the molecule from dissociation [98]. From the measurement one can thus conclude that the potential well becomes deeper from CH_3F^{2+} is unstable. Higher-charged parent ions were absent from all measured spectra.

For all molecules and intensities H^+ , H_2^+ and CH_x^+ with x = 0-3 fragments can be observed. For the highest laser peak intensity also C^{2+} and CH_2^{2+} appeared. All fragments can be the result of dissociative ionization or Coulomb explosion of the singly- or multiply-charged parent ion. Reference [98] showed for methyl iodide that CH_x^+ with x = 0-2 are the result of a stepwise



Figure 6.8: Same as figure 6.6 but for CH₃Br.

dissociation of the CH_3^+ fragments. We thus assume that this is also the case for the other methyl halides. At high intensity also the carrier gas is ionized leading to the peak at m/q = 4 (He⁺). In all spectra peaks appear at m/q = 16 and m/q = 18 which is the result of the ionization and dissociative ionization of residual water molecules. In some spectra also traces of nitrogen (m/q = 28) and oxygen (m/q = 32) can be found. But the signals coming from water, nitrogen and oxygen were so small that they did not affect the actual measurements. For CH₃Cl and CH₃Br, H₃⁺ appeared at intermediate laser intensities (figure 6.7(b) and 6.8(b)). H₃⁺ is the result of the Coulomb explosion of the doubly-charged parent ion whereas three hydrogen bonds are broken and newly formed [99].

In all spectra also charged halogen atoms were observed. For CH_3F , F^+ and F^{2+} could be identified in the spectrum. Unfortunately F^{3+} which should appear at m/q = 6.33 overlaps with the peak of C^{2+} . But based on the yield ratio between F^{2+} and F^+ one would expect that the F^{3+} yield is very small. For CH_3Cl molecule the Cl^+ and Cl^{2+} peaks are clearly visible in the TOF spectrum whereas the Cl^{3+} is too close to the C^+ peak to be resolved. However, in the imaging mode where MCP gain can be switched as fast as 100 ns it was possible to restrict the observation to either C^+ or Cl^{3+} . For methyl chloride also very little Cl^{4+} ions (m/q = 8.75) have been observed for



Figure 6.9: Same as figure 6.6 but for CH₃I.

the highest laser peak intensity (figure 6.7(c)). For CH_3Br halogen ions from Br^+ to Br^{4+} and for CH_3I from I^+ to I^{5+} were observed. The observation of multiple-charged halogen atoms indicates that highly charged parent ions were produced in the laser pulse. Multiply-charged parent ions were only observed up to CH_3X^{2+} . This shows that multiply-charged parent ions are very unstable and decay rapidly to different fragments. From all the possible decay channels we focused on those of the form

$$\operatorname{CH}_{3} \mathbf{X}^{(p+q)+} \to \operatorname{CH}_{3}{}^{p+} + \mathbf{X}^{q+}.$$
(6.8)

These reactions are usually referred to as Coulomb-explosion channels. The $\rm CH_3^{p+}$ ions can further decay to smaller fragments and therefore we restricted the observation to $\rm CH_3^{+}$ and $\rm X^{q+}$ ions. Because of the rapid dissociation of the multiply-charged parent ions one can assume that the angular distribution of these fragments are mainly defined by the orientation of the molecule at the time of ionization. Hence, it is possible to obtain the head-to-tail asymmetries of (dissociative) ionization from the angle-resolved momentum distribution spectra of the $\rm CH_3^{+}$ and $\rm X^{q+}$ ions [92]. The result of these measurements will be presented in the next section.

6.4.2 Asymmetric Emission of Charged Fragments

For each measurement session the relative phase $\Delta \phi$ was calibrated by measuring the asymmetric emission of the C⁺ and O⁺ ions from CO molecules. We define the emission asymmetry as

$$\alpha(E) = \frac{\int_{0^{\circ}}^{180^{\circ}} Y(E,\theta) d\theta - \int_{180^{\circ}}^{360^{\circ}} Y(E,\theta) d\theta}{\int_{0^{\circ}}^{360^{\circ}} Y(E,\theta) d\theta}$$
(6.9)

where E stands for the kinetic energy of the fragment and $Y(E,\theta)$ for the energy- and angle-dependent fragment yield [92]. The emission direction θ is defined such that $\theta = 90^{\circ}$ and $\theta = 270^{\circ}$ correspond to the emission of the fragment parallel to the polarization axis of the two-color laser field. The emission asymmetry $\alpha(E)$ should not be confused with the ionization asymmetry a defined in section 6.3. Considering dissociative ionization of the molecule a direct relation between a and $\alpha(E)$ is only given if the first ionization step is the decisive quantity and the influence of the two-color field on the subsequent dissociation is small. Because there are several different ionization mechanisms which can lead to a doubly-charged parent ion (like non-sequential double ionization, sequential double ionization or charge-resonance-enhanced ionization) it is not obvious how $Y(E,\theta)$, obtained from Coulomb-explosion channels, is related to the first and second ionization step. For the Coulomb explosion of higher-charged parent ions it is even more complex. In a first approximation one can assume that $Y(E,\theta)$ is the product of the ionization asymmetry of the different ionization steps. $Y(E, \theta)$ was obtained from the VMIS operated in the ion imaging mode (for further details see section 6.2).

