Applications of Ultrafast Pulse Shaping to Molecular Control and Strong-Field Ionization

A Dissertation Presented

by

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to

The Graduate School

in Partial Fulfillment of the Requirements

for the Degree of

Doctor of Philosophy

in

Physics

Stony Brook University

May 2013
Stony Brook University
The Graduate School

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This thesis studies the interactions of intense laser pulses with small polyatomic molecules \( \text{CH}_2\text{XY} \) (with \( X,Y = \text{Cl}, \text{Br}, \text{I} \)). It is divided into two sections: In the first part, two schemes - photon-locking and hole-burning - are used to control the evolution of a nuclear wave packet on the lowest ionic state of \( \text{CH}_2\text{BrI} \). The experimental results are compared with theoretical predictions and show good qualitative agreement. This is also the first observation of photon-locking in a polyatomic molecule. The second part focuses on controlling strong field ionization. Here a combination of pulse shaping and velocity map imaging of ions and electrons is used to characterize molecular wave packets after ionization with IR ultrafast pulses (central wavelength 780nm). In these experiments basic parameters of the pump pulse like intensity, second/third order phase, or pi-phase flip are systematically scanned. The measurements reveal a superposition of electronic states created by strong field ionization and in certain cases their contributions can be quantified. Last
but not least this technique is extended to photo-electron spectra
and helps to associate specific features (freeman-resonances) with
ionic states.
To my family
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Acknowledgements

First of all I would like to thank my advisor Professor Thomas Weinacht, for his support and guidance. I have very much appreciated our fruitful discussions, his ability to bring light into the most confusing data sets, his great technical expertise, after-hour support in the lab and most of all his optimism. I have greatly benefited from the collaborations with two theory groups, Professors Tamás Rozgonyi (Hungarian Academy of Sciences, Budapest) and the group of Professor Letitia Gonzáles at the University of Vienna with Philipp Marquetand and Jesús González-Vázquez. Many results presented in this thesis would have not been possible and far less interesting without their help.

Many thanks go to the former and current members of this group. They have not only been a very valuable resource for my PhD work, but generally made my stay in Stony Brook much more enjoyable. Thanks to Brett Pearson, Sarah Nichols and Carlos Trallero for introducing me to ultrafast physics and being patient with my questions and mistakes. Special thanks go to my long-term office mate Marija Kotur for her scientific insights, help with my experiment and – maybe most of all – many memorable times in and outside the lab. I have appreciated the input of Martin Cohen, especially his technical knowledge regarding optics and lasers. And, I have enjoyed working together with Péter Sandor on my setup and also the other group members, Arthur (Xin Zhao), Coco (Chien-Hung Tseng), Oumarou Njoya, Steven Clow, Spencer Horton, Uvo Hölscher, and Will Lunden.

I would like to thank the neighboring AMO groups of Professors Schneble and Metcalf, not only for being a great reservoir of lab equipment, but also for providing a friendly and cooperative atmosphere in the basement. I am grateful for the administrative support of the physics department main office staff, especially Sara Lutterbie and Pat Peiliker. Special thanks also go to the electronics shop, machine shop and the former advanced technology lab. Without their quick help and very useful advice, my experiments would have run a lot less smoothly.

I am thankful to the committee, Professors Maria Victoria Fernandez-Serra, Louis DiMauro, Dominik Schneble and Michael G. White, for making
my last minute defense possible and contributing comments and corrections to this thesis.

On a personal level, I am very grateful for passing through the years of grad school, not alone, but together with some very special people. Thanks to Cameron Crowe, David Morris, Marija Kotur, Francis Paraan, and many others. Finally, I thank my parents Gabriele and Wolfgang, and my brother Benjamin for a lifetime of encouragement. I really would not have made it without them.

I would like to acknowledge the Studienstiftung des Deutschen Volkes for their partial graduate school stipend.

Dominik Geißler
Stony Brook, NY
February, 2013
Chapter 1
Introduction and Overview

The development of ultrafast light sources [1-4] provides methods to study the fastest processes occurring in ‘normal’ matter: electronic and nuclear motion in solids, molecules and single atoms. Large scale structural motion, e.g. folding of proteins, can last several seconds, but nuclear evolution, which governs chemical reactions usually happens much faster, i.e. in the order of 100 fs or less. Valence electron motion is even quicker and occurs on a timescale of 1 fs or less. The challenge to develop universal tools that can study matter on an atomic level in the time-domain has been compared to one of the big projects and achievements of the 20th century, namely spatially resolving matter (e.g. x-ray crystallography or NMR).

Among the available tools, strong field ionization (SFI) has become a key ingredient in ultrafast science. There are various definitions of ‘strong’ used in literature. In this thesis, it is used to refer to all cases of ionization, that are non-linear in the applied laser field strength. Strong field ionization offers multiple different applications: It can be used as a probe of evolving systems, as done in the now standard pump-probe ionization experiments. In this kind of experiments the atom/molecule is prepared in an initial state by a pump pulse, and ionized by a probe pulse later on. The created ions [5] and/or photoelectrons (time resolved photo-electron spectroscopy, TRPES [6, 7]), are collected and yield information on the system’s evolution. The usage of ionization as the probe mechanism provides many advantages [8]: (a) Charged particles are easy to detect. Unlike optical detection schemes, a collection volume of 4π is easily implemented. (b) Ionization is always possible, provided that the laser intensity is high enough. Optical schemes can suffer from dark states, detuning or - in general - low interaction cross-sections (e.g. in the X-ray region). This is further aggravated by the fact that ultrafast pulse sources are most readily available in the near-IR region. By now other central frequencies are available, but usually at the cost of a lower photon flux (using non-linear
frequency conversion tools) or technical complexity, e.g. synchrotrons and free electron lasers [8]. (c) Last but not least, SFI is a highly non-linear process. Ionization takes place in less than one optical cycle (at sufficiently high electric field strength), which corresponds to a few femtoseconds or even attoseconds. Thus SFI opens the door to attosecond physics and the emerging field of ultrafast dynamic imaging [4, 9–12]: The process of high harmonic generation, which is based on SFI, can generate broadband, deep UV pulses, and extends classical pump-probe spectroscopy into the attosecond regime, allowing for the study of fast nuclear and electron dynamics [9, 13, 14]. Other experiments directly make use of SFI: Both the outgoing attosecond electron wavepacket, as well as electrons that are re-scattered on the ion core after the electric field reverses, carry information about the electronic configuration and nuclear geometry of the studied system [15–20].

These promising applications of SFI motivate a considerable theoretical effort to model the ionization step. In the weak field limit one can treat ionization successfully as multiphoton absorption [21]. However, this approach becomes futile in the limit of strong fields. A theoretical treatment of this regime was initiated by Keldysh [22] in 1964. His work belongs to the group of quasi-static models of SFI, which is illustrated in figure 1.1: The ionization pulse temporarily tilts the binding potential of the atom/molecule, such that the bound electrons are energetically allowed to escape into the continuum. This can happen either on a classical trajectory, if the barrier is suppressed sufficiently (black line), or quantum mechanically by tunnelling through the reduced barrier (green line). Keldysh also introduced the Keldysh parameter $\gamma$ as follows:

\[ \gamma = \omega_{\text{laser}} \cdot \tau \]

\[ \tau = \frac{\sqrt{2m_e I_p}}{eE_0} \]  

(1.1)

Here $E_0$ refers to the peak field strength of the laser pulse, $I_p$ is the ionization potential of a particular electronic state and $\omega_{\text{laser}}$ to the central frequency of the pulse. $\tau$ is simply a classical estimate for the time it would take an electron to travel through the system’s barrier of height $I_p$ tilted by an electric field of strength $E_0$, arriving in the continuum with zero velocity. In this sense, $\gamma$ much smaller than one is equivalent to the electron escaping the molecule much faster than the time it takes for the electric field to reverse. This is usually the criterion for the applicability of quasi-static ionization models.

The original work of Keldysh has been extended to include multi-electron atoms, and is now referred to as ADK-Theory [24–26]. Further theoretical treatment focussed on generalizing the $1/r$-potential of the ADK approach to
Figure 1.1: This cartoon illustrates the binding potential of an H atom in an external electric field. The dashed red line corresponds to a bound 1s state inside the unperturbed potential well (blue). The electric field of a laser pulse tips the potential and the formerly bound electron can tunnel into the continuum (green line). This requires the tunnelling rate to out-compete the reversal of the electric field, which is characterized by the Keldysh parameter $\gamma$ being $< 1$. The black line refers to the extreme case of over-the-barrier ionization; in this case the barrier is suppressed sufficiently for the electron to leave the system on a classical trajectory, which represents the high-intensity-limit of the validity of the tunnel-ionization picture [23].
more realistic cases, e.g. the Keldysh-Faisal-Reiss (KFR) theory \cite{27,30} allows multiple atomic centres as sources for the electron current, or the ‘bucket’-model considers a spatially extended well \cite{31,32}. Similarly the molecular ADK theory (MO-ADK) uses an expansion of the real molecular ground state wavefunction into hydrogen-atom wavefunctions and calculates strong field ionization for diatomic molecules \cite{33}. Besides this large group of quasi-static theories for SFI, other models approach the problem by solving the Schrödinger equation numerically \cite{34,40}.

Despite theoretical progress, there are still many aspects of molecular strong-field-ionization that are poorly understood \cite{31}. Electron spectra, as the ones shown in chapter 6, exhibit a very rich structure that is not captured by theoretical models. All parts (besides chapter 3) of this thesis focus on the development of methods to characterize strong field ionization of polyatomic molecules. This involves determining the molecular state after SFI, identifying various ionization pathways*, associating them with particular features in the photoelectron and fragment ion distributions, and demonstrating their dependence on ionization pulse shape.

This thesis is divided into the following chapters:

Chapter 2 introduces the experimental apparatus. It begins with a brief discussion of the main laser system, i.e. Ti:Sapphire oscillator and amplifier, frequency up-conversion to the deep UV and pulse shaping. It then continues with some discussion of the velocity map imaging detector, including a characterization of the ion and electron imaging quality.

The first experimental chapter, chapter 3, makes use of SFI to launch a vibrational wavepacket on the ground ionic state of CH\textsubscript{2}BrI. Two methods to control the evolution of a nuclear wavepacket are demonstrated: photon-locking and hole-burning. The former, control scheme utilizes a long laser pulse to freeze the evolution of a vibrational wave packet. The latter, control scheme can manipulate its center of gravity, by selectively removing ‘slices’ of the wave packet. Further, the experimental results are contrasted with full theoretical simulations, which show a good qualitative agreement. This work has been published in reference \cite{41}.

The next three chapters focus on details of strong-field ionization. Most of the described work uses an IR pump with a field strength corresponding to $\gamma \approx 1$, which puts this work into an intermediate regime of multi-photon ionization with some features typical for tunnelling ionization. Chapter 4 is based on publication \cite{42}. It describes a proof-of-principle experiment and verifies that multiple ionization pathways play a role during SFI. In all experiments, pulse-shaping is an essential tool to gain further knowledge: Since SFI

*Please refer to section 4.1 for a precise definition of this term
usually leaves the molecule in a superposition of various electronic states, the experimentally accessible observables (photoelectrons and -ions) are difficult to interpret. Shaping the ionization pulse provides an additional control to the experimentalist, and helps to isolate out independent features. Chapter 5 - published in reference [43] - uses this technique to associate ionization pathways with different sub-structures in the CH$_2$Br$^+$ momentum distributions. This can be used to both characterize the molecular state after SFI, but also to study the pulse shape dependence of SFI. An ongoing project, described in chapter 6 utilizes a similar approach to understand features in the photoelectron spectra.

Some final remarks are given in chapter 7 followed by the appendix.
Chapter 2

Experimental Setup

2.1 Laser System

The backbone of the lab is a two-stage ultrafast laser system: An oscillator to generate extremely short (but weak) laser pulses and an amplifier to subsequently increase the pulse intensity. The commercial oscillator (KM Labs Ti:Sapphire laser kit) utilizes soft Kerr-lens modelocking and is pumped by a Coherent Verdi V5 Continuous Wave (CW) laser. The oscillator pulses are sent through the multi-pass amplifier system (KM labs, model HAP-AMP), which is pumped by a pulsed Quantronix Falcon (CW-pumped, Q-switched, Nd:YLF) laser system. The output is an ultrafast pulse train with a repetition rate of 1 kHz, which is centred around 780 nm. The pulses have a minimum time duration of 30 fs, with a maximum energy of about 1 mJ. Both the oscillator and the amplifier use Ti:sapphire as laser gain medium, which can be tuned within a narrow window of about (772, 792) nm. A more detailed description of the setup can be found in earlier theses of this group (e.g. [44, 45]).

The setup is also equipped with an ultrafast pulse shaper. The details are given in references [45, 47]. Figure 2.1 shows a schematic setup: A 4f geometry is used to map the individual frequency components of the original beam into a horizontal line inside an acousto-optical modulator (AOM, Brimrose TED7-150-50-.800) and then back to a collimated beam after the AOM. The AOM diffraction angle and efficiency can then be controlled by sending a sound wave through the AOM, which effectively turns the AOM into a transmission grating. The sound wave is generated by a piezo-electric crystal attached to the end of the AOM, which is modulated by an electronic signal (a RF wave around 150 MHz) synthesized by an analog-digital (A/D) converter (Gage CompuGen 1100). This individually modifies the amplitude and phase of the frequency components of the ultrafast laser pulse. Due to various technical limitations
(laser focus spot size on the AOM, A/D board resolution, conversion of RF wave to sound wave, etc.), the pulse shaper can only control amplitude and phase of about 40 separate frequency bands (i.e. has a resolution of about 1 nm) out of the whole pulse. The AOM itself has a maximum diffraction efficiency of \( \approx 65\% \) which is reduced to an overall efficiency of the pulse shaper of \( \approx 40\% \) including the other optics.

There are various techniques to measure the temporal structure of the laser pulses (see [48]): FROG, GRENOULLIE, SPIDER and MIPS\(^*\). The method used for the experiments described in this thesis is second harmonic FROG (SHG-FROG). A more detailed description of it can be found in [44].

The ultrafast UV pulses (centred around 260 nm) are generated after splitting the main beam into two pulses, where one of beams subsequently passes through several non-linear crystals. The tripling setup consists of a 250 \( \mu m \) thick \( \beta \)BBO crystal, which generates a 2nd harmonic pulse. The 2nd harmonic pulse and the IR pulse are approximately collinear and then sent through a 100 \( \mu m \) \( \beta \)BBO crystal and mixed to generate the UV pulses. A thin 100 \( \mu m \) calcite crystal is added in between to compensate for the different IR and blue (390 nm) group velocities. Depending on the used IR pulse energy, UV pulses of up to 21 \( \mu J \) (starting with 650 \( \mu J \) of IR) can be generated. The pulse duration can be measured with a self-diffraction FROG (SD-FROG) and is determined to be 40 – 50 fs.

All experiments described study molecular systems in the (very dilute) gas phase. Two different vacuum chambers were used: A conventional time-of-flight (TOF) chamber, built by a previous student [45], and a velocity-map-imaging (VELMI, described in section 2.3) system, based on a molecular apparatus of a previous student [49].

### 2.2 Time of Flight Vacuum Chamber

A detailed description can be found in [45]. The baseline vacuum pressure of this chamber is about \( 2 \cdot 10^{-6} \) torr and is maintained by a turbo molecular pump. The sample is injected through a manifold section, which can be alternatively connected to the "outside" or the "inside" and can be pumped down to about 10 mtorr by a roughing pump. During an experiment the pressure is raised by about an order of magnitude to \( 10^{-5} \) torr. At this pressure the mean free collision time is much longer than the time delay between interac-

\(^*\)Acronyms for "frequency-resolved optical gating", "grating-eliminated no-nonsense observation of ultrafast incident laser light e-fields", "spectral phase interferometry for direct electric-field reconstruction", and "multiphoton intrapulse interference phase scan", respectively.
Figure 2.1: Pulse Shaper in 4f-Configuration: The incoming beam first encounters a grating (grating 1). This grating and the AOM are both in the focal spot of curved mirror 1. Together they map the incoming beam into a frequency resolved line inside the AOM. By applying a sound wave to the AOM it acts as a controllable transmission grating, whose line spacing and transparency can be adjusted locally. The phase of a specific color is adjusted by diffracting it onto a longer/shorter path. The diffraction efficiency of a specific color is controlled by changing the ‘grating’ depth, i.e. the local amplitude of the sound sound wave. The second pair of curved mirror 2 and grating 2 reverse the action of the first pair and recombine all colors into a collimated beam.
tion with the laser pulse and detection, i.e. the molecules can be thought of as isolated. The laser beam is focused by a lens directly in front of the vacuum chamber and enters/exist it through thin vacuum windows. Depending on the IR mode/lens used the laser focus can be as tight as 20 µm at beam waist in the focal spot (for IR). In this setup only ions formed by the interaction between molecules and laser are detected with a TOF spectrometer. The ions are created by the ultrafast laser pulse within a stack of extractor plates, that accelerate them towards a stack of micro-channel-plates (MCPs). Those create a shower of $10^5 \sim 10^6$ electrons per ion impact. The electron current is collected by an anode behind the MCP stack, digitalized (Gage CompuScope CG11G) and is proportional to the absolute number of particle hits. Different ion types (i.e. H$^+$, CH$^+$, etc.) can usually be distinguished by their charge-to-mass $\frac{q}{m}$ ratios and thus can be and thus can be identified by their various arrival times at the detector.

### 2.3 Velocity Map Imaging Chamber

A schematic view of the whole chamber can be seen in figure 2.2. This vacuum chamber exceeds a conventional TOF setup, as described in the previous section, in various regards: the chamber operates with a molecular beam instead of a diffuse gas, the detector is position sensitive and the extractor plates are replaced by an electrostatic lens that can image the velocity of ions at their origin onto position space at the detector. This way it is possible not only to measure the absolute ion yield, but also the momenta of the various ions. At a later point the chamber was upgraded with µmetal shielding allowing also to measure the yield and momenta of photo-electrons.

The sample can be injected into the vacuum system through a manifold, in a similar way as in the TOF chamber. Originally the chamber was constructed to use a molecular beam rather than an effusive gas. A design as described in publications 49, 50 is used: The gas is first injected through a nozzle into an expansion cube, but only its very central portion can enter the interaction cube through a skimmer. The pressure in the expansion cube is maintained by a diffusion pump (Varian VHS-6), and in the interaction cube with a turbo pump (Varian Turbo V301 Navigator). With no sample load present the baseline pressure in the small cube is about $9.5 \cdot 10^{-9}$ torr. The maximum ratio of transversally cold beam molecules to total signal is estimated to be about 12 %. The relatively low ratio is due to the large distance between the interaction point and the molecular beam skimmer (several cm), as can be seen in figure 2.2 This convolves the observed momentum distributions with a Maxwell-Boltzmann distribution, which is acceptable for the
Figure 2.2: Schematic view of the VELMI chamber (not to scale). The upper right image shows the a typical "data point" as taken with the camera. Each spot corresponds to one ion/electron hit on the detector front. If the electrostatic lens is used in VELMI mode, zero kinetic energy particles hit in the center of the image and the distance from the center is proportional to the particle’s velocity (see [2.1]).
Figure 2.3: Simulation of the VELMI lens in SIMION. The red trajectories refer to ions with 0 eV kinetic energy at origin, the green trajectories refer to ions ejected with 1 eV along the y-axis at origin. Note that the points of origin extend over 2 mm but are mapped to one single point on the detector front. The repeller plates are labelled by their approximate voltage needed (as ratio of the maximum voltage) to achieve velocity map imaging properties. Typically a maximum voltage of \( \approx \pm 1 \) kV is used.

experiments described in this thesis, since they only study features with a width of \( \approx 100 \) meV.

2.4 The VELMI Lens System

The velocity map imaging lens closely follows the design described in [51, 52]. The design is shown in 2.3. It is a cylindrically symmetric assembly and is composed of four stainless steel doughnut-like plates (grade 316L, to prevent magnetisation over time), separated by ceramic spacers. Besides the fourth plate, which is always grounded, the other 3 plates can be adjusted to an individual potential of up to 950 V. In principle, two non-grounded disks can form a VELMI-lens, but adding a third adjustable plate provides an additional degree of freedom to change the magnification and reduce astigmatism [53]. Since the potentials of all plates can be set independently, the whole assembly acts like an electron/ion lens with an adjustable focal length and flexible magnification. Most of the time it is used in VELMI mode, i.e. the lens images the momentum space at the laser focus, where the ions are created, to position space at the detector plane. The optical analogue is a spherical lens, with the detector being positioned at focal distance. For alignment purposes it is convenient to adjust the electrostatic lens to ”spatial” mode, and image the
spatial distribution of ions at the laser focus plane into spatial position on the
detector. The laser beams inside the chamber can be 'seen' by the detector
since they leave a trace of ions on their path. This way one can easily overlap
and center several beams in the chamber for the experiments. The magnifica-
tion in spatial mode is between 20 and 40, which allows a positioning accuracy
up to 7 µm (given the finite resolution of the detector).

The imaging properties in VELMI mode can be described with the follow-
ing expression. Here $R$ refers to the (x,y) coordinates of the particle impact
on the detector and $v_\perp$ to its transverse velocity (i.e. parallel to the detector
surface) at the ion source.

$$v_\perp \sim R$$  \hspace{1cm} (2.1)

$$E_{\text{kin,}_\perp} = C |R|^2$$  \hspace{1cm} (2.2)

The term $E_{\text{kin,}_\perp}$ refers to the part of the particle’s kinetic energy (i.e.
$E_{\text{kin}} = 1/2m(v_x^2, v_y^2, v_z^2)$), that is perpendicular to the detector surface. One
important consequence is that the detector is 'blind' to the longitudinal veloc-
ity of the detected particles. For this reason, the three dimensional velocity
distribution of photo-ions/electrons is simply projected onto the two dimen-
sional surface of the detector. This leads to a smearing out of the real velocity
distributions, but can be corrected by various methods (see section 2.8 and
appendix A).

It should be stressed that the constant $C$, as defined in 2.2 is independent
of the particles’ mass $m$ and and scales proportionally to the square root of
the applied repeller plate voltages - as long as their relative values are kept
constant. This feature is indeed shared by all electrostatic lens systems [54].
In this sense, one could describe electrostatic-lenses as perfectly achromatic,
i.e. its focal length is independent of particle momentum. Experimentally
this is very convenient, since the conversion 2.2 from detector hit-position to
particle energy holds independently of the particle type. Furthermore, the
imaging properties are not affected if one scales the voltages on all plates by
the same constant. In the used setup this is easily achieved, since all voltages
are generated from only one high voltage power supply by a dynamic voltage
divider. This allows us to overpower any possible electric stray field by simply
turning up the main repeller plate voltage.

### 2.5 Charged Particle Detection

A commercial assembly (BIS, Model BOS-40-6) of a Chevron stack of mi-
icrochannel plates (MCPs) and a phosphor screen (P43) is used to detect ions
and electrons. The phosphor screen has a diameter of 4 cm and the signal is digitized with a CCD camera (The Imaging Source, DMK 31BU03) with a 1024x768 pixel resolution. Both the minimum exposure time of the camera (0.1 ms) and the decay time of the phosphor screen (P43, 300 ns) are sufficiently short to allow single shot detection, although this is not advisable since the camera has a limited frame rate much slower than the laser repetition rate. The second MCP can be gated to single out a specific ion type for detection. This is necessary as the phosphor screen does not allow to distinguish between ion type or electrons. For this purpose a fast high voltage switch is used (DEI, Model PVX-4150), whose minimum window width is about 60 ns. If spatial resolution of the detector is not required, the chamber can also be run in time-of-flight-mode (tof-mode). For this purpose the MCP gating is switched off and the ion/electron yield signal is decoupled directly from the phosphor screen via a HF bandpass filter. This signal can be digitized with a fast A/D board. Its sampling rate is 500 MHz, which is high enough to capture the response of a single particle impact (≈ 4 ns). Furthermore it can acquire data at a repetition rate of 1 kHz, such that the ion yields of different laser shots can be read out individually. In this case the spatial resolution of the detector is lost, but one can measure the yields of all ion types at the same time.

MCPs suffer degradation with continuous usage. The specifications for this type of MCP estimate that about 30 C of charge can be extracted per square-centimetre of surface during its life-span, accompanied by an exponential decay in brightness per detected ion/electron. With the ion/electron beam densities used in experiments in this thesis, the MCPs should be replaced about every two years. This is especially the case for the second MCP, as it provides most of the current. This can be partially circumvented by applying a flat field correction that normalizes the gain across the whole detector. For this purpose we regularly created 'sensitivity maps', which are long-exposure images while the VELMI-lens is unfocussed to uniformly illuminate the detector. An example is shown in figure 2.4.

2.6 Kinetic Energy Calibration

The constant $C$ as defined in formula 2.2 is essential in connecting the spatial images on the phosphor screen with physical momentum distributions of the detected particles. We have been using four methods to achieve this: (1) ion trajectory simulations in SIMION, (2) comparison of a background gas velocity distribution with the Maxwell-Boltzmann distribution and - after the $\mu$metal shielding upgrade - (3) Above-Threshold-Ionization (ATI) peaks in the photo-electron spectra (for some explanation, see chapter 6 or reference[21]).
Figure 2.4: This plot shows a typical sensitivity map used to flat field correct the detection efficiency. The color axis is normalized to 1 and represents the gain versus position on the screen. The dark blue spot in the center represents the zero velocity region, where most ions hit the detector and it degrades most quickly. The faint blue vertical line through the center is damage caused by using the detector in spatial mode, which focuses all particles into a narrow line on the screen.
(4) comparison of the observed photoelectron spectra with older CW based measurements.

For method (1) a detailed model of the vacuum chamber, the lens system and the time-of-flight-tube were created. Since all physical dimensions are well known and the repeller plate voltages can be easily measured, one should in principle be able to determine the VELMI-lens properties. The only parameter that is not easily accessible is the exact position of the laser focus inside the vacuum chamber. Simulations show that it can be moved slightly (especially along the time-of-flight axis) with the ions/electrons still being in focus while the magnification constant $C$ changes. For this reason this method is less reliable than the other techniques and suffers from a systematic error of up to 20%. Method (2) measures the full width half max of the velocity distribution of background gas (e.g. the very dilute water vapour in the interaction cube), that is ionized but not fragmented. These ions simply keep their initial thermal spread, which is dictated by the Maxwell-Boltzmann distribution and the temperature of the environment. By comparing both distributions one can extract $C$, although particular care has to be taken to avoid space charge broadening. Since this method is based on ions, magnetic stray fields can be neglected. The next two methods became available after upgrading the chamber with $\mu$metal shielding, since they are based on electron kinetic energies. There is method (3): If the absolute energy difference between any two features is known (for physical reasons), $C$ can be determined. An excellent way for this is using the first and second above threshold ionization order (ATI order) in photo electron spectra: If two features can be unambiguously identified with the same process, their distance is per definition one photon in energy $^{[21]}$. Freeman peaks arising from resonances with Rydberg states - which will be the topic of chapter 6 - are naturally narrow features and easy to identify and thus provide the best results. This method is susceptible to magnetic stray fields, which distort the image, e.g. the calibration constant based on the spacing between first and second ATI order is systematically higher than the result based on the second and third ATI ring. Last but not least method (4) compares the position of certain photoelectron peaks with values known from literature. For this purpose the photoelectron spectrum of CS$_2$ is measured as function of laser intensity. Since the difference of the ionization potentials of its first and second ionic state is $\approx 2.7$ eV $^{[55]}$, the spectrum is dominated by ionization to the lowest ionic state (at low intensities). The position of the associated peak in the photoelectron spectrum (extrapolated

$^{[1]}$Due to their low mass (at least a factor of 2000 compared to ions), electrons are much more strongly affected by magnetic fields than ions: they are accelerated to faster velocity by the repeller plates and they are more easily deflected
to zero intensity), provides a measure for the first IP of this molecule, which can be cross-calibrated with the value given in literature.

It should be noted that all four methods lead to slightly different values for $C$ and suffer from different systematic error sources. While the two first methods agree within their error margin, and the two electron based methods yield consistent results, the latter calibration is systematically higher than results based on method (2) and (1). All four methods group around the result from approach (2) within a spread of 18%. The exact cause is unknown, but is presumably due to the fact that electrons additionally are subject to residual magnetic fields. In this thesis method (2) is used as a reference for the ion based data, since it is the only experimental approach based on ions. By contrast, (3) and (4) are also sensitive to magnetic fields and are thus used as the basis for calibrating the photoelectron spectra. Here the statistical spread is about 7%.