The asymmetry $\alpha(E)$ as a function of the phase delay $\Delta\phi$ between the two fields for C⁺ from CO is shown in the middle panel of figure 6.10(a). A clear modulation of the asymmetry is visible. The amplitude of this modulation is shown in the right panel whereas on the left panel the ion yield as a function of the kinetic energy is given. The energy scale is identical in all panels. In the yield spectrum two peaks near 0 eV and 4 eV are visible which corresponds to the fragmentation of the ionized CO molecule into C⁺ + O and C⁺ + O⁺, respectively. Hence, one also expects a modulation of the emission asymmetry of the O⁺ ions which can be associated with the C⁺ + O⁺ dissociation channel. The asymmetry of the emission of the O⁺ ion is given in figure 6.10(b) together with the yield spectrum and the modulation amplitude. As expected one observes the opposite modulation of the asymmetry compared to the C⁺ ions. The ion yield spectrum of O⁺ also shows two peaks. With the relation of the kinetic energies for a two-body fragmentation

$$m_{\rm X} E_{\rm X} = m_{\rm Y} E_{\rm Y},\tag{6.10}$$

where $m_{\rm X}$ ($m_{\rm Y}$) and $E_{\rm X}$ ($E_{\rm Y}$) stand for the mass and energy of the two differ-



Figure 6.10: Density plot of the asymmetric emission $\alpha(E)$ (middle panel) of C⁺ (a) and O⁺ (b) from CO as a function of the phase delay $\Delta\phi$ between the 800- and 400-nm fields. In the left panel the ion yield as a function of the fragment kinetic energy and in the right panel the modulation amplitude of the asymmetry are shown. The energy axis is identical in all panels. The laser peak intensity was $(1.9 \pm 0.7) \cdot 10^{14}$ W/cm².

ent fragments, one can check whether the peaks close to 4 eV correspond to the dissociation channel leading to $C^+ + O^+$ ions. In the figures 6.10(a) and (b) the corresponding energies are indicated in the left panels as green horizontal lines. The position of the green line in the spectrum of O^+ , calculated from the peak position of the C^+ yield, is very close to the peak maximum. One can thus conclude that these peaks indeed correspond to the Coulomb explosion of the CO molecule. This has been observed by Li *et al.* [92]. They have also shown that the C^+ ions are preferentially emitted in the direction opposite to the electric field maximum. Based on this result we have assigned the phase $\Delta \phi$ in the density plots of the emission asymmetry $\alpha(E)$.

The phase-dependent asymmetry of the emission of CH_3^+ fragments from CH_3F is shown in figure 6.11(a)-(c) for three different laser peak intensities. At low intensities a single peak at 1 eV is visible in the yield spectrum. For the highest intensity (figure 6.11(c)) a second peak at 3.4 eV appears. The position of this peak is marked with a green line. In the yield spectra the red lines mark the expected fragment kinetic energies assuming a dissociation as given in equation 6.8. The labels (p, q) indicate the charge of each fragment.



Figure 6.11: Density plot of the asymmetry, yield spectrum and modulation amplitude similar to figure 6.10, but for CH₃⁺ ions from CH₃F. The laser peak intensity was $(5 \pm 2) \cdot 10^{13}$ W/cm² (a), $(1 \pm 0.4) \cdot 10^{14}$ W/cm² (b) and $(1.6 \pm 0.6) \cdot 10^{14}$ W/cm² (c). Figure (d) represents the same data as shown in (c) but the asymmetry is calculated based on the raw spectra (not Abel inverted). The green line marks the position of the peak at 3.4 eV. The red lines indicate the kinetic energy $E_{(p, q)}^{CH_3^+}$ calculated using equation 6.11 for different dissociation channels.



Figure 6.12: Momentum-resolved modulation amplitude (left) and modulation phase (right) of the CH₃⁺ ion yield from CH₃F. The laser polarization was parallel to p_z . The laser peak intensity was $(5 \pm 2) \cdot 10^{13}$ W/cm² (a), $(1 \pm 0.4) \cdot 10^{14}$ W/cm² (b) and $(1.6 \pm 0.6) \cdot 10^{14}$ W/cm² (c).

The energies were calculated assuming two point charges q_p and q_q , separated by the equilibrium distance R_e between the C and F atom of the neutral CH₃F molecule, i.e.

$$E_{\rm (p,q)}^{\rm frag} = \frac{m_{\rm mol} - m_{\rm frag}}{m_{\rm mol}} \frac{q_{\rm p} q_{\rm q} e^2}{4\pi\epsilon_0 R_{\rm e}}$$
(6.11)

where $m_{\rm mol}$ is the mass of the molecule, $m_{\rm frag}$ is the mass of the fragment, e is the electron charge and ϵ_0 is the permittivity of vacuum [101]. The distance $R_{\rm e}$ for CH₃F is listed in the table 6.1. For the (1, 1) dissociation channel one obtains for the CH_3^+ fragment a kinetic energy of 5.83 eV. This is about 2.4 eV above the center of the peak marked by the green line. Corrales et al. [101] have also observed that the measured kinetic energy of CH_3^+ for the Coulomb explosion of CH₃I was smaller than the energy predicted by a similar estimation. But this is not surprising because the values obtained from equation 6.11 represent an approximate upper limit since they rely on the assumption of purely Coulombic repulsion. Corrales et al. also calculated the adiabatic potential energy curve along the C-I bond for the neutral and doubly-charged CH₃I molecule. Based on this data they obtained kinetic energies for the CH_3^+ fragments which are in agreement with the experimental results. In this way they could assign the peak in the CH_3^+ spectrum of CH_3I to the (1, 1) dissociation channel. We thus assume that equation 6.11 also overestimates the fragment energy for CH_3F and one can assign the peak at 3.4 eV to the (1, 1) Coulomb-explosion channel and the peak at 1 eV to the dissociation of the singly charged parent ion to $CH_3^+ + F$. In figure 6.11(a) and (b) one can see that the modulation of the asymmetry for the (1, 0) dissociation is large. The sign of the modulation is identical with the sign of the C⁺ fragment from CO. This means that the dissociation of the parent ion is faster if the electric field points from the methyl group to the fluorine atom. This was also ob-