2.7 Imaging Accuracy

The image quality in all charged particle applications suffers from the fact, that all particles interact also with each other via their electric field. In the literature this is referred to as ‘space charge’, which usually leads to a smearing out of an otherwise crisp image. For VELMI detectors usually a value of 100 particles or less per laser shot is stated as the upper tolerable limit \[52\]. A momentum distribution with sufficiently high quality (as used in the experiments described in this thesis) is usually based on between $10^5$ and $10^6$ counts, i.e. one data point (using a 1 kHz laser repetition rate) accumulates signal in between 1 s and 10 s. Space charge distortions can be large compared to the kinetic energy release of the studied system (a few eV), but are much smaller than the kinetic energy acquired in the lens system ($\approx 1000$ eV). If the setup is only used in tof-mode, the sample density and data acquisition rate can be much higher.

Besides space charge, there are also ‘true’ lens errors. Possible concerns are a breakdown of the paraxial approximation (i.e. aberrations) and electric and magnetic stray fields. Several experimental checks have been performed to asses these lens errors. One important question is to what extend the VELMI lens is capable to collect all ions of the same velocity class from the whole source area and image them to one single spot. The optical analogue is sometimes referred to as the ‘circle of confusion’ or the ‘point spread function’. This can be easily evaluated using the parent ion (of an arbitrary sample) and only analysing transversely cold ions (i.e. after subtracting the contribution of thermal background ions), since they are created with zero kinetic velocity.
(besides the negligible electron/photon recoil). The result can be seen in figure 2.5. It turns out that the bluriness is actually limited by the size of one hit on the phosphor screen (HWHM ≈ 4.5 pixels), which is less than 1 meV at the center of the screen and reaches 95 meV for the fastest particles.

Another concern are lens aberrations, i.e. equation 2.2 might not be a pure $R^2$ dependence. This concern was addressed in the initial set of publications (e.g. reference [51]), demonstrating the current lens design to be aberration free. But also SIMION simulations for the current setup were used to independently verify the lens properties. Nevertheless these simulations cannot take all parts of reality into account, most notably electric and magnetic stray fields. To address this issue a simple test can be performed, providing an upper limit: If the laser polarization is turned perpendicularly to the detector screen, the ions/electrons exhibit a centrally symmetric distribution, visible as a set of concentric rings on the detector screen. Any deviations from this must be due to an imaging error. On the other hand any electric/magnetic stray field will cause some distortions; this is particularly true for fields that break the rotational symmetry around the time-of-flight axis, i.e. all inhomogeneous stray fields and transverse (i.e. perpendicular to the tof axis) fields; with a longitudinal homogeneous magnetic field being an exception since it - to first order - adds a term proportionally to the particle’s velocity, i.e. just changes the effective calibration constant $C$. This test has been performed both for electrons and ions and is summarized in figure 2.6. This graph shows the distance $R(\alpha)$ (normalized to the average) of a certain selected feature versus angle $\alpha$ (polar angle of the detector screen). A perfect lens would image the ion/electron source to a perfect circle. Thus, the deviations shown can be used as an upper estimate on the imaging errors. As can be seen in the figure, the electron images are much more distorted than the ion images, which indicates that indeed magnetic stray fields are the main source for the inaccuracies. Altogether the error in the kinetic energy measurement can be estimated (taking the mean $(\Delta R/R)^2$ value of figure 2.6) be about 0.5% and 2.6% for ions and electrons, respectively. It should be noted that this is only the averaged error, over all angles. An estimate for the imaging error of narrow features, which are limited to a limited angular range (e.g. Freeman resonance peaks) should be based on the extrema of figure 2.6. This is about 1.6% and 4% for ions and electrons, respectively.

2.8 Inverse Abel Transform and DC Slicing

As has been mentioned before the three dimensional ion/electron distribution is projected onto the detector and the information about the momentum
Figure 2.5: This figure shows an angularity averaged radial lineout of the CH$_2$I$_2^+$ parent ion momentum distribution. DC slicing was employed to isolate the transversally cold molecular beam fraction, and achieved a purity of $\sim 79\%$. Since parent ions exhibit only a negligible recoil from electron emission and photon absorption, this distribution can be used to estimate the image quality of the VELMI lens. The observed HWHM spread was 4.5 pixels, which corresponds to less than 1 meV close to the center and only about 95 meV for the fastest detectable particles. The author wishes to point out that this blurriness not only includes the imaging accuracy of the VELMI lens, but also takes into account the finite spot size associated with a particle impact on the MCP/phosphor screen detector.
Figure 2.6: This figure shows the image distortions for electrons and ions versus polar angle $\alpha$ for one fixed distance to the image center; the y-axis is normalized to the distance at 0 deg. The laser polarization has been turned perpendicular to the screen, which enforces a centrally symmetric electron/ion distribution at the source. The lines are based on the center of gravity versus $\alpha$ of one prominent feature in a sample electron/ion distribution. Any deviations from a constant value must be due to imaging inaccuracies. Based on this graph the imaging error for the kinetic energy ($\sim R^2$) is estimated to be $0.5 \sim 1.6\%$ and $2.6 \sim 4.0\%$ for the ion and electrons, respectively. It should be noted, that this graph only shows the distance $R$ to the electron/ion center, which are distinct. Precisely speaking, the electron distribution center is about 1 mm offset from the ion distribution center.
component parallel to the tof-axis is lost. This leads to mixing in of fast ions/electrons into slower velocity classes and effectively lowers the contrast of the acquired distributions. In the literature, this problem has been solved by mostly one of two following techniques: physically via DC slicing \cite{53} or by post-processing the data by applying the inverse Abel transform or related algorithms \cite{52,56,58}. The former technique gates the MCP in a way that only particles are detected that were created with zero momentum perpendicular to the detector. They separate from the other particles during their flight, because of their slightly lower longitudinal kinetic energy. Literature \cite{53} states that it is necessary to cut off 90\% of the ion cloud in order to avoid the projection effect. This corresponds to a gating window of 20 ns (for ions), which is technically challenging, since it requires to switch the voltage bias for at least one MCP by \( \approx 1 \) kV within a few ns. This is barely feasible with the described set-up, but it also leads to a reduction of the S/N ratio by the same amount. For electrons this technique is not applicable, since the electron cloud created by the laser pulse spreads out only to a few nanoseconds altogether. Latter post-processing techniques are based on the assumption that the real (un-projected) momentum distribution is centrally symmetric around the laser polarization axis. This is absolutely correct when using a CW laser beam, but it is also sufficiently valid in our case, since the pulse envelope is only slowly varying compared to one optical cycle. For this reason we chose to use only post-processing methods to correct the signal. Further, in most described experiments (besides chapter \( \Box \)), this turned out to be unnecessary and provided only marginal benefits. The data presented in this thesis is usually the 'raw', not post-processed, data, if not stated otherwise. Appendix \( \Box \) gives further information on the inverse Abel transform.
Chapter 3

Control of Vibrational Dynamics in CH$_2$BrI$^+$

3.1 Introduction

In contrast to the other projects described in this thesis, this chapter focuses rather on nuclear dynamics than on electronic dynamics. It has been an ongoing theme in the ultrafast community to work on methods to selectively modify the nuclear evolution of molecules, with possible long-term applications to quantum computing [59, 60], and using ultrafast laser pulses as a ‘catalyst’ for desired chemical reactions [61, 62]. There are heuristic approaches, which often use a closed-loop learning algorithm in combination with pulse shaping, to find optimal control pulses that have the targeted effect on the molecular evolution. Interpreting the mechanism underlying control in those experiments is difficult and requires the aid of further insights from ab-initio electronic structure and quantum dynamics calculations [63–65]. In addition, there are various ‘bottom-up’ approaches, described and implemented in the literature (see references [66–76]). They have been designed with a particular mechanism in mind, based on a detailed understanding of the molecular potential energy surfaces involved. The work described in this chapter belongs to the latter category and uses a strong IR pulse to change the evolution of a nuclear wave packet, while key parameters of the control pulse (timing, intensity and duration) are systematically varied. We demonstrate two different schemes for control over the evolution of a vibrational wave packet. One scheme has been termed ‘photon locking’ (originally referred to as ‘optical paralysis’) [77–83], and mixes (or dresses) two potential energy surfaces in order to lock a vibrational wave packet in position. The other scheme, termed ‘hole burning’, uses strong field population transfer to reshape a vibrational wave packet by
population transfer in a spatially narrow window\textsuperscript{*}. Similar approaches, using position dependent ionization or strong field driven AC Stark shifts, have been used to create or reshape molecular wave packets in diatomic molecules \cite{84,87}. Possible applications are coherent cooling of hot molecules to their ground state \cite{88} or using vibrational levels for storing quantum information \cite{59}. Other work using strong fields focussed on using light-dressed states to control the branching ratio in dissociation \cite{89,93}. The experiment utilizes a three pulse sequence composed of a strong IR (780nm) 'pump' pulse, an intermediate IR 'control' pulse (whose parameters are scanned) to influence the evolution of a nuclear wave packet on the lowest ionic state of CH\textsubscript{2}BrI, and a weak UV (260nm) 'probe' pulse. The results are compared with a theoretical model of this system developed by the groups of Leticia González et al. and Tamás Rozgonyi. This model simulates the evolution of the nuclear wave packet under the influence of the control field by solving the time dependent Schrödinger equation using potentials calculated with \textit{ab-initio} methods \cite{94}.

This chapter is organized into six sections. Section 3.2 discusses the nuclear dynamics under consideration, introduces the two main control schemes and demonstrates how they can be observed experimentally. Sections 3.3 and 3.4 describe the experimental data acquisition and the corresponding theoretical simulations. Sections 3.5 and 3.6 continue with discussing the results of the two control schemes in detail. Finally section 3.7 describes the main error sources and provides upper limits on their magnitude.

### 3.2 Basic Scenario and no-control case

The control mechanisms are implemented in CH\textsubscript{2}BrI\textsuperscript{+} and the basic scenario is summarized in figure 3.1. This system has been subject of several previous publications, which studied the evolution of a nuclear wave packet on the ionic ground state $V_1$ and the coupling to neighbouring ionic states both experimentally and theoretically \cite{43,94,95}. Further details are discussed in chapter 5 of this thesis. In brief, the IR pump pulse launches a vibrational wave packet on the lowest ionic state $V_1$ via strong-field ionization, at the position of the ground state equilibrium (from here on referred to as FC\textsubscript{pump}). The wave packet evolution can be well described as a one-dimensional motion along the I-C-Br bending coordinate ($u$) - details on the theoretical framework and its interpretation will be given in section 3.4. Without the control pulse, the wave packet.

\textsuperscript{*}The literature seems not yet to have converged on a standard phrase. Other names suggested are 'lochfrass' or 'R-dependent-excitation' (see \cite{84}). Both terms allude to the fact, that a (spatially) narrow hole is burned into the wave function using a strongly position ('R')-dependent excitation process.
packet will exhibits nearly harmonic motion in the $V_1$ potential well, with a calculated round trip time of 350 fs. This motion can be directly observed with the UV probe pulse, which can promote parts of the $V_1$ population to a higher lying, dissociative state (labelled $V_n$ in figure 3.1). The Frank-Condon point for this transfer is referred to as $FC_{\text{probe}}$. Any population on this state is several eV above the dissociation threshold [96] and leads mostly to fragmentation into $\text{CH}_2\text{I}^+$ and Br or further fragmentation into I$. Thus varying the pump-probe delay can modulate the parent and fragment ion yields, which are shown in figure 3.1 panel (b) or the Fourier transform of the parent signal in panel (c). Please note that the parent ion and $\text{CH}_2\text{I}^+$ signals are phase shifted by almost $\pi$, which is to be expected when the probe transfers population between a bound and dissociative state (leading to $\text{CH}_2\text{I}^+$ formation).

The measured period (in $\text{CH}_2\text{BrI}^+\text{, CH}_2\text{I}^+$ and $\text{I}^+$) with a UV probe pulse is $(346 \pm 30)$ fs and agrees well with the calculated period of motion in the $V_1$ potential, 350 fs (see section 3.4). This is analogous to the modulation period observed with an IR probe $(351 \pm 11)$ fs reported in previous publications [94, 95] and chapter 5. The dephasing time is remarkably long and more than several ps.

These modulations also provide a method for studying the effects of the control pulse. In order to characterize the wave packet on $V_1$ (modified by the action of the control pulse), we Fourier transformed the pump probe signal. We define two observables, the amplitude $A(\alpha)$ and the phase $\Phi(\alpha)$ (corresponding to a period of 351 fs), that refer to the amplitude and phase of the parent ion modulations as a function of the control pulse shape $\alpha$. Here $\alpha$ is a generic variable, capturing all varied parameters of the control pulse, i.e. intensity, second order phase and time delay. We want to point out that, since the modulations in $\text{CH}_2\text{BrI}^+$, $\text{CH}_2\text{I}^+$ and $\text{I}^+$ reflect the same wave packet motion, any of them - in principle - contains the same amount of information. Yet as is discussed in the remaining chapters of this thesis, strong field ionization effectively populates several ionic states, and only the lowest two are bound. The fragment ion modulations are superimposed with a significant background signal from dissociative ionization via the pump pulse (see reference [97] for a representative time of flight mass spectrum) and the parent-ion signal is selected because of its favourable signal-to-noise ratio. $A$ relates directly to the depth of modulation of the $V_1$ wave packet. Without the control pulse, $\phi$ is close to zero, which indicates that $FC_{\text{pump}}$ and $FC_{\text{probe}}$ are very nearby - the exact time delay is used in section 3.4 to determine the absolute position of $FC_{\text{probe}}$. Deviations from the no-control values of $\phi$ relate to a displacement of the center of gravity of the $V_1$ wave packet. In the following sections the experimental values for amplitude and phase will be compared with the
theoretical predictions, which justifies the given interpretation of the observed control schemes.