Figure 6.13: Similar to figure 6.11 but for F⁺ (a) and F²⁺ (b) from CH₃F. The laser peak intensity was $(1.6 \pm 0.6) \cdot 10^{14}$ W/cm². The red lines indicate the calculated kinetic energy for different dissociation channels. The green line in (a) is drawn at 2.7 eV.

served for the (1, 1) Coulomb-explosion channel in figure 6.11(c) and even for CH_3^+ ions with energies up to 15 eV. In the same figure one can also observe a continuous shift of the modulation phase and a decrease of the modulation amplitude for energies below 5 eV. In principle these kinds of effects can be caused by an inaccurate Abel inversion of the raw spectra. This can be seen in the figures 6.12(a)-(c). They show the momentum-resolved modulation amplitude and modulation phase of the CH₃⁺ fragments from CH₃F for the same data as shown in the figures 6.11(a)-(c). The polarization vector of the $\omega + 2\omega$ field was parallel to the p_z axis. The frequency for which the amplitude and phase was evaluated was determined using the asymmetry plots. In the figures 6.12(a)-(c) the relative amplitude is shown for $p_x < 0$ and the corresponding phase for $p_x > 0$. For the highest intensity (figure 6.12(c)) one can clearly distinguish the two patterns which correspond to the (1, 0) and (1, 1) dissociation channel. For both channels the phase changes from positive to negative for $p_z > 0$ to $p_z < 0$ (as expected from the evaluation of the asymmetry $\alpha(E)$) except for momenta close to $p_x = 0$. In this region the Abel inversion induces large signal fluctuations and the retrieved values can be negative. As explained in section 6.2 negative values were not considered in the analysis. Therefore, it was not possible to retrieve the correct phase for momenta close to $p_x = 0$.



Figure 6.14: Similar to figure 6.12 but for F^+ (a) and F^{2+} (b) from CH_3F . The laser peak intensity was $(1.6 \pm 0.6) \cdot 10^{14} \text{ W/cm}^2$.

These values are left white in the momentum-resolved modulation phase spectra. But the shift of the modulation phase is also observed if the asymmetry is calculated based on the raw data. This is shown in figure 6.11(d). The phase shift is less pronounced compared to figure 6.11(c). The fact that the shift only appears at high laser intensities for fragments with little kinetic energy could be an indication for a dissociation channel which changes its dissociation preference depending on the field strength. It may also be due to a different channel which only becomes dominant at higher laser intensities. From the ion time-of-flight spectrum of $CH_{2}F$ (figure 6.6(c)) it was known that for the highest laser intensity F^+ and F^{2+} ions appear. The asymmetric emission of these two fragments is shown in the figures 6.13(a) and (b), respectively. The position of the green line in figure 6.13(a) is calculated from the peak at 3.4eV in the spectrum of the CH_3^+ fragment by using equation 6.10. The green line is close to the maximum of the F^+ yield at 3.0 eV. Hence, this peak corresponds to the (1, 1) Coulomb-explosion channel of CH_3F . The asymmetry is just the opposite as for the CH_3^+ fragments. The shift of the modulation phase for energies below 1.2 eV was also observable at lower intensities. Therefore, this shift may originate from a second dissociation channel leading to F⁺ fragments with kinetic energies close to zero whereby the dissociation asymmetry is opposite compared to the Coulomb-explosion channel. An even stronger modulation was observed for the F^{2+} fragments which also show the opposite asymmetry compared to CH_3^+ . The maximum of the F^{2+} yield is at 7.1 eV, very close to the energy $E_{(1,2)}^{F^{2+}}$ which is obtained from equation 6.11 for the (1, 2) channel. This shows that the ionization asymmetry does not change even if more than two electrons are removed. Unfortunately it was not possible to measure the emission asymmetry for the F^{3+} fragments because of the low detection rate and the interference with the C^{2+} ions (due to the limited switching speed of the MCP gain). For completeness, the momentum resolved modulation amplitude and phase for F^+ and F^{2+} are given in figure



Figure 6.15: Similar to figure 6.11, but for CH_3^+ ions from CH_3Cl . The laser peak intensity was $(5 \pm 2) \cdot 10^{13} \text{ W/cm}^2$ (a), $(1.0 \pm 0.4) \cdot 10^{14} \text{ W/cm}^2$ (b) and $(1.6 \pm 0.6) \cdot 10^{14} \text{ W/cm}^2$ (c). The green solid line is plotted at 4.3 eV and the green dashed line at 7.7 eV. The dashed black line in the yield spectrum of (c) shows the magnified yield spectrum.

6.14(a) and (b), respectively.

In figures 6.15(a)-(c) the asymmetric emission of CH_3^+ from CH_3Cl is shown for different laser intensities. Similar to CH_3F one observes a prominent peak in the yield spectrum at 0.5 eV for all intensities. Due to the low energy this peak can only correspond to the dissociation of the singly-charged parent ion to $\text{CH}_3^+ + \text{Cl}$. Compared to the emission of CH_3^+ from CH_3F the asymmetry has the opposite sign meaning that dissociation occurs preferentially if the field asymmetry points from the chlorine atom to the methyl group. In the density plot of the asymmetry in figure 6.15(a), which shows the result for



Figure 6.16: Similar to figure 6.13, but for Cl^+ (a), Cl^{2+} (b) and Cl^{3+} (c) from CH_3Cl . The laser peak intensity was $(1.6 \pm 0.6) \cdot 10^{14} \text{ W/cm}^2$. The positions of the green solid and dashed line are related with the position of the green lines shown in the figure 6.15(c) through equation 6.10.