The IR control pulse arrives in between the pump and the probe. The two control mechanisms are illustrated in figure 3.2. For an IR control pulse there are two closely spaced one-photon resonances between $V_1$ and $V_3$ and $V_4$, which distort $V_1$ and facilitate the control of the $V_1$ wave packet by dressing these states. As will be justified in section 3.4 we can simplify this picture by jointly referring to $V_3$ and $V_4$ as one state $V_{3/4}$, with one resonance to $V_1$ at ‘FC$_{control}$’. The control is most pronounced when the wave packet is in proximity of FC$_{control}$ during the control pulse, which happens twice per round trip but results in two qualitatively different effects: When the wave packet is moving from the outer (FC$_{pump}$) turning point towards smaller bending angles, ‘photon-locking’ is observed. This can be seen in cartoon 3.2, panel (a) and will be discussed in detail in section 3.5. As long as the molecule is exposed to the control pulse, the $V_1$ population will rather evolve on a dressed potential $V_1$-$V_{3/4}$, referred to as $V_+$. In this case the wave packet will encounter a ‘wall’ close to FC$_{control}$, which - if sufficiently high, i.e. if the control is intense enough - will lock the wave packet in its position. By contrast, panels (b) and (c) illustrate the control mechanism that can be applied to wave packet while it is moving from the inner turning point - towards larger bending angle. Here the control pulse removes a spatially narrow slice out of the $V_1$ population around FC$_{control}$ by transferring it to $V_{3/4}$. Depending on the exact arrival time of the wave packet, the control cuts off its ’leading edge’, ’center’ or ’trailing edge’, leading to a displacement of its center of gravity. Alluding to the ’hole’ in the wave packet after the interaction with control pulse, this method is referred to as ’hole burning’ and further discussed in section 3.6.

3.3 Experimental Setup and Data Acquisition

The CH$_2$BrI molecule was not only chosen in an effort to study control mechanisms in polyatomic systems, but it also provided several benefits. First, its potential energy surfaces are partly known and the $V_1$ nuclear evolution can not only be modelled theoretically. Second, there are only two one-photon IR resonances between $V_1$ and other low lying ionic states, which simplifies the understanding of the control pulse influence. Third, we were able to use UV light as a probe, which also only has one one-photon resonance with $V_1$. This further allowed us to disentangle the influence of the control and probe pulse, since optical interference between both pulses can be ruled out directly in the experiment. Fourth, while population transfer by IR from $V_1$ leads predominately to CH$_2$Br$^+$ formation, UV excitation predominately leads to CH$_2$I$^+$.
Figure 3.1: This figure summarizes the basic picture used in this experiment. Panel (a) is a cartoon of the relevant potential energy surfaces and their relevant couplings versus the molecular bending I-C-Br coordinate (u). The strong IR (780 nm) pump launches a vibrational wave packet at FC\textsubscript{pump} on the lowest ionic surface V\textsubscript{1}. This can be excited with the following UV (260 nm) probe pulse to a higher lying dissociative surface V\textsubscript{n}, which will result in fragmentation to CH\textsubscript{2}I\textsuperscript{+} and Br and further fragmentation into I\textsuperscript{+}. Since V\textsubscript{1} is bound the wave packet will exhibit a near-harmonic motion with a period of (346 ± 30) fs. The probe is most efficient in promoting population within the narrow Frank-Condon region FC\textsubscript{probe}. Panel (b) shows the ion signal, when the pump-probe delay is systematically scanned. In this case the probe timing modulates the fragmentation of the parent ion, which leads to anti-correlated oscillations between CH\textsubscript{2}BrI\textsuperscript{+} and CH\textsubscript{2}I\textsuperscript{+} (and I\textsuperscript{+}) matching the V\textsubscript{1} round trip time. Panel (c) shows frequency spectrum of the parent-ion signal of panel (b) and directly verifies that there is only one-dominant frequency component (highlighted in red) and that the wave packet motion can be understood as population evolving in a nearly harmonic potential. The amplitude and phase of this frequency component is a direct measure of the amplitude and phase (position) of the V\textsubscript{1} wave packet, respectively. A second IR pulse, the ‘control’, can couple V\textsubscript{1} with two neighbouring ionic states V\textsubscript{3} and V\textsubscript{4} (only V\textsubscript{3} is shown here), which distorts V\textsubscript{1} and thus affects the wave packet evolution. This can be observed as a change in amplitude and phase of the modulations in the parent ion pump-probe signal.
Figure 3.2: This figure summarizes the two control schemes implemented in this experiment. The control pulse couples $V_1$ to $V_{3/4}$, with qualitatively different consequences on the $V_1$ wave packet evolution depending on its direction of motion. Panel (a) illustrates the photon locking control scheme in the Floquet-Picture: Here $V_1$ (dashed orange line) and $V_{3/4}$ (dashed violet line, shifted by one IR photon in energy) form the light-dressed $V_+$ (solid green line) potential. On this effective potential the wave packet will encounter a 'wall', which blocks its propagation towards the inner turning point, i.e. it is locked close to the outer turning point. Panels (b) and (c) describe the case, when the control pulse arrives while the wave packet moving through $FC_{control}$ coming from the inner turning point. This happens around 610 fs, with panel (b) referring to just before 610 fs ($t_1$) and panel (c) referring to a time just afterwards ($t_2$). The control 'burns' a hole into the wave packet, which effectively shifts its center of gravity backwards (panel b) or forward (panel c). This can be observed as shift in magnitude of parent ion modulation depth and phase.
and I⁺ formation, and thus one can distinguish between fragmentation by the control and fragmentation via the probe. And last but not least, the near periodic motion of the V₁ wave packet, showing only little dephasing within the first few ps after the pump pulse, gives some degree of freedom for choosing the time delays between pump, control and probe, since their relative timing only matters modulo one period. This was very convenient in demonstrating the 'hole burning' effect, since the time delays between the different laser pulses could be chosen long enough to avoid any optical interference.

Experimentally, the strong 'pump' pulse and the weaker 'control' pulse were generated from a single beam with the AOM pulse shaper and then later collinearly combined with the UV arm, which provided the 'probe' pulse. As mentioned before, two different control schemes, that used differently designed 'control' pulses, were employed. In both scenarios, the pump pulse ionized the molecules and launched a vibrational wave packet on the ground ionic state V₁. This PES was then distorted by the following control pulse, which affected the evolution of the nuclear wave packet. The result was read out with the probe pulse. It promoted a portion of the wave packet evolving on the ground ionic state to a higher lying dissociative state of the ion (Vₙ), allowing to study the wave packet evolution by monitoring the parent and fragment ion yields. In both cases the 'pump' pulse had a pulse duration of ≈ 40 fs and a peak intensity of 5.1 · 10¹³ W cm⁻² (corresponding to a Keldysh parameter γ of about 1.3), and the 'probe' pulse had a pulse duration of about 50 fs with a intensity of about 4.5 · 10¹² W cm⁻². The probe delay relative to the pump pulse was also scanned within the intervals (-200 fs, 2000 fs) and (900 fs, 2400 fs) for the 'photon-locking' data set, and 'hole-burning' data set respectively.

The control pulse parameters differed for both scenarios. For the photon-locking scheme the control pulse was centered at the same time delay as the pump pulse. The pulse was artificially stretched in time by adding second order phase ('chirp'), such that its duration varied between ≈ 75 fs and 240 fs. The intensity was scanned from 0 to a maximum peak intensity (for an unshaped control pulse) of 1.7 · 10¹³ W cm⁻². In the hole-burning scheme the control pulse was kept at a transform-limited pulse duration (i.e. ≈ 40 fs), but its time delay (relative to the pump) was varied. Further the intensity was fixed at 1.7 · 10¹³ W cm⁻². The parameters were chosen in order to avoid systematic errors overwriting the desired control, as will be discussed in section 3.7.

For this experiment no momentum resolution of the different ions was needed. For this reason the data was acquired in tof-mode. In this case space charge (as described in section 2.7) was not a concern and a relatively high sample pressure of about 6 · 10⁻⁴ Pa could be used.
3.4 Simulations

The picture outlined in the previous section is supported by quantum dynamics calculations. These simulations consist of both ab-initio structure calculations of the relevant potential energy surfaces and simulating the (nuclear) time-evolution of the molecule under interaction with the laser pulses. The ground work of calculating the electronic structure of the \( \text{CH}_2\text{BrI} \) was provided by the groups of Tamás Rozgonyi and Letitia Gonzáles \[94\]. The normal mode coordinates were determined by density functional theory \[98\], while the potential energy curves (PEC), transition dipole moments (TDM) and spin-orbit couplings (SOC) were determined by the state averaged complete active space self consistent field (SA-CASSCF) method \[99\]. Only the five lowest PES were calculated. According to experimental evidence \[96\] and theoretical results (shown in figure 5.2), only the two lowest ionic states are below the dissociation threshold. Higher states are known to be dissociative \(^\dagger\). The ground state equilibrium position defines \( \text{FC}_{\text{pump}} \), which is located at \( u = 0.85 \) a.u. Further, \( \text{FC}_{\text{control}} \) refers to the two very closely spaced one-photon IR resonances of \( V_1 \) with \( V_3 \) and \( V_4 \), around \( u = 0.34 \) a.u.. The position of \( \text{FC}_{\text{probe}} \) is reconstructed from experimental data, as mentioned in section 3.2. The phase of the modulations in the \( \text{CH}_2\text{I}^+ \) ion signal in the no-control case, together with the known round trip time, locates \( \text{FC}_{\text{probe}} \) around \( u = 0.76 \) a.u. On top of these ‘electronic’ calculations, simulations regarding the nuclear evolution were performed, partly by Philipp Marquetand and the author. Those were restricted to one degree of freedom, the I-C-Br bending coordinate, which has proven to be successful in comparison between experiment and theory in other projects \[43, 94, 95\]. Theoretically the validity of this simplification can be motivated by the fact that the equilibria of the ground states of \( \text{CH}_2\text{BrI} \) and \( \text{CH}_2\text{BrI}^+ \) (i.e. \( V_1 \)) happen to differ mostly along the I-C-Br bending angle: the angle is smaller for the ion than for the neutral. According to reference \[94\], ionization to \( V_1 \) induces a wave packet in \( \text{FC}_{\text{pump}} \) with a mean vibrational quantum number of 7 and a spread (full width at half max) of about 5 levels. The details of the simulations for the nuclear wave packet evolution are described in references \[41, 94\], which solve the time-dependent Schrödinger

\(^\dagger\)The states \( V_3 \) and \( V_4 \) are indirectly dissociative, i.e. they are energetically above the dissociated system (I + \( \text{CH}_2\text{Br}^+ \)), and a trajectory connecting the bound with the dissociated geometry must exist. But this pathway is not known, e.g. these states appear to be bound along the bending mode in figure 3.1.

\(^\dagger\)Correctly speaking \( \text{FC}_{\text{pump}} \) is the projection of the neutral ground state equilibrium coordinate onto the one-dimensional model. As mentioned before this can be justified, theoretically by the relatively small deviation of the ‘real Frank-Condon point’ from \( \text{FC}_{\text{pump}} \) along other coordinates (the C-I and C-Br equilibrium bond lengths differ less than 1% between neutral and ionic ground state.) and experimentally a posteriori.
The electromagnetic field of the pump and the control pulse were included explicitly in the TDSE. The TDSE is solved on a grid of 128 points with the help of the Split-Operator method [100] and the fast Fourier technique. A time discretization of 0.01 fs and a spatial discretization of 0.025 a.u. is employed. The grid size was checked for convergence. Here only the population on the potentials $V_1$ to $V_5$ were included. The interaction with the probe was not included in the simulations. Since it is a one-photon process in a weak field, perturbation theory implies that its excitation to $V_n$ is simply proportional to the $V_1$ population within a window around FC$_{\text{probe}}$. This is supported by the fact that the oscillation period of the experimental CH$_2$I$^+$ signal is the same as that of the calculated bending mode frequency in $V_1$. The borders of the probe window were defined as $u = 0.56$ a.u. and $u = 0.96$ a.u. to match approximately the width of the moving wave packet.

In the photon-locking simulations, the control pulse field strength was scanned between 0 and 4 GV/m. The time delay was fixed at 0 fs and the pulse duration was varied by adding second order phase. The bandwidth was assumed to be the equivalent of a 47 fs pulse. In the hole-burning scenario, the peak field strength of 4 GV/m was used, the duration was kept constant at 40 fs, but the time delay was scanned between 0 and 900 fs.

In addition to the detailed quantum dynamics calculations, a simplified set of calculation allowed to test the interpretation of the hole burning control mechanism. This simulation – using the split-operator method, as described in the appendix of [49] – only included $V_1$ explicitly. The interaction with the control pulse was implemented by removing all population from $V_1$ at FC$_{\text{control}}$ in the window $0.325 \pm 0.225$ a.u. at the arrival time of the control pulse.

As mentioned in section 3.2, two observables are defined, the amplitude $A(\alpha)$ and phase $\phi(\alpha)$ of the parent ion modulations (in the pump-probe signal), versus control pulse shape $\alpha$. These observables could also be calculated based on the simulated data and were defined in a similar way. Let $Y(t, \alpha)$ be the total $V_1$ population within FC$_{\text{probe}}$ at time delay $t$ and after control pulse $\alpha$; in the simulation the molecule was assumed to be oriented parallel to the TDM between $V_1$ and $V_{3,4}$. The fragment ion yield should be proportional to the parent ion population that is promoted to $V_n$ by the probe, and one expects (with $C$ as the appropriate normalization constant):

\[
A(\alpha) = 0.5 \cdot \left[ \max_{t \in (t_0, t_0 + 351)} Y(t, \alpha) - \min_{t \in (t_0, t_0 + 351)} Y(t, \alpha) \right] \quad (3.1)
\]

\[
\Phi(\alpha) = C (351 \text{ fs})^{-1} \int_{t_0}^{t_0 + 351} t Y_c(t, \alpha) \, dt \quad (3.2)
\]
The time interval \((t_0, t_0+351)\) fs was chosen such that it covered one complete round trip of the wave packet on \(V_1\) (starting from \(FC_{\text{pump}}\)), but had no overlap with the control pulse. The core of the interpretation of this experiment is summarized in figures 3.3 and 3.4 which compare the experimental values of \(A\) and \(\Phi\) with their theoretical predictions.

### 3.5 Control by Photon-Locking

This section discusses further details of the photon-locking scheme (as illustrated in figure 3.2, panel a), which refers to the case of \(V_1\) wave packet propagating towards the inner turning point during the control pulse. Experimentally, the control pulse is superimposed with the IR pump pulse, i.e. they are both centred around 0 fs time delay. Its energy was varied between 0 and 19.6 \(\mu\)J and its duration was manipulated by adding second order phase such that it changed between 75 fs\(^2\) and 240 fs\(^2\) (FWHM). These intervals were selected to restrict the intensity of the control pulse to a regime where it cannot act as an additional pump and complicate the interpretation.

As indicated in panel (a) of figure 3.2 while the interaction with the molecule, the wave packet propagates on the light dressed state \(V_+\), instead of the bare state \(V_1\). \(V_+\) differs from \(V_1\) mostly by adding a ‘wall’ around FC\(_{\text{control}}\). If the control pulse is sufficiently intense, this wall is high enough to hold and/or reflects the wave packet. Simulations and experimental data show that population transfer to \(V_{3/4}\) is negligible in this case. The distinction between holding and reflecting is partly a question of definition, since the distance between the \(V_+\) minimum and \(FC_{\text{pump}}\) can be smaller than the FWHM of the wave packet, which is 0.35 au at FC\(_{\text{pump}}\).

In order to qualitatively understand this effect it is helpful to consider two extremal cases, when the control pulse is either turned off instantaneously or turned off adiabatically. In the former case, \(V_+\) ‘jumps back’ to \(V_1\) instantaneously and the wave packet resumes its usual harmonic-oscillator-like evolution on \(V_1\). One would expect a phase offset in the parent ion modulations, i.e. an offset in \(\Phi(\alpha)\), corresponding to how long the wave packet was frozen in the minimum of \(V_+\). The amplitude \(A(\alpha)\) would be unaffected. In the adiabatic case the minimum of \(V_+\) slowly converges to the intersection point of \(V_1\) and \((V_4 - h\nu)\). The wave packet, which has been locked in the minimum of \(V_+\) follows the minimum, until the control pulse is weak enough, such that it can leak through the residual ‘wall’ via non-adiabatic coupling. After the control pulse is over, one expects the wave packet again to resume its unperturbed motion, but it has acquired a phase offset and also a reduced amplitude, since it was re-launched closer to FC\(_{\text{control}}\), not from FC\(_{\text{pump}}\). From
the energetic point of view, the wave packet is losing energy to the control field, since it is slowly ‘dropping’ with the wall towards the unperturbed $V_1$. Further, the wave packet is expected to be broader (spatially), since parts of it have been leaking through the wall while interacting with the control pulse.

Original versions of the experiment aimed to implement the ‘instantaneous’ case described above, but encountered two main problems. One technical and one fundamental issue: First, the bandwidth of the control pulse is not short enough to allow an instantaneous turn-off. The bandwidth supports 40 fs, which is barely enough for turning on within the time the wave packet takes to propagate from $FC_{pump}$ to $FC_{control}$ (60 fs). Further, the wall needs to be already fully formed when the wave packet reaches $FC_{control}$ in order to avoid population transfer to $V_{3/4}$, allowing little freedom for the control pulse timing. In addition, the molecular sample is not aligned to the control laser pulse polarization. Earlier experiments showed that ionization to $V_1$ is not sensitive to the angle between pump polarization and molecular alignment. But there is a well defined transition dipole moment between $V_1$ and $V_{3/4}$, i.e. independently how intense the control pulse is, a large fraction of the total $V_1$ population only experiences a low intensity control pulse and forms a ‘wall’ too shallow for photon-locking. This contributes a strong no-control signal to the pump-probe signal, regardless of the exact control pulse parameters and makes determining a possible phase shift more difficult. As a result, we do not observe a significant phase shift in the pump probe signal proportional to the control pulse duration\footnote{We do measure a small phase shift in the pump probe signal with the control pulse, but the sign and size of the phase advance are consistent with a minor systematic error, rather than photon locking.}.

The modulation depth in the pump probe signal from calculations is shown in figure 3.3 (a). As described above it shows a decrease for both longer and more intense control pulses. This is in qualitative agreement with the experimental data presented in panel (b) of figure 3.3. One quantitative disagreement is the less pronounced decrease in modulation depth for even higher intensities in the experimental data. We believe this could be resolved by a more detailed modelling of the volume and angle averaging in the sample. But this would require a exact characterization of not only the IR and UV modes in the vacuum chamber, but also their overlap, which was beyond the scope of this work.
Figure 3.3: These plots shows the results of the numerical simulations (panel a) and experimental data (panel b) for the photon-locking scheme as described in section 3.4. The x-axes refer to the peak field strength of the control pulse (rescaled to TL duration). The y-axes refer to the predicted decrease in modulation depth of the CH$_2$BrI$^+$ pump-probe signal. The modulation depth is normalized to the unperturbed case. Also the simulation result is intensity averaged, trying to mimic the different effective control pulse intensities due to volume and angle averaging. The main prediction is a decrease in modulation depths both with increasing control pulse duration (by adding second order phase) and intensity. The increase in modulation depth with field strength for the shortest control pulse duration is an artifact of the simple model used to describe the ionization process. Experimentally, for control pulse durations less than 100 fs, no significant decrease in modulation amplitude is observed.
3.6 Control by Hole-Burning

If the control pulse interacts with the molecule during the second half of the wave packet’s round trip in $V_1$, the situation is very different, as illustrated in panels (b) and (c) of figure 3.2. The effect is most pronounced in the time interval when the wave packet is crossing $FC_{control}$, which is at around 610 fs. Experimentally the control pulse delay was varied (in this case with a transform-limited duration) in the interval (560,660) fs, i.e. ±50 fs around the passage through $FC_{control}$. The probe pulse delay was scanned between 900 fs and 2400 fs. As mentioned before and indicated in section 3.3 the timing of the individual pulses can be shifted modulo one round trip time, which was exploited for this experiment to avoid optical interference between the different pulses. We also acquired similar data sets with control and probe shifted one period closer to the pump pulse, with qualitatively similar results.

As described in section 3.2 the measured amplitude and phase of the parent ion pump probe signal are used to characterize the $V_1$ wave packet and compared with their simulated predictions as a benchmark for the validity of our interpretation. Panel (b) of figure 3.4 presents the experimental results of this control scenario.

The change in amplitude can be explained by the loss of population to $V_{3,4}$ due to removing a slice from the wave packet. A simple estimate implies that a strong-field picture, instead of perturbation theory, needs to be applied: The control pulse peak intensity of $1.7 \cdot 10^{13}$ W cm$^{-2}$ corresponds to a peak field strength $E_0$ of 11 V/m (for molecules aligned with the laser polarization and in the center of the beam focus). After neglecting nuclear motion and only considering the part of the $V_1$ wave packet at $FC_{probe}$, one can approximate $\Omega(t) \approx \frac{\mu E(t)}{\hbar}$ for the Rabi frequency $\Omega$, and the dipole element $\mu \approx 8.4 \cdot 10^{-30}$ Cm. Assuming a pulse with Gaussian temporal profile ($\tau = 40$ fs), this yields a pulse area much larger than $\pi$:

$$1/2 \int \Omega(t') dt' = \frac{\sqrt{\pi} \tau E_0}{2\mu \hbar} \approx 300$$

The decrease in modulation depth is most pronounced when the center of the wave packet is at $FC_{control}$ (i.e. at 610 fs) when the control pulse arrives. If the wave packet arrives early or late, only the leading or its trailing edge are removed and the decrease in amplitude is less visible; this is reflected by the wings in figure 3.4 (b) approaching unity. Further, a phase shift of up to 0.15 rad at about 30 fs before and after the amplitude minimum is observed: removing the leading or the tailing edge of the wave packet shifts its center of gravity backwards or ahead respectively. Removing the center slice does not
Figure 3.4: The hole-burning scheme removes a narrow slice of the $V_1$ wave packet, which results in a change in both phase and the amplitude of the modulations in the $\text{CH}_2\text{BrI}^+$ pump probe signal. Panel (a) displays the predictions on amplitude and phase versus control pulse timing based on numerically solving the TDSE. Two different simulations have been performed. A ‘full’ simulation, which includes the five lowest ionic states and treats the interaction with the control explicitly - the results are shown in the solid lines. The dashed lines refer to a simplified calculation that only includes $V_1$ and treats the interaction with the control by removing all population from a narrow window around $\text{FC}_{\text{control}}$. The decrease in amplitude reflects the hole-burning effect, which leads to an absolute minimum if its center slice is removed at 610 fs. The phase advance/delay corresponds to removal of the tail or head of the wave packet. Panel (b) shows the experimentally determined values for amplitude and phase. The amplitude is normalized to 1 at its maximum. The phase is shown relatively to the no-control case.
show any net effect, as well as control pulse timings too early or late to remove any significant part of the wave packet.

There are two different kinds of simulations to verify this interpretation: Both calculate amplitude and phase by numerically propagating the $V_1$ wave packet and modeling the effects of the control pulse (for details see section 3.4). This is shown in panel (a) of figure 3.4. The solid lines refer to a ‘full’ simulation, which includes the five lowest ionic states and solves the TDSE including the electromagnetic field of pump and control pulses. They qualitatively reproduce the experimental data, but the predicted changes in magnitude and phase are much larger. As in the case of quantitative disagreement between experiment and theory for the photon-locking scenario, this is expected to be resolved by including the intensity and angle averaging effects. In addition to the ‘full’ simulation, a second set of simplified calculations is carried out, whose results are also shown in figure 3.4 (a) as dashed lines. Both types of simulations agree quantitatively, which implies that the simpler type of simulation already includes all relevant effects. But in contrast, the second type of simulation only includes one electronic surface, $V_1$. Further, the coupling with the control pulse is only treated phenomenologically by setting all population to zero within a narrow window around FC$_{\text{control}}$ at the control pulse arrival time. Since both types of simulation make almost identical predictions, this further supports that spatially selective population transfer - hole burning - is responsible for the phase advances and delays seen in the full calculations and measurements.

3.7 Systematic Experimental Error Checks

Several experimental checks have been performed, in order to rule out systematic effects that also could affect the depth of modulation. We considered two additional possibilities: (1) Additional ionization to $V_1$ from the molecular ground state by the control, and - in the photon-locking scheme - (2) population transfer to $V_{3/4}$ via the control pulse.

The modulation depth of the pump probe signal is found to increase monotonically with increasing pump intensity after exceeding a threshold intensity. This concern sets the upper limit on the maximum usable intensity for the experiment. In the photon-locking control scheme issue (1) would lead to an increase in the modulation depth with increasing control pulse intensity, which is opposite to the observed behaviour. For the hole-burning experiments a larger range of different control intensities is explored. For the highest control pulse intensities additional ground state ionization is indeed observed, but this can be easily recognized since it leads to qualitatively different behaviour of
Φ(α). For this reason, the control intensity is restricted to the lower intensity range.

With regard to (2): while population transfer to V_{3,4} via F_{control} is the key element in the hole-burning control scheme, it is undesirable in the photon-locking case. In principle it could mimic the decrease in amplitude as observed in panel (b) of figure 3.3. But as is described in chapter 5, the population transfer (indirect V_{3,4}) from V_{1} to V_{3/4} can be measured directly using momentum resolved detection of CH_2Br^+. It is found that the total indirect V_{3,4} population is roughly constant for control pulse energies above 9 \mu J and a pulse duration longer than 127 fs, which covers most of the range shown in figure 3.3 (a). For this reason we can rule out a significant contribution of population transfer in the photon-locking scenario.

Last but not least it should be pointed out that the described experiments were performed both with the probe and control polarizations parallel and perpendicular, resulting in similar degrees of control. This implies that the TDMs for the transitions accessed by the control (V_{1} to V_{3,4}) and by the probe (V_{1} to V_{n}) are not parallel. Since the molecular sample is not aligned, this further reduces the magnitude of the observed control since only a subsection of the 'controlled' molecules is also probed. Experimentally this would be very challenging to address: The two non-collinear TDMs of control and probe, impose two restrictions on the molecular orientation, i.e. a full three-dimensional alignment would be required.

3.8 Conclusion

In conclusion, this experiment implemented two control mechanisms photon-locking and hole-burning in a small polyatomic molecule. To the author’s best knowledge this is also the first observation of photon-locking in a molecule. In both cases, a strong laser field is used to modify the evolution of a nuclear wave packet by distorting the associated electronic state. The results are shown to be in qualitative agreement with theoretical simulations.
Chapter 4

Multiple Ionization Pathways in Strong-Field Ionization

4.1 Introduction

This and the following chapters discuss ways to quantify the molecular state after SFI. ADK theory \[101,102\] suggests a simple relationship between ionization yield \( W_{ab} \) from initial state \( |\Psi_N^i\rangle \) to final state \( |\Psi_{N-1}^f\rangle \) - here the exponent indicates that it is a \( N \) or \((N - 1)\) electron wave function - separated by an energy gap of \( E_{if} \) in a linearly polarized laser pulse with peak field strength \( F_0 \):

\[
W_{ab} = C(E_{if}, F_0, \Psi_D) K(E_{if}, F_0) G^D
\]

\[
K(E_{if}, F_0) = \exp \left( -\frac{2(2E_{if})^{3/2}}{3F_0} \right)
\]

\[
|\Psi_D\rangle = \langle \Psi_{N-1}^f | \Psi_N^i \rangle
\]

\[
G^D = \langle \Psi_D | \Psi_D \rangle
\]

In formula 4.1 the dominant contribution is \( K \), while \( C \) depends only weakly on its parameters, i.e. sub-exponentially. The wave function defined in 4.3 is called the Dyson-Orbital and reflects the electronic wavefunction overlap between initial and final state. In the systems studied in this thesis, usually several ionic states are located within the first 1 eV above the ionization potential. With a peak intensity of about \( 10^{14} \) W cm\(^{-2} \), formula 4.1 implies that the ionization pulse should result in a superposition with significant contributions from several states. The question of the distribution of population among the various molecular states SFI has been studied in numerous publica-
tions in the recent years. Many techniques involve high harmonic generation \[103-107\]. Other approaches interpret special features in the photo electron spectrum \[108, 109\] - this method is generalized in chapter 6, or focus on the relation between ionization current and molecular axis \[110, 111\], or utilize more sophisticated electron-ion coincidence techniques \[112, 113\].

The work described in this chapter follows a different approach, which combines pump-probe scans with insights from ab-initio structure calculations. It discusses the final molecular state as a superposition arising from the contribution of multiple 'ionization pathways' (see below for an exact definition). The system under consideration is CH$_2$I$_2$, and exhibits at least three different ionization pathways, when ionized with a strong IR (780 nm) pulse. When using an IR pump, the Keldysh parameter $\gamma$ is slightly less than 1, which corresponds to an intermediate regime of multi-photon ionization and SFI. These IR pump - IR probe scans are contrasted with UV pump - IR probe scans, which can be treated as a pure multi-photon interaction ($\gamma \approx 20$). The experiment further demonstrates SFI features that are not captured by simple ADK models (e.g. as shown in equation 4.1), that only include the intensity profile of the ionization pulse: the relative importance of the identified pathways also depends on the sign of the applied second order phase.