the lowest laser intensity, one observes a clear modulation of the asymmetry between 0 eV and 4.2 eV. Within this energy range the phase of the modulation does not change. If the intensity is increased to $(1 \pm 0.4) \cdot 10^{14}$ W/cm² (figure 6.15(c)) a peak appears in the yield spectrum at 4.3 eV and a modulation of the asymmetry up to 9.5 eV becomes visible. But the sign of the asymmetry changes at 4.2 eV. In figure 6.15(c) the largest modulation amplitude is observed at 7.7 eV and is marked as green dashed line. The width of the peak at 7.7 eV indicates that the energy distribution of the fragments is broad. In the magnified yield spectrum (dashed black line) of figure 6.15(c) one can identify a shoulder at 7.7 eV. Therefore, one has to assume that at



Figure 6.17: Similar to figure 6.12, but for CH_3^+ from CH_3Cl . The laser peak intensity was $(5 \pm 2) \cdot 10^{13} \text{ W/cm}^2$ (a), $(1.0 \pm 0.4) \cdot 10^{14} \text{ W/cm}^2$ (b) and $(1.6 \pm 0.6) \cdot 10^{14} \text{ W/cm}^2$ (c).

least two channels with a different sign of the emission asymmetry contribute to the ion yield within the energy range between 2.4 eV and 10 eV. From the position of the green solid line shown on top of the yield spectrum in figure 6.15(c), which marks the peak at 4.3 eV, and from the position of the green dashed line at 7.7 eV one can calculate the energy of the corresponding chlorine ion using equation 6.10. The obtained energies for the $^{35}\text{Cl}^+$ ions are 1.9 eV and 3.3 eV, respectively. The two energies are indicated as green solid and green dashed lines in the yield spectra in the figures 6.16(a)-(c). These data were taken at a laser peak intensity of $(1.6 \pm 0.6) \cdot 10^{14}$ W/cm² and show the result for Cl^+ , Cl^{2+} and Cl^{3+} ions, respectively. In figure 6.16(a) the green solid line at 1.9 eV in the yield spectrum coincides with the yield maximum. Therefore, one can conclude that the peak at 4.3 eV in the yield spectrum of CH_3^+ in figure 6.15(c) corresponds to the (1, 1) dissociation channel. In the yield spectrum of figure 6.16(a) no distinct peak at the position of the dashed green line (3.3 eV) is visible. In the asymmetry plot of figure 6.16(a) one can further see that at 1.7 eV the sign of the asymmetry changes. For energies between 1 eV, the local yield minimum, and 1.7 eV the asymmetry is negative and for energies above 1.7 eV the sign is positive at zero phase delay. Assuming (1, 1) Coulomb explosion of the molecule, this result is in agreement with the observation in CH_3^+ where we could measure the opposite change of the sign when the corresponding CH_3^+ fragments exceeds a kinetic energy of 4.3 eV. A shift of the modulation phase was also observed for energies between 0 eV and 1 eV. The same shift was observed for an intensity of $(5 \pm 2) \cdot 10^{13}$ W/cm². Hence, it might be an indication that there are two channels with different dissociation asymmetries leading to CH_3 and Cl^+ fragments. In figure 6.16(b) the green dashed line is close to the Cl^{2+} yield maximum at 4.4 eV. The sign of the asymmetry at this energy is the opposite compared to the CH_3^+ fragments with energies higher than 4.3 eV. One can



Figure 6.18: Similar to figure 6.12, but for Cl^+ (a), Cl^{2+} (b) and Cl^{3+} (c) from CH_3Cl . The laser peak intensity was $(1.6 \pm 0.6) \cdot 10^{14} \text{ W/cm}^2$.

thus not exclude that the high-energy CH_3^+ fragments are solely the result of the (1, 1) Coulomb explosion of the molecule. The (1, 2) Coulomb explosion of the molecule also has to be considered as a source of high-energy CH₂⁺ fragments and even the (1,3) Coulomb-explosion channel is possible. This is shown in figure 6.16(c) for the Cl^{3+} fragment. The prominent peak at 7.3 eV in the yield spectrum coincides with the expected fragment kinetic energy (red solid line) for the (1, 3) Coulomb-explosion channel. The width of the peak covers a large energy range. Within this range the modulation phase of the asymmetry changes continuously. This shows that there are at least two channels with different emission asymmetries which contribute to the Cl^{3+} fragment yield. At zero phase delay the asymmetry is positive for 0 eV and becomes negative for high energies. At the position of the green dashed line $(3.3~{\rm eV})$ the sign of the asymmetry is opposite to the sign of the asymmetry of the high-energy CH_3^+ fragments. The change of the asymmetry for CH_3^+ fragments with high energies is also clearly visible in the figures 6.17(a)-(c) which show the momentum-resolved modulation amplitude and phase. The corresponding momentum-resolved spectra for Cl^+ , Cl^{2+} and Cl^{3+} are shown in the figures 6.18(a)-(c), respectively.

For CH_3Cl we have also measured the asymmetric emission of H_3^+ and CCl^+ fragments coming from the Coulomb explosion of the parent ion. The result



Figure 6.19: Similar to figure 6.11, but for H_3^+ (a) and CCl⁺ (b) from CH₃Cl. The laser peak intensity was $(1.6 \pm 0.6) \cdot 10^{14}$ W/cm². The position of the green line is 4.0 eV in (a) and 0.26 eV in (b), respectively.

is shown in figure 6.19(a) and (b), respectively. The yield maximum of the H_3^+ fragments is at 4.0 eV (indicated as green solid line). The signal of H_3^+ shows a very weak modulation of the asymmetry. At zero phase delay the asymmetry is positive which means that the Coulomb explosion of the parent ion to H_3^+ and CCl⁺ is slightly faster when the field maximum points from the halogen atom to the methyl group. As expected for a two-body fragmentation the modulation asymmetry of CCl⁺ has the opposite sign compared to H_3^+ . Using equation 6.10 one obtains from the peak position of H_3^+ a corresponding energy of 0.26 eV for CCl⁺. This energy is indicated as green solid line in figure 6.19(b). At this position the yield spectrum of CCl⁺ has a shoulder on the high-energy side of the main peak at 0.05 eV. For completeness, the momentum-resolved amplitude and phase spectra for the two fragments are given in figure 6.20(a) and (b), respectively.

The asymmetric emission of CH_3^+ from CH_3Br for different laser peak intensities are given in the figures 6.21(a)-(c) and the corresponding momentum-resolved spectra of the modulation amplitude and phase are shown in the figures 6.23(a)-(c), respectively. Just as CH_3Cl , CH_3Br also tends to dissociate faster to CH_3^+ + Br if the field asymmetry points from the halogen atom to the methyl group.



Figure 6.20: Similar to figure 6.12, but for ${\rm H_3}^+$ (a) and CCl⁺ (b) from CH₃Cl. The laser peak intensity was $(1.6\pm0.6)\cdot10^{14}~{\rm W/cm^2}.$



Figure 6.21: Similar to figure 6.11, but for CH_3^+ ions from CH_3Br . The laser peak intensity was $(5 \pm 2) \cdot 10^{13} \text{ W/cm}^2$ (a), $(1.0 \pm 0.4) \cdot 10^{14} \text{ W/cm}^2$ (b) and $(1.6 \pm 0.6) \cdot 10^{14} \text{ W/cm}^2$ (c). The green solid line corresponds to an energy of 5.1 eV and the green dashed line to an energy of 9.2 eV.



Figure 6.22: Similar to figure 6.11, but for Br^+ (a), Br^{2+} (b) and Br^{3+} (c) from CH_3Br . The laser peak intensity was $(1.6 \pm 0.6) \cdot 10^{14}$ W/cm². The positions of the green solid and dashed line are related with the position of the green lines in figure 6.21(c) through equation 6.10.

The same is also true for the Coulomb explosion of the doubly-charged parent ion which leads to the prominent peak at 5.1 eV. A change of the sign of the asymmetry for CH_3^+ fragments with high kinetic energies was also observed. One can use again equation 6.10 to find the energy of the corresponding bromine ions for the different channels. For the (1, 1) channel at 5.1 eV (indicated as green solid line in figure 6.21(c)) one obtains an energy of 0.97 eV for ⁷⁹Br and for the second channel at 9.2 eV, (indicated as green dashed line in figure 6.21(c)) one obtains 1.75 eV. The two energies are marked with green lines in the figures 6.22(a)-(c) which show the result for Br⁺, Br²⁺ and Br³⁺, respectively. The green solid line in figure 6.22(a) for Br⁺ is very close to the peak maximum at 1.1 eV. The asymmetry at this energy has the



Figure 6.23: Similar to figure 6.12, but for CH_3^+ from CH_3Br . The laser peak intensity was $(5 \pm 2) \cdot 10^{13} \text{ W/cm}^2$ (a), $(1.0 \pm 0.4) \cdot 10^{14} \text{ W/cm}^2$ (b) and $(1.6 \pm 0.6) \cdot 10^{14} \text{ W/cm}^2$ (c).

opposite sign compared to the corresponding CH_3^+ peak and we can conclude that the peak at 1.1 eV in the Br⁺ yield spectrum is indeed the result of the Coulomb explosion of the doubly-charged parent ion. A change of the asymmetry for Br⁺ at 9.2 eV (indicated as dashed green line) cannot be observed in figure 6.22(a). However, in the momentum-resolved spectrum given in figure 6.24(a) one can observe a change of the modulation phase. In the spectrum the momentum which corresponds to an energy of 1.75 eV is indicated as green dashed circle. Starting at $p_z = 137$ a.u. and $p_x = 0$ a.u. and following the dashed circle the sign of the modulation changes from negative to positive. But the momentum range where the phase is negative is limited to momenta with small p_x values. Similar to Cl⁺ fragments from CH₃Cl one can also observe a shift of the modulation phase for Br⁺ fragments with kinetic energy < 0.5 eV. This might be the result of the dissociation of the parent ion through channels with different emission asymmetries. Phase shifts of the modulation were also observed for Br^{2+} and Br^{3+} fragments. For both fragments the modulation phase at the position of the green dashed line is opposite to the phase obtained for the high-energy CH_3^+ fragments. It is therefore very likely that the high-energy CH_3^+ fragments are the result of the Coulomb explosion of the multiple charged parent ion. The change of the modulation phase is also clearly visible in the figures 6.23(b) and (c), respectively.

Also for CH₃Br the asymmetric emission of H_3^+ and CBr⁺ fragments was measured. The result is shown in figure 6.25(a), (b) and the corresponding momentum-resolved modulation amplitude and phase spectra are given in figure 6.26(a) and (b), respectively. The green line in the yield spectrum of figure 6.25(a) marks the position of the yield maximum at 4.0 eV. This corresponds to an energy of 0.13 eV for the CBr⁺ fragment assuming a two-body fragmentation of the parent ion.



Figure 6.24: Similar to figure 6.12, but for Br^+ (a), Br^{2+} (b) and Br^{3+} (c) from CH_3Br . The laser peak intensity was $(1.6 \pm 0.6) \cdot 10^{14} \text{ W/cm}^2$.

The sign of the emission asymmetry of H_3^+ is identical to the low-energy CH_3^+ fragments from CH_3Br and hence also to the emission asymmetry of H_3^+ from CH_3Cl . However, the modulation amplitude is much larger in contrast to the amplitude obtained for H_3^+ from CH_3Cl . As expected, the modulation of CBr^+ is opposite to the modulation of H_3^+ .