Intuitively the term 'ionization pathway' refers to 'how' population is transferred from the initial neutral state to the final ionic state of the molecule, e.g. as described in chapter 5 regarding SFI in CH$_2$BrI and indicated by the orange arrows in figure 5.2. A more formal definition can be given as follows (similar to the treatment described in reference [81]): Let $\Psi_{after}(r; R)$ denote the complete wavefunction of the molecule after SFI with the generalized electronic and nuclear coordinates $r$ and $R$. It can be expanded into a double sum, using the diabatic potentials (at $R_0$) $\psi_k(r)$ as a basis for the electronic part and Gaussians wavefunctions $g_l(R)$ as basis for the nuclear part, yielding (with the appropriate coefficients $c_{kl}$):

$$\Psi_{after}(r; R) = \sum_{k,l} c_{nk} \psi_k(r) g_l(R)$$  \hspace{1cm} (4.5)

This sum is the formal representation of a molecule whose population is coherently distributed among several nuclear wave packets, which are not necessarily located all on the same electronic energy surface. At the same time, one can interpret SFI in a multiphoton picture, and expand the interaction with the ionization pulse into a Dyson series – corresponding to the time-dependent
perturbation $V(t)$ on the field-free molecular Hamiltonian $H_0$:

$$\Psi_{\text{after}}(r; R) = \sum_{n=0}^{\infty} (-i)^n \int_{t_{\text{after}} \geq t_1 \geq \cdots \geq t_n \geq t_{\text{before}}} dt_1 \cdots dt_n e^{-iH_0(t_{\text{after}}-t_1)} \cdot V(t_1)e^{-iH_0(t_1-t_2)} \cdots V(t_n)e^{-iH_0(t_n-t_{\text{before}})} \Psi_{\text{before}}(r; R).$$

(4.6)

Each of the populations, i.e. each of the terms in sum 4.5 with a significant non-zero coefficient $c_{kl}$, has a 'history', i.e. one or several terms of the Dyson expansion are contribution to it. Those terms in the Dyson expansion form an 'ionization pathway' leading to the creation of the wavepacket $\psi_k(r)g_l(R)$.

Since our laser pulses are long compared to a single (tunnel-) ionization event (lasting less than half an optical cycle), the following discussion further distinguishes between 'direct' and 'indirect' ionization pathways. With the difference being, whether any of time differences $(t_a - t_b)$ in the expansion 4.6 being long enough for the nuclear part of $H_0$ to matter or not. If nuclear evolution during the ionization step can be neglected, a particular ionization channel is referred to as 'direct', otherwise it shall be called 'indirect'.

### 4.2 Calculations and Experimental Setup

The electronic levels of CH$_2$I$_2$ were calculated by the groups of Tamás Rozgonyi and Letitia Gonzáles [42]. Similarly to CH$_3$BrI$^+$, the equilibrium positions of the neutral and ionic ground state differ mostly along the bending coordinate $u_B$ (the I-C-I angle changes from 116.0° to 96.2°), whereas differences between neutral and ionic equilibrium positions for rest of the internal coordinates are less than 4%. The potential energy curves for the four lowest ionic states are shown in figure 4.1. It displays the adiabatic states along the bending coordinate. Also the positions of the one-photon resonance between $V_1$ and $V_4$, accessed by the IR probe, is labelled as $\text{FC}_{\text{probe}}$. Similarly $\text{FC}_{\text{pump}}$ shows the position of the neutral equilibrium, from which the wavepackets are launched (by vertical excitation). The label gives the vibrational (bending) frequency of the various electronic states close $\text{FC}_{\text{pump}}$.

The neutral ground state was calculated by single state complete active space self consistent field method (CASSCF), whereas the lowest eight ionic states were determined using the the state-averaged state complete active space self consistent field (SA-CASSCF) method [114]. In this case the active space consisted of eleven electrons on eight orbitals including two lone pairs on each Iodine atom and the $\sigma$ and $\sigma^*$ for each C-I bond. The ab-initio structure results were compared with experimental data based on photo electron spectra...
and the ground state vibrational frequency is in agreement with earlier calculations \cite{116}.

This experiment only required tof resolution and a high sample pressure (similarly as in experiment \textsuperscript{3}) could be used. We performed two different sets of pump-probe scans on CH\textsubscript{2}I\textsubscript{2}. In the first set, an IR pump pulse was used, with a transform-limited peak intensity of $1.3 \times 10^{14}$ W cm\textsuperscript{-2} and pulse duration of 55 fs. Its second order phase was also scanned from -120 fs\textsuperscript{2} to +280 fs\textsuperscript{2}. In the second data set we used a UV pulse as pump. Its pulse duration was about 60 fs and its peak intensity was about $1.6 \times 10^{12}$ W cm\textsuperscript{-2}. In both cases we used an IR probe with a peak intensity of $5 \times 10^{13}$ W cm\textsuperscript{-2} and a pulse durations of 60 fs.

\section*{4.3 Interpretation - UVpump/IRprobe}

The UV pump data is shown in figure 4.2 along with an IR pump - IR probe scan (for a second order phase of -120 fs\textsuperscript{2} of the pump). It exhibits clear modulations in the parent ion yield, which are also visible in the CH\textsubscript{2}I\textsuperscript{+} yield having about the same modulation depths but are $\pi$ out of phase. Other fragments also exhibit modulations (which is partly discussed in reference \cite{117}), but their modulation depth is much smaller. The UV pump - IR probe scan is less structured than the IR pump case, exhibiting only one dominant frequency component. This case is discussed first. The result is not surprising, considering the high Keldysh parameter for the UV pump - IR probe ($\gamma \sim 20$), which puts this data set well in the perturbative regime and only ionic states close to resonance with a small number of integer number of photons will be populated. While the absorption of one UV photon leads to a quickly dissociative neutral state, the ionization with three of more photons becomes increasingly unlikely. Further, among all lower lying ionic states only the ionization potential of V\textsubscript{1} is close to resonance (detuned by 0.02 eV from a two UV photon absorption), which enhances UV ionization to V\textsubscript{1} over all other ionic states \cite{118}. Last but not least, the measured frequency of $112 \pm 3$ cm\textsuperscript{-1} in the CH\textsubscript{2}I\textsubscript{2}\textsuperscript{+} yield agrees very well with the calculated I-C-I bending frequency in the ground ionic state of the molecule (108 cm\textsuperscript{-1}) and previous calculations (e.g. $\approx 114$ cm\textsuperscript{-1} in \cite{116}).

Older data \cite{96,119} based on photo-electrons and electron impact gives an appearance energy of 10.5 eV and $\gtrsim 13.2$ eV for CH\textsubscript{2}I\textsuperscript{+} and I\textsuperscript{+}, respectively. This indicates (see figure 4.1), that while V\textsubscript{1} to V\textsubscript{3} are bound ionic states, V\textsubscript{4} is dissociative into CH\textsubscript{2}I\textsuperscript{+} only, and higher lying ionic states also can fragment into I\textsuperscript{+} (if excited at FC\textsubscript{pump}). Since among all fragments only CH\textsubscript{2}I\textsuperscript{+} has a comparable modulation depth to the parent, this further implies that the
Figure 4.1: This figure shows the four lowest lying ionic potentials of CH$_2$I$_2^+$ versus the nuclear bending coordinate I-C-I, $u_B$. The y-axis shows their energy relatively to the ground state minimum. There is a one-photon resonance between $V_1$ and $V_4$, which is highlighted with a vertical dotted line (left) and will be referred to as FC$_{probe}$. The right dotted line marks the position of FC$_{pump}$, i.e. the position of the ground state equilibrium. Higher lying electronic states were calculated but are not shown, since they are separated by at least another $\sim 2.1 \text{ eV}$ from $V_4$ (at $u_B = 0$). The inset also notes the bending mode frequencies associated with each state. Since the states are an-harmonic, those were calculated around the launch position of the vibrational wave packets, i.e. around FC$_{pump}$. The states $V_1$ to $V_3$ are bound (when excited at FC$_{pump}$). Higher lying ionic states are above the dissociation threshold.
probe mostly transfers population from $V_1$ to $V_4$ using the single photon resonance at $FC_{\text{probe}}$. The transfer dipole matrix element (TDM) between $V_1$ and $V_4$ at this point is about 1 au, which allows an efficient population transfer. Since $FC_{\text{probe}}$ is not located at either turning point, one expects - in principal - two maxima in the ion yield per period in the pump-probe signal, as has been observed in CH$_3$BrI (compare to chapter 3). Alternatively, one should see a second harmonic signal in its Fourier transform. This has not been observed here, which is presumably for a combination of the following factors: (1) A relatively intense IR probe has been used, which might lead to an asymmetric population transfer as has been discussed in the context of probing vibrational wavepackets in CH$_3$BrI$^+$ (see chapters 3 and 5). (2) $FC_{\text{pump}}$ and $FC_{\text{probe}}$ are closer than the estimated width of the $V_1$ wavepacket. (3) As already mentioned, there are other (multi-photon) probe pathways leading to I$_2^+$ and I$^+$ formation, whose FC points are at a different location and will reduce the contrast of the dominating modulations due to the $V_1$-$V_4$ probe pathway. These details are also given in other publications [95, 117, 120].

4.4 Interpretation - IRpump/IRprobe

In contrast to the UV pumped experiments, which can be understood in a multiphoton picture, the IR pumped data is expected to exhibit some tunnel ionization character ($\gamma \gtrsim 1$). Figure 4.2 shows the pump probe response. Its inset reveals the presence of another frequency component at 96 cm$^{-1}$ next to the ‘usual’ modulation at 113 cm$^{-1}$. We also systematically scanned the second order phase of the IR pump between $-120$ fs$^2$ and $+280$ fs$^2$, while the pulse energy was kept constant. The result is summarized in figure 4.3 and demonstrates that depending on the chirp value, yet another frequency component at 130 cm$^{-1}$ becomes visible. Further, the different frequency components show a systematic dependence on chirp. Following the terminology of the previous section, the 113 cm$^{-1}$ modulations, can be interpreted as ‘direct $V_1$’ population created by SFI. Similarly, the two ‘new’ components can be associated with vibrational wavepackets on other ionic surfaces. The uncertainty of frequency is about $\pm 3$ cm$^{-1}$.

Since the modulations are observed in the fragment CH$_2$I$^+$ and the parent CH$_2$I$_2^+$, both the 98 cm$^{-1}$ and the 130 cm$^{-1}$ modulation have to due to transfer between a bound ionic state $V_3$ (or lower) and $V_4$ (or higher). As one can see in figure 4.1, the predicted modulation period (128 cm$^{-1}$) in $V_4$ matches the measured component of 130 cm$^{-1}$. The probe pulse can modulate the parent ion fragmentation by using $FC_{\text{probe}}$ to transfer population back to the bound state $V_1$. $V_3$ also is predicted to have a similar bending motion frequency, but
Figure 4.2: This graph contrasts the parent ion yield in an IR pump scan (-120 fs²) with a similar plot based on the UV pump scan. Both scans exhibit clear modulations, which are $\pi$ phase shifted relative to the CH$_2$I$^+$ fragment ion yield, indicating that the probe is transferring population between a bound state and an ionic state mostly leading to CH$_2$I$^+$ formation. The inset displays the associated Fourier transform of the time-domain data. The three vertical lines are located at 96 cm$^{-1}$, 113 cm$^{-1}$ and 130 cm$^{-1}$. The Fourier transform for the complete IR data set is shown in figure 4.3. All data sets share a strong modulation component at 113 cm$^{-1}$, which corresponds to a wavepacket evolving in $V_1$ launched at FC$_{pump}$. While the UV scan exhibits only one clear modulation, the IR data is clearly a superposition of at least two frequency components, which is reflected by the presence of a second component in its Fourier transform.
Figure 4.3: Fourier transform of the CH$_2$I$_2^+$ yield in a series IR pump - IR probe scans for various pump pulse chirps. The associated pump chirps are given in fs$^2$. All spectra are normalized to their maximum at 113 cm$^{-1}$. Also we decided to correct for the DC offset of the pump probe signal, but Fourier transforming the derivative rather than the raw data. The three vertical lines highlight the frequencies 96 cm$^{-1}$, 113 cm$^{-1}$ and 130 cm$^{-1}$. As argued in section 4.4 they can be interpreted as a linear measure of the (direct) population in V$_2$ and V$_1$ (created at FC$_{pump}$) and (indirect) population in V$_4$ (created at FC$_{probe}$, respectively. The inset on the right displays the relative strength of the 96 cm$^{-1}$ and 130 cm$^{-1}$ component (normalized to the 113 cm$^{-1}$ component) virus pump chirp. They exhibit a systematic dependent con the pump pulse chirp. The authors want to point out that the dependence is monotonic with chirp, which rules out a purely intensity-driven effect.
the launch point of the wavepacket on \( V_3, FC_{pump} \), is close to the \( V_3 \) minimum (along the bending coordinate). This implies that any vibrational wavepacket on \( V_3 \) will explore only a small part of this surface, while there is no one-photon IR resonance to a dissociative state (\( V_4 \) or higher) is in its proximity. For these reasons the 130 cm\(^{-1} \) frequency component can be associated with population evolving on \( V_4 \).

Although — according to the argument made in the introduction (see for formula 4.1 and following) — one expects strong field ionization to occur to \( V_4 \), population created at FC\(_{pump} \) directly by the pump cannot reach FC\(_{probe} \) for energetical reasons. This direct \( V_4 \) population will dissociate independently of the probe pulse timing. Population on \( V_4 \) is energetically above the dissociation threshold, yet there is no known direct pathway from FC\(_{pump} \) into the continuum. Any bond cleavage presumably is 'slow' and relies on non-adiabatic crossings to other states. In principle, AC-Stark shifts could distort the adiabatic PES sufficiently to launch the direct \( V_4 \) population with enough energy that it can reach FC\(_{probe} \). Nevertheless, a different mechanism, which already has been observed in CH\(_2\)BrI and is described in chapters 3 and 5, is more plausible: A vibrational wavepacket is launched at FC\(_{pump} \) on \( V_1 \) (i.e. 'direct \( V_1 \)' ) and then (post-ionization-) excited in the tail of the pump pulse at FC\(_{probe} \) to \( V_4 \). Similarly to the situation in CH\(_2\)BrI, this also is supported by simulations in CH\(_2\)I\(_2\). Thus, following the terminology introduced above, the vibrational wavepacket on \( V_4 \) is created via an indirect ionization pathway.