For low intensities similar results were obtained for CH_3I . Due to the low ionization potential of CH_3I the data presented in figure 6.27(a) was measured at an intensity of $(3 \pm 1) \cdot 10^{13}$ W/cm² instead at $(5 \pm 2) \cdot 10^{13}$ W/cm² like the other three molecules. For CH_3I and intensity of $(3 \pm 1) \cdot 10^{13}$ W/cm² is enough to induce Coulomb explosion of the parent ion. This leads to the peak at 4.7 eV (indicated as green solid line) in the yield spectrum of CH_3^+ . This peak was assigned to the (1, 1) Coulomb explosion channel in reference [101]. In fact, there are two peaks close together at 3.94 eV and 4.68 eV which appear in the spectrum as a single peak. The peak at 0 eV corresponds to the (1,0) dissociation channel [98]. In figure 6.27(a) one can see that the two channels have the same asymmetry as observed for CH_3Cl and CH_3Br meaning that the ionization and subsequent dissociation is faster if the maximal amplitude of the field points from the iodine atom to the methyl group. At higher intensity we could observe that the asymmetry of the CH_3^+ emission



Figure 6.25: Similar to figure 6.11, but for H_3^+ (a) and CBr^+ (b) from CH_3Br . The laser peak intensity was $(1.6 \pm 0.6) \cdot 10^{14}$ W/cm². The position of the green line is 4.0 eV in (a) and 0.13 eV in (b), respectively.



Figure 6.26: Similar to figure 6.12, but for H_3^+ (a) and CBr^+ (b) from CH_3Br . The laser peak intensity was $(1.6 \pm 0.6) \cdot 10^{14}$ W/cm².

changes several times within the energy range between 4.7 eV and 15 eV. The first change of the asymmetry was at 7.5 eV (indicated as green dashed line). It is less pronounced in figure 6.27(c) which shows the result measured at $(1.6 \pm 0.6) \cdot 10^{14}$ W/cm² but it is clearly visible in figure 6.27(b). Also in the corresponding momentum resolved spectra given in figures 6.29(a)-(c) the change of the modulation phase can be observed. The green dashed circle on top of the spectra marks the same energy as the green dashed line in figure 6.27(7.5 eV). Remarkable is also the change of asymmetry for the low-energy



Figure 6.27: Similar to figure 6.11, but for CH_3^+ ions from CH_3I . The laser peak intensity was $(3 \pm 1) \cdot 10^{13} \text{ W/cm}^2$ (a), $(1.0 \pm 0.4) \cdot 10^{14} \text{ W/cm}^2$ (b) and $(1.6 \pm 0.6) \cdot 10^{14} \text{ W/cm}^2$ (c).

 $(<3 \text{ eV}) \text{ CH}_3^+$ fragments if the intensity is increase from $(3 \pm 1) \cdot 10^{13} \text{ W/cm}^2$ to $(1.0 \pm 0.4) \cdot 10^{14} \text{ W/cm}^2$. If we consider the corresponding energy range in the momentum resolved spectra (main structure in the center of the 2D spectra) one can get the impression that a different dissociation channel with the opposite emission asymmetry becomes dominant at higher intensities. But it is also possible that this is the result of a field induced inversion of the emission asymmetry. A contrary indication is the fact that also at an intensity of $(3 \pm 1) \cdot 10^{13} \text{ W/cm}^2 \text{ CH}_3^+$ fragments with the opposite modulation phase are observed. As expected from the CH_3^+ results different emission asymmetries for different fragment energies were observed for I⁺ as well as for I²⁺, I³⁺, and I⁴⁺. The results for the emission asymmetry are shown in figure 6.28 and



Figure 6.28: Similar to figure 6.11, but for I⁺ (a), I²⁺ (b), I³⁺ (c) and I⁴⁺ (b) from CH₃I. The laser peak intensity was $(1.6 \pm 0.6) \cdot 10^{14} \text{ W/cm}^2$.

the corresponding momentum resolved spectra are given in figure 6.29. In the yield spectrum of I^+ (figure 6.28(a)) the position of the green solid line at 0.56 eV (calculated from the position of the green solid line in figure 6.27 using equation 6.10) almost coincides with the yield maximum at 0.65 eV. Hence,

this peak corresponds to the (1, 1) Coulomb dissociation of the doubly-charged parent ion. The sign of the asymmetry is opposite to the corresponding CH_3^+ fragments. A change of the asymmetry for higher energies cannot be observed. Also the momentum resolved spectrum given in figure 6.29 shows no indication for a phase change of the modulation for high-energy I⁺ fragments. It follows that the CH_3^+ fragments with an energy of 7.5 eV (dashed green line in figure 6.27(b) and (c)) cannot be the result of the (1, 1) Coulomb explosion of the molecule. However, in the asymmetry spectrum of I²⁺ (figure 6.28(b)) a phase change at the position of the green dashed line (0.89 eV, calculated assuming a two-body fragmentation where the CH_3^+ fragment acquires a kinetic energy of 7.5 eV) can be observed. The phase change of the modulation is better visible in the momentum resolved spectrum of I²⁺ given in figure 6.30(b). One can thus conclude that the emission asymmetry of the (1, 2) dissociation channel is opposite to the (1, 1) dissociation channel.