The most interesting feature are the observed 96 cm\(^{-1} \) modulations. The chirp dependence of amplitude of this signal, as shown in the inset of figure 4.3, suggests that it must be traced to a different ionization channel as described above. It seems unlikely that two wave packets are launched utilizing the same ionization pathway, but these relatively small applied chirps to the pump pulse could control their relive amplitude. In addition, for \( V_1 \) there are (both theoretical and experimental) results available, that argue against evolution along other vibrational modes, since those are generally much faster - the bending mode being the slowest. Further, the UV pump based experiments demonstrate that simply exciting \( V_1 \) at FC\(_{pump} \) does not lead to nuclear motion along any other coordinate. As mentioned beforehand, a direct \( V_3 \) wavepacket is to be expected (due to the tunnel-ionization character of the ionization), but is likely to 'be stuck' close to its launch point in the minimum of \( V_3 \) and thus not visible in pump probe scans. A similar explanation as for the 130 cm\(^{-1} \) modulations, e.g. an indirect \( V_3 \) excitation pathway also can be ruled out: Such a wavepacket would predominantly evolve along the bending coordinate, but the associated vibrational frequency (as given in figure 4.1)
does not match the observations. The same mismatch between calculated and observed modulation frequency also argues against population evolving on V2. The best explanation is provided by a wavepacket initially created at FC\textsubscript{pump} on V\textsubscript{2} (i.e. the direct V\textsubscript{2} ionization), but continuing on V\textsubscript{1} via non-adiabatic coupling between both states. Both potentials approach each other in energy for large bending angles, which makes diabatic coupling efficient. Further V\textsubscript{1} is an an-harmonic potential and higher dimensional ab-initio structure calculations (including also the I-C stretch) show that population launched on V\textsubscript{1} from coordinates at about 1.8 au. indeed has a vibrational spacing close to 96 cm\textsuperscript{-1} (predicted is 105 cm\textsuperscript{-1} with 10\% error). Therefore, the 98 cm\textsuperscript{-1} modulations can be interpreted as population created using the direct V\textsubscript{2} pathway.

4.5 Conclusion and Outlook

The described experiment is a proof-of-principle result demonstrating that during SFI multiple ionization pathways must be considered. This interpretation is supported by associating features - modulations at 96 cm\textsuperscript{-1}, 113 cm\textsuperscript{-1} and 130 cm\textsuperscript{-1} in the CH\textsubscript{3}I\textsuperscript{+} and CH\textsubscript{2}I\textsuperscript{+} yields with various wavepackets on different ionic states. In addition it is demonstrated that their relative contribution is affected by subtle pump pulse parameters as its second order phase. Although a complete understanding of this control mechanism, i.e. an extension of ADK theory to include strong-field control, is beyond the scope of this work, some contributions are resolved in chapter 6. In this experiment, it is shown that Freeman-resonances play an important role in SFI and can be used to bias excitation towards certain electronic states.
Chapter 5

Characterization of Strong Field Ionization with Velocity Map Imaging and Pulse Shaping

5.1 Introduction

The previous chapter provides a proof-of-existence for multiple excitation pathways in strong field ionization. This is achieved by associating features in the pump probe signal with different vibrational wavepackets on various electronic states. This chapter explores ways to quantify the populations in the different pathways. The approach of the previous chapter can be generalized: First velocity map imaging is employed to momentum resolve the ionic fragments. The kinetic energy release of each fragment depends partly on the point where the wavepacket was launched. One can identify different structures in the momentum distribution of ionic fragments with different launch points. Further pulse shaping is employed to change the relative population following with each excitation pathway; this way independent sub-structures in the acquired momentum distributions can be identified.

Experimentally, the molecule is excited and fragmented with a shaped laser pulse and the kinetic energy release distribution \( Y(E, \alpha) \) of a particular fragment is recorded as a function of pump pulse shape \( \alpha \) and fragment kinetic energy release* (KER) \( E \). In general this distribution carries contributions

\*The kinetic energy release refers to the total amount of kinetic energy of all fragments involved in a certain dissociation process as viewed in the lab frame. In this chapter only two-body dissociation processes are considered. In this case – neglecting photon and electron recoil – obtaining the KER distribution associated with a dissociation channel is equivalent to measuring the momentum distribution of one of the fragments.
from several electronic states (e.g. 'direct $V_1$' and 'direct $V_2$', as described in chapter 4), and possibly even with multiple vibrational wave packets launched at different positions on the same electronic state (e.g. 'direct $V_4$' vs. 'indirect $V_4$'). Let $P_k(\alpha)$ denote the total population following a certain excitation pathway. Here $k$ simply serves as an index numbering the associated ionization pathway. The addition of the argument $\alpha$ reflects the fact that the excitation probability for each pathway is generally a function of the excitation pulse as has been seen in figure 4.3. The working hypothesis of this chapter is that the (normalized) KER distribution $S_k(E)$ (associated with each initial wavepacket $k$) to the total momentum distribution $Y$, is not affected by the exact details of the pump pulse shape. Or in brief, that one can factorize:

$$Y(E, \alpha) = \sum_k P_k(\alpha) S_k(E)$$

(5.1)

Here the sum covers all indices $k$, which reflects the fact that SFI usually leaves the molecule in a superposition of several states. This factorization is an a-priori hypothesis, but it can motivated by making a time scale argument: If the excitation between different electronic levels occurs faster – i.e. the ionization pulse duration is shorter – than the reaction time of the nuclei, the final shape of the nuclear wavepacket does not depend on the details of the excitation pulse. The systems under investigation exhibit nuclear evolution on a few 100 fs time scale, which is 10% or less of the ionization pulse duration and makes them a suitable candidate. Yet, this experiment would profit from short pump pulses\footnote{It is also easy to image situations when this assumption is not valid, e.g. by definition SFI is accompanied by large AC-Stark shifts which distort the unperturbed electronic states, which can affect the original shape and the following evolution of the launched vibrational wavepacket. The photon-locking scenario, which involved control pulses of up to 200 fs, described in chapter 3 is one direct counter example, since there the momentum of the wavepacket on $V_1$ after the pump clearly depends on the characteristics of the pump/control combination.}.

In general neither $P_k(\alpha)$, nor $S_k(E)$ are known and only their sum $Y(E, \alpha)$ can be measured directly. Even though it is to be expected that each ionization pathway $k$ has an individual 'fingerprint', i.e. leads to a different KER distribution $S_k(E)$ after dissociation, their identification is complicated: Due to the many internal degrees of freedom of a polyatomic molecule the various $S_k(E)$ usually are broad and they overlap. Further, some dissociation channels can lead to excited fragment ion states (which cannot be experimentally distinguished from another with the described setup), i.e. the majority of available energy can be invested in electronic excitation, such that some $S_k(E)$ associated with ionization to a higher lying ionic state may actually lead KER.
distributions that are overall slower than \( S_k(E) \) produced from a lower lying ionic state. On the other hand knowledge of the 'pure' distributions \( S_k(E) \) is of great value, since it provides a method to determine the populations \( P_k(E) \) associated with the various excitation pathways directly by decomposing a measured total distribution \( Y \).

This chapter demonstrates that under certain circumstances not only assumption 5.1 holds, but also \( P_k(\alpha) \) and \( S_k(E) \) can be reconstructed if a large enough parameter space of \( Y(\alpha, E) \) is explored. In this experiment, the \( \text{CH}_2\text{Br}^+ \) KER distribution resulting from ionizing \( \text{CH}_2\text{Br}I \) is studied. This fragment has been chosen since it is by far the most dominant among all ionic fragments and shows the lowest appearance energy, i.e. even the lowest lying (dissociative) state contributes to it [96]. The factorization described above requires no \textit{ab-inito} knowledge of the molecule. But together with additional information from \textit{ab-inito} structure calculations, it is possible to identify the different ionization pathways \( k \). Last but not least, the experimentally retrieved functions \( P_k(\alpha) \) and \( S_k(v) \) are compared with their theoretical expectations and show good qualitative agreement.

\subsection*{5.2 Experimental Setup and Data Acquisition}

This experiment was a single beam experiment, with only one shaped IR pulse (sequence) to ionize the molecule. The \( \text{CH}_2\text{Br}^+ \) yield was measured KER resolved as a function of several pulse parameters. The pump pulse was generated by our pulse shaper and three different data sets were, which are discussed individually in the following sections: (a) an intensity scan, where the intensity of single transform limited pulse was scanned between \( 1.8 \cdot 10^{13} \) W cm\(^{-2} \) and \( 5.0 \cdot 10^{13} \) W cm\(^{-2} \), (b) a pump-probe-type experiment, for which a double pulse (both transform limited) was used, while their time separation was varied. In this case their intensities were fixed to \( 3.9 \cdot 10^{13} \) W cm\(^{-2} \) and \( 7.2 \cdot 10^{12} \) W cm\(^{-2} \) for the 'pump' (the first pulse in the double sequence) and probe pulses respectively. And (c) a chirped pulse data set, for which the second order phase of a single pulse was scanned between \(-2000 \) fs\(^2 \) and \(+2000 \) fs\(^2 \). In this case the peak intensity changed by a factor of 1.6 between the extrema (\( \pm 2000 \) fs\(^2 \)) and a transform limited pump.

A typical image of the \( \text{CH}_2\text{Br}^+ \) velocity distribution is shown in figure 5.1. The molecular sample was not aligned and a diffusive gas instead of the molecular beam was used, i.e. all measured distributions are only precise down to a convolution with a room temperature Maxwell-Boltzmann distribution. Singular data points were repeated at a lower pressure in order to verify that space charge broadening was not a significant contribution. As described in
a flat-field correction was used to compensate areas on the detector with degraded sensitivity.

For the interpretation of the data it proved useful not only to analyse the CH$_2$Br$^+$ yield momentum resolved, but also to include the dissociation direction. For this the total KER distribution was split into into two sectors: A 'parallel' P-sector, referring to all ions ejected along the laser polarization axis within ±45 deg, and an 'orthogonal' O-sector for ions ejected orthogonally to the laser polarization 180 deg ±45 deg. This is also indicated in figure 5.1. Further the following sections discuss an asymmetry parameter, which is defined as

$$Y_p(E) - Y_o(E)$$

$$Y_p(E) + Y_o(E)$$

where $Y_{p,o}(E)$ refers to the CH$_2$Br$^+$ yield kinetic energy resolved in sector P or O, respectively.

5.3 Theoretical Predictions

The experimental results were compared with theoretical predictions, provided by the groups of Tamás Rozgonyi and Leticia González. These are shown in figure 5.2. Three different sets of calculations have been performed: (a) Ab-initio structure calculations to determine the adiabatic potential energy surfaces along the I-C-Br bending coordinate (u) of the ground neutral and the first five ionic states. These include spin-orbit-coupling and the dipole matrix moments between various states. More details are given in chapter 3 or published in reference [94]. The results are summarized in figure 5.2 on the left panel. (b) Additionally the lowest electronic states of the (I + CH$_2$Br$^+$) unbound system were computed by the multireference configuration interaction (MRCI) method using the Molpro program package [122]. The MRCI excitation energies for CH$_2$Br$^+$ were then combined with available experimental data (i.e. experimental values are used when available): the ionization potential (9.692 eV) of CH$_2$BrI [96], the appearance energy (10.813 eV) of CH$_2$Br$^+$ [96], and the SO-splitting (0.94 eV) of neutral iodine [123]. The details are described in publication [43]. The results are shown as the 'dissociative limit' in the right panel of figure 5.2. The different electronic levels of the dissociated (I + CH$_2$Br$^+$) system are labelled A, B, etc. (c) Last but not least the evolution of the nuclear wavepacket on the various ionic states of CH$_2$BrI was calculated by numerically solving the time dependent Schroedinger equation (similarly to chapter 3).

In this experiment three different ionization pathways contributing to CH$_2$Br$^+$ formation were identified. They are indicated by the orange arrows in figure 5.2. Starting from the right to to the left, these are - using the same terminology as introduced in section 4.3, direct ionization to $V_{3,4}$ launching a wavepacket at FC$_1$’ on $V_{3,4}$, indirect ionization on $V_{3,4}$ at FC$_2$ by re-exciting
Figure 5.1: This figure shows a non inverse Abel transformed two-dimensional velocity distribution of CH$_2$Br$^+$, when the sample is excited with a single transform-limited pulse. The color axis is on an logarithmic scale and represents the wave function density versus velocity (vector). The x and y axis represent the x and y component of the velocity, while being averaged over all possible z components, i.e. the data has not been inverse abel transformed, as discussed in section 2.8. The laser polarization was oriented along the x-axis. The sample was prepared at room temperature, which lead to an inherent spread of the distribution by the Maxwell-Boltzmann distribution. This figure also defines the orthogonal sector and the parallel sectors, labelled with 'O' and 'P'; their borderline is at ±45 deg. One can see that the complete distribution can be roughly disassembled into a 'slow' part and a 'fast' part. Further while the 'fast' part exhibits a strong asymmetry with ions being preferentially ejected along the laser polarization (i.e. into sector P), the slow peak is mostly symmetric besides its 'fast' wings.
Figure 5.2: These graphs summarize the results from the calculations described in section 5.3. Panel (a) (based on SA-CASSCF computations) shows the energy of the five lowest adiabatic states of CH$_2$BrI$^+$ along the bending normal mode coordinate $u$. The states are labelled $V_1$, $V_2$, etc. by increasing energy at FC$_1$. The black arrows indicate the position of several FC points - FC$_1$ for vertical ionization from the neutral ground state, FC$_2$ for the close lying $V_1/V_3$, $V_1/V_4$ resonances, and FC$_3$ for the three photon $V_1/V_5$ resonance. Panel (b) (based on MRCI combined with experimental values) states the first few electronic energies at FC$_1$ of CH$_2$BrI$^+$ (left column, referenced to 0 for $V_1$) and also the energies of the unbound system (I + CH$_2$Br$^+$) in the right column. They are referred to as: A, B, C, D and E.
population from $V_1$, and indirect ionization to $V_5$ by re-exciting population from $V_1$ at $FC_3$. The latter one exploits a three IR-photon resonance between $V_1$ and $V_5$. The two states $V_3$ and $V_4$ are very closely spaced and could not be resolved experimentally, and are jointly referred to as $V_{3,4}$; the same is true for the two one-photon resonances $V_1-V_3$ and $V_1-V_4$, which are simply labelled as $FC_2$. There is a subtle distinction between $FC_1'$ and $FC_1$. While former refers to the 'real Frank-Condon point of the pump pulse' - the coordinate of the neutral ground state equilibrium - $FC_1$ is its projection onto the one-dimensional model along the bending coordinate. The difference can be neglected when simulating the evolution of the $V_1$ wavepacket without compromising the agreement between theory and experiment. Not highlighted in this figure, but observed in the experiment, was also one direct ionization pathway to $V_5$ and its closely neighbouring states.