In summary, it follows from the measured asymmetry that the ionization of CH₃F is faster when the maximum of the asymmetric field points from the methyl group to the fluorine atom. For CH₃Cl, CH₃Br and CH₃I the opposite is the case. This observation is consistent with the theoretical result of the WFAT given in section 6.3. Although Ohmura et al. [94] have reached the same conclusion, their measurements had a much lower kinetic-energy resolution. They could therefore not resolve the contributions of multiple fragmentation channels and their opposite asymmetries. We conclude that the kinetic-energy resolution typical of VMI experiments is therefore essential to properly analyze and interpret two-color Coulomb-explosion experiments. We further observed for the first time that the Coulomb-explosion rate of CH₃Cl and CH_3Br to $CCl^+ + H_3^+$ and $CBr^+ + H_3^+$, respectively, is increased when the field points from the halogen atom to the methyl group. From the modulation amplitude of the asymmetry of CH_3^+ one can further conclude that the ionization asymmetry is larger for CH₃F compared to CH₃Cl, CH₃Br and CH₃I. This observation agrees with the prediction of the WFAT calculations. In contrast to the WFAT, the result obtained from the Stark-corrected PFT calculations disagree with the experimental results. For CH₃F and CH₃Cl the predicted sign of the asymmetry is wrong whereas for CH₃Br and CH₃I the predicted sign is in agreement with the experimental results. But for CH_3I the absolute value of the asymmetry stands in contrast to the experimental observation. However, for the high-energy CH_3^+ fragments which are the result of the Coulomb explosion of the parent ions we could observe a flip of the asymmetry for CH₃Cl, CH₃Br and CH₃I. To the knowledge of the author this was not observed until now. An explanation for this observation can be given under the following assumptions: first, the wave functions shown in figure 6.4 represent the orbitals of molecules in an intense two-color laser field and second, one electron is removed from HOMO-1 or HOMO-2. The latter



Figure 6.29: Similar to figure 6.12, but for CH_3^+ from CH_3I . The laser peak intensity was $(3 \pm 1) \cdot 10^{13} \text{ W/cm}^2$ (a), $(1.0 \pm 0.4) \cdot 10^{14} \text{ W/cm}^2$ (b) and $(1.6 \pm 0.6) \cdot 10^{14} \text{ W/cm}^2$ (c). The green dashed circle indicates a kinetic energy of 7.5 eV.



Figure 6.30: Similar to figure 6.12, but for I⁺ (a), I²⁺ (b), I³⁺ (c) and I⁴⁺ (d) from CH₃I. The laser peak intensity was $(1.6 \pm 0.6) \cdot 10^{14}$ W/cm². The green dashed circle indicates an energy of 0.89 eV. This energy is obtained assuming a two-body fragmentation where the CH₃⁺ fragment acquires a kinetic energy of 7.5 eV.

assumption implies that ionization from low-lying orbitals can occur although higher-lying orbitals are not completely empty. If we consider the shape of the HOMO-2 (see figure 6.4) one can see that the wave-function amplitude is larger on the methyl side for all molecules. Due to the large asymmetry of the HOMO-2 of CH_3Cl , CH_3Br and CH_3I one can further assume that the angular distribution of the fragments is mainly dominated by the ionization step from HOMO-2. Hence, the dissociation rate is higher if the maximal amplitude of the asymmetric field points from the methyl group to the halogen atom. This is the opposite direction as observed at low laser intensities for the (1, 0) dissociative ionization channel in CH₃Cl, CH₃Br and CH₃I but the identical direction in CH₃F. This is a plausible explanation. However, the question arises why ionization from HOMO-2 should dominate over ionization from HOMO or HOMO-1 although they still contain electrons. But without the help of an extended theory which considers multi-electron ionization from multiple orbitals in a strong laser field it remains difficult to answer this question. However, the development of such theories is an active area of research.

6.5 Conclusion

We have measured the fragmentation of the methyl halides (CH_3X) where X =F, Cl, Br, I) in a two-color laser pulse. The field asymmetry was characterized using the fragmentation of CO molecules as a reference. Further, ion time-offlight spectra were recorded for all methyl halides for three different intensities. For the highest intensity multiply-charged fragments were observed indicating that the parent ion was initially in a multiply-charged state. With a VMIS in the ion imaging mode the angle-resolved momentum distributions of the CH_3^{+} and halogen ions were measured. In the kinetic energy spectra obtained from these measurements we could assign fragment energies to the dissociative ionization and Coulomb-explosion channel of the singly and doubly-charged parent ions, respectively. For CH₃Cl, CH₃Br and CH₃I we concluded from the sign of the emission asymmetry that ionization was faster if the maximal amplitude of the asymmetric field points from the halogen atom to the methyl group whereas for CH₃F this situation is opposite. This observation was in agreement with the prediction of the WFAT theory. However, for CH₃Cl, CH₃Br and CH₃I we could observe a change of the emission asymmetry of the high-energy CH_3^+ fragments. We propose that the change of the asymmetry is due to ionization from lower-lying orbitals.

Chapter 7 Conclusion and Outlook

In a pump-probe experiment we could observe a mixed electronic-rotational wave packet in NO induced by a Raman scattering and probed by strongfield ionization. We identified pump-probe delays where the wave packet was dominated either by the electronic or nuclear coherence. In a subsequent experiment, momentum-resolved photoelectron spectra were measured for the different pump-probe delays. With these spectra we could show that the holographic pattern is very sensitive to the time-dependent electronic structure of the wave packet whereas only minor effects of the electronic coherence on the high-energy electrons were observed. However, for pump-probe delays close to the alignment revival we could also observe a change of the momentum distribution of the high-energy photoelectrons. By comparison of the experimental results with ab-initio calculations based on the R-matrix theory, this observation is attributed to the orientation dependence of the elastic-scattering differential cross section. This experiment is the first demonstration of the potential of strong-field ionization, rescattering and holography to observe both electronic and nuclear dynamics in molecules.

From the ion TOF measurements of H_2 , D_2 , CH_4 and CD_4 we could clearly show isotope effects on the fragmentation processes of the ionized molecules in an intense femtosecond laser field. For H_2 and D_2 we could observe that the dissociation through charge-resonance enhanced ionization compared to the dissociation through bond-softening is faster in H_2 compared to D_2 . For CH_4^+ we could observe a higher H^+ fragment yield and a lower CH_3^+ fragment yield relative to the parent ion yield as compared to the relative yields of the corresponding fragments from CD_4^+ . We concluded that the rate of the reactions $CX_4^+ \rightarrow CX_3^+ + X$ and $CX_4^+ \rightarrow CX_3 + X^+$ is different for CH_4^+ and CD_4^+ . From the yield ratios it follows that the latter reaction is faster for CH_4^+ compared to CD_4^+ . Because of the lack of a sufficiently accurate method to calibrate the gas density in the detection volume, reliable results of the absolute ionization rates were not obtained. However, the development of an accurate and sample-independent method to measure the gas density in

the detection volume would make these measurements feasible in the future. The observation of nuclear dynamics in the same molecules by LIED using 800-nm and 1800-nm laser pulses was made difficult by long-term instabilities of laser-pulse parameters. However, within the accuracy of the measurement we could not observe the significant differences between the high-energy photoelectron momentum-distribution spectra of isotopologues that were predicted by our ab-initio scattering calculations. The low-energy photoelectron momentum-distribution spectra did show differences but it was not clear whether these were caused by the long-term laser intensity fluctuations or by the different nuclear dynamics. In the near future the laser stability will be improved by moving the laser to a separate room which should make it possible to acquire spectra during several hours under identical conditions. These measurements should then provide unambiguous results. Another promising approach is to increase the scattering energy of the electrons up to several hundred electronyolts which would increase the resolution of the LIED. This would require small modifications of the electrostatic lens system and the dimension of the flight tube in order to be able to detect electrons with energies of several hundreds of electron volts.

Through strong-field ionization of methyl halides with a phase-controlled twocolor laser field we observed that the formation of $\rm CH_3F^{2+}$ and subsequent dissociation to $CH_3^++F^+$ is enhanced when the maximum of the electric field amplitude points towards the halogen atom. We concluded that this was due to an enhanced tunneling ionization rate for this particular orientation of the molecule, with respect to the laser field. This conclusion was also consistent with the prediction of the WFAT. However, for CH₃Cl, CH₃Br and CH₃I enhancement of the dissociative ionization to $CH_3^+ + X^+$ was observed for the opposite direction but only if CH_3^+ fragments with low kinetic energies were formed. Under the assumption that the orientation dependence of the dissociative double-ionization process is dominated by the tunneling ionization rate of the molecule this result was also in agreement with the WFAT. The observation of the dissociation of $\rm CH_3 Cl^{2+}$ and $\rm CH_3 Br^{2+}$ to $\rm H_3^{+}+\rm CCl^{+}$ and $H_3^++CBr^+$, respectively, led to the same conclusion. However, from the highenergy CH₃⁺ fragments different kinetic-energy dependencies of the asymmetric fragmentation were observed. One explanation could be that ionization occurred from low-lying orbitals with a different electronic structure and hence different orientation-dependent ionization rates. To further complete the description of these processes it might be useful to measure the momentum of all ion fragments and electrons which result from the dissociation of a single molecule. This is possible with a photoelectron-photoion coincidence spectrometer which is currently under construction.

In this thesis experiments were presented where the VMIS was used in the TOF, ion-imaging and electron-imaging mode. During the execution of the different experiments we could extend our expertise regarding the VMIS en-

abling us to perform versatile experiments. Unfortunately, we never reached the point where we could use the VMIS in combination with the attosecond XUV beam line which was under construction during the time of this thesis. However, the spectrometer will soon be attached to the attosecond XUV beam line which will open the possibility of using isolated attosecond pulses. Especially the observation of charge migration in molecules would be very interesting not least because this process is of great importance in biological systems and also in applications where (single) molecules are used, for example, as transistors or in photovoltaic elements.

If it may turn out that the performance of the VMIS in the current state does not meet the requirements of these experiments, there are several modifications which can be easily implemented. A better vacuum, for example, can be achieved by connecting additional turbomolecular pumps to the chamber. Currently it would be possible to connect two additional pumps which would improve the vacuum by a factor of ten. Also the separation of the flight tube from the source chamber can be improved to reduce the pressure in the flight tube. The electrostatic lens system could also be extended by additional lenses to improve the imaging quality. There are still unused HV feedthroughs welded into the top flange to which these lenses can be connected.

However, also without any further modification of the VMIS several new experiments are possible. For example one could study the electronic wave packet in Xe⁺. The electronic ground $({}^{2}P_{3/2})$ and first excited state $({}^{2}P_{1/2})$ of Xe⁺ are separated by 1.3 eV [102]. The period of the quantum beat of a coherent superposition of the two states is thus 3.2 fs. Xe^+ ions in this state can be obtained through tunnel ionization of neutral xenon atoms with an intense laser pulse. With a second, delayed laser pulse with a center wavelength of 1900 nm one can ionize the Xe^+ ions further to Xe^{2+} . However, due to the electronic wave packet the efficiency of this process is expected to be dependent on the time delay between the first and second laser pulse. In another experiment one could study a nuclear wave packet in CH₂Br₂ where the CBr₂ vibrational scissor mode can be exited through an impulsive stimulated Raman transition. The vibrational levels of this mode are separated by 169 cm^{-1} [83]. Hence, the dynamic of the wave packet of these vibrational modes happens on a time scale of ≈ 200 fs. In a pump-probe experiment similar to the experiment on nitric oxide presented in this thesis one could study the effect of the nuclear motion on the angle- and momentum-resolved photoelectron and photoion spectrum. By combining a UV or XUV source with the VMIS many more experiments, for example on photoelectron circular dichroism in chiral molecules, become feasible. However, the interpretation of photoelectron spectra becomes increasingly challenging for complex samples. But coming back to the experiments done by Heinrich Hertz, since then far more complex problems have been solved in this context.
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