A complete calculation of the various $S_k(E)$ would require knowledge of the wave packet trajectory from its launch point into the continuum. This is beyond the scope of ab-initio structure calculations on CH$_2$BrI$^+$. Nevertheless it is possible to make predictions on the high energy cutoff of $S_k(E)$: The energy difference between the (electronic) potential energy at the initial position of the wavepacket and the ionic fragments after dissociation provides an upper limit on the energy which can be converted into kinetic energy of the fragments. This can be measured as the high energy cutoff of the functions $S_k(E)$, and corresponds to the special case that all available energy is concentrated in the translational degrees of freedom, but none into rotational$^4$ or internal degrees of freedom. Table 5.1 summarizes the predictions for the various ionization pathways and dissociation channels. It should be noted that the analysis is limited to (CH$_2$Br$^+$ + I) dissociation channels, but other channels involving I$^+$ or I$^-$ are also possible. While the former possibility can be neglected since it requires ionization to much higher lying, doubly ionized states, the latter one is formed by a dissociating neutral state. Nevertheless, no negative ions were observed and this case does not need to be considered. This observation is consistent with the picture developed in reference [101], which implies that ionization with a laser pulse of medium high intensity ($\leq 5 \cdot 10^{14} \text{ W cm}^{-2}$) tends to 'skip' neutral states and transfer population directly to ionic states.

The accuracy of the ab-inito structure calculations is estimated to be about $\pm 100$ meV. But also other possible sources of error are considered: (a) since the molecular sample was not cooled, all measured distributions are only accurate down to a convolution with the Maxwell-Boltzmann distribution, which adds 25 meV to all cutoffs. Further (b), exact measurements [96] of the appearance of CH$_2$BrI rotations can actually absorb a large fraction of the total energy available, up to 86% of the translational energy.

---

$^4$In CH$_2$BrI rotations can actually absorb a large fraction of the total energy available, up to 86% of the translational energy.
energy of various fragments indicate that in a thermal sample the energy stored
in numerous internal degrees of freedom can accumulate to 100-200 meV, aid-
ing fragmentation and allowing for extra KER of the same amount. And (c),
the energies as listed in §5.2 represent the field-free electronic levels. AC-Stark
shifts associated with field strengths of 6 GV/m can be a few hundred 300 meV
and shift the PES, as stated in reference [94]. On the other hand, since the
vibrational wavepacket is not expected to propagate much during the laser
pulse duration, only a small fraction of the AC-Stark shift will contribute to
the molecule’s vibrational energy. The energies listed in table 5.1 do not take
these additional effects into account, i.e. the measured cutoffs can be up to
300 meV larger than the mere electronic energy difference between bound and
dissociative geometries.

As stated in reference [96], the electronic energy of V₃ (at FC₁) is below
the appearance energy of the second easiest to form fragment CH₂I⁺, even
V₄ is only marginally above the required amount. This means any (direct)
population on V₃ can only dissociate into CH₂Br⁺. Further, V₄ is known
from previous chapters to contribute to CH₂Br⁺ formation. Higher lying ionic
states are well above the CH₂I⁺ appearance energy, and – from an energetical
perspective – there is no need to fragment into CH₂Br⁺. Nevertheless all higher
lying ionic states (V₆ and above) correspond (at least partly) to a configuration
with an excitation to the iodine anti-bonding orbital, $\sigma^*_I$, which facilitates the
breaking of the C-I bond and indicates that also higher lying states decay into
CH₂Br⁺.

5.4 Single Pulse Analysis - Intensity Scans

The simplest pulse shape dependence to study is the peak intensity of a single
transform limited pulse. The KER resolved CH₂Br⁺ yield is recorded as a
function of a peak intensity between $1.8 \cdot 10^{13}$ W cm⁻² to $5.0 \cdot 10^{13}$ W cm⁻².
Some of the distributions are shown in figure 5.3. All distributions can be
decomposed⁸ into a ‘slow’ peak, centred at about 50 meV, and a ‘fast’ peak,
centred at around 3.1 eV; this even holds for all other pulse shapes studied.
Interestingly, there are no further structures beyond the ‘fast’ peak up to the
limit of our detector, which is at $\approx 15$ eV.

The two peaks differ by their associated asymmetry parameters, as can
been by comparing the dashed with the solid red line ($Y_p - Y_o$ versus $Y_p + Y_o$) in

⁸The data shown in the figures of this chapter is not inverse abel transformed, i.e. fast
features exhibit a long tail that mixes into slower features. When applying the inverse abl
transform there are no ions between 1.1 eV and 2.5 eV, clearly separating the ‘fast’ and
‘slow’ peak.
<table>
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<th>initial/final state</th>
<th>avail. Energy</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
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<tr>
<td>direct $V_3 / V_4$</td>
<td>1.22 / 1.43</td>
<td>0.1</td>
<td>0.31</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>indirect (via FC$<em>2$) $V</em>{3,4}$</td>
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<td>0.46</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
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<td>0.1</td>
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<td>2.68</td>
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<tr>
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<td>3.27</td>
<td>2.33</td>
<td>0.66</td>
<td>0.56</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 5.1: This table summarizes the predicted cutoff energies (in eV) for the various KER distributions $S_k(E)$. They are determined for the extreme case, that the complete electronic energy difference between initial position of the wavepacket and final asymptotic electronic state ($I + CH_2Br^+$, labelled as A, B, C...) is invested into translational kinetic energy. The distinction 'direct'-'indirect' refers to whether the ionization step does not require nuclear motion (i.e. the wavepacket is created at FC$_1$), or does require nuclear motion. For the direct populations, the quartet states $V_6$ and $V_7$ are neglected due to their poor Dyson overlap with the ground state. The values are based on the numbers provided in figure 5.2 and are expected to be only accurate to 100 meV. In addition, they ignore AC-Stark [94] shifts which can contribute up to 300 meV. Last but not least, the calculations assume cold molecules; additional thermal energy [96] can increase the cutoff by up to 200 meV.

They are very similar for the 'fast' peak, which reflects the fact that its ions are almost exclusively ejected only along the laser polarization, i.e. the parallel sector. By contrast the slow peak is very symmetric, only in its 'fast' tail the dashed line deviates from zero and indicates a bias towards dissociation into sector P. More importantly, both peaks differ in their dependency on pulse peak intensity. The fast/slow ratio converges to zero for low intensities, as it is shown in figure 5.3 in the 'low intensity' line.

The 'fast' peak exhibits a very uniform intensity scaling, i.e. only its amplitude changes with increasing intensity, but not its shape (with a relative error of 2.2% or better). This indicates that most of the ions contributing to this feature are created from population on one or several closely spaced ionic states; typically states with very different ionization potential exhibit very different scaling with pulse intensity, as suggested by formula [4.1] where the ratio out of field strength and ionization potential contributes exponentially. Since the predicted cutoffs for $V_3$ and $V_4$ are well below the slow tail of the fast peak (compare to table 5.1), they cannot explain this feature. $V_5$ alone cannot account for all ions of the fast peak, since its cutoff at 4.7 eV exceeds the theoretical prediction for this state. But already $V_8$ – separated by only 460 meV – is associated with a cutoff at 3.3 eV, which is further extended by
the several systematic errors discussed above and can explain 89% of the fast peak (assuming an extension of the cutoff by 300 meV). For this reason, one can assign the 'fast' peak predominantly to the group of neighbouring states $V_5$ and $V_8$. The states $V_6$ and $V_7$ are neglected, since due to their (dominant) quartet character they have poor Dyson overlap (see equation 4.3) with the neutral ground state and are most likely not effectively populated. It is interesting that there are no ions measured with a KER between 1.1 eV and 2.5 eV, which suggests that the dissociation channel B is not favoured for $V_5$ and $V_8$.

By contrast the center of gravity of the slow peak shifts towards higher KER with increasing intensity and comparing distributions of different intensity shows that the slow peak not purely rescales with increasing intensity. This implies at least one of the two following statements: either (a), the slow peak is comprised of two or more sub-distributions, which exhibit a different intensity dependence, or (b) the assumption described in the introduction 5.1 is not correct. The experimental cutoff of the slow peak is at about 1.1 eV, with 98% or more of the ions corresponding to a KER of 550 meV or less. Out of the different dissociation pathways listed in table 5.1 the direct $V_3$, direct $V_4$, direct $V_5$ (channel C & D), direct $V_8$ (channel C & D) and indirect $V_{3,4}$ fall energetically into this region. The possibility of population created indirectly on $V_5$ does not need to be considered, since it would require the evolution of $V_1$ population from FC$_1$ to FC$_3$, which takes about 180 fs and exceeds the pump pulse duration by far.

For the lowest intensities at the ionization threshold (the 'low intensity' line in figure 5.3), one expects the distribution to be dominated by population from the lowest dissociative ionic state only, which is the direct $V_3$ and direct $V_4$ population. If a basis set is formed based on this 'lowest intensity' distribution and the reconstructed distribution (as described in section 5.3) associated with the indirect $V_{3,4}$ pathway, then a linear combination of both distributions is capable of describing the 'slow' peak with an accuracy of 1.5% and better. Even though possibility (b) cannot be completely ruled out, this is consistent with explanation (a): the slow peak is mostly a combination of fragment ions from direct $V_{3,4}$ population, with some $V_1$ population being also promoted indirectly to $V_{3,4}$, if the pump pulse is intense enough. This is further discussed in the following sections.

Further an upper bound can be derived on the contribution of other populations (i.e. direct $V_5$ and $V_6$) to the slow peak: if one assumes that the fitting error (i.e. 1.5%) is only due to the other dissociation channels contributing to the slow peak, this implies a branching ratio of 6.5% or less from $V_5$ and $V_6$ following channel C and D. Even though population from $V_5$ and $V_8$ could dis-
Figure 5.3: This graph displays three KER distributions of CH$_2$Br$^+$ taken at a pulse peak intensity of $1.8 \cdot 10^{13}$, $3.2 \cdot 10^{13}$, $4 \cdot 10^{13}$ W cm$^{-2}$. They are labelled low, medium and high intensity respectively. The dashed red line is the 'asymmetric' counterpart of the solid red line. While the solid lines show the total distribution of both sectors, the dashed line refers to the difference yield $Y_p(E) - Y_o(E)$. All three lines are normalized to the maximum yield at high intensity. Clearly the total distribution can be disassembled into a 'fast' peak and a 'slow' peak. This generic feature has been observed independently of pulse shape. Further, no ions have been observed beyond the fast peak up to an energy of $\sim 15$ eV.
associate into electronically excited fragment ions, dissociation channel A - i.e. forming I and CH$_2$Br$^+$ in their ground state - is clearly preferred ($\gtrsim 93.5\%$).

### 5.5 Pump-Probe Parameterization

In order to separate out the contributions of indirect excitation pathways, a pump-probe parametrization of the excitation pulse was chosen. In this data set a double pulse was generated. Both pulses (referred to simply as pump and probe), had a transform limited duration and a fixed peak intensity of $3.9 \cdot 10^{13}$ and $7.2 \cdot 10^{12}$ W cm$^{-2}$. The CH$_2$Br$^+$ yield $Y(E,t)$, KER resolved, was recorded as a function of the pump-probe time delay $t$, which was varied between -200 and +2000 fs. As in the previous section, the dependence of the signal on pulse shape (in this case time) allows us to disassemble the total distribution into its sub-distribution $S_k(E)$. Further, each of these pure distributions could be associated with a particular ionization pathways, which are identified as indirect excitation to $V_{3,4}$ and $V_5$. Their observed cutoffs are in good agreement with the prediction in section 5.3. Further, with the knowledge of the $S_k(E)$ one can reconstruct the populations $P_k(t)$ as a function of time. These match the theoretically expected behaviour qualitatively.

The raw data $Y(E,t)$ is shown in figure 5.4. It displays clear modulations with a periodicity of $(95 \pm 3)$ cm$^{-1}$ (corresponding to a period of 351 fs), which already has been discussed in chapter 3. The measured decay time of the oscillations is on the order of several picoseconds. The modulations can be interpreted as a nuclear wavepacket, that is created by the pump pulse on the nearly harmonic $V_1$, and evolves along the nuclear bending coordinate until it is promoted to a dissociative state by the probe, via FC$_2$ or FC$_3$.

The indirect pathways involving the nuclear motion on $V_1$ can be isolated by applying the Fourier transform to the total signal $Y(E,t)$ and studying only the frequency component that matches the observed 95 cm$^{-1}$. This analysis has been performed separately for both the parallel and the orthogonal sectors. The results are denoted as $\tilde{Y}_p(E,95\text{ cm}^{-1})$ and $\tilde{Y}_o(E,95\text{ cm}^{-1})$, respectively and are shown in figure 5.5. Here the data was restricted to pump probe delays larger than 200 fs, in order to avoid contributions near zero time delay. The amplitude in both graphs exhibits a clear double peak structure, which is mirrored by a double plateau in the corresponding phase, i.e. the phase is nearly constant, but distinctly different, in the intervals (0,175) meV.

---

*If the $V_1$ modulations were not periodic, a comparable analysis still could be performed, e.g. taking the difference between two extremal distributions (along the time axis) or applying a non-negative-matrix-factorization method [124]. The Fourier transform includes all data points along the time axis and thus provides the best S/N ratio.*
Figure 5.4: This figure shows the CH$_3$Br$^+$ yield $Y(E,t)$ as a function of kinetic energy release $E$ and pump-probe time delay $t$. The data has been summed over both sectors. The slow peak exhibits clear modulations with a period of $\approx 351$ fs corresponding to a wavepacket motion in $V_1$. There are several maxima per round-trip, with dominant maximum being highlighted by horizontal dashed lines.
Figure 5.5: The raw data as shown in figure 5.4 has been Fourier transformed and its component at a periodicity of 95 cm\(^{-1}\) are plotted. The signal is split into its amplitude (solid lines) and phase (dashed lines), for both sectors individually: \(\tilde{Y}_{o,p}(E, \omega = 95 \text{ cm}^{-1})\). These reflect the KER distributions associated with indirect excitation pathways - or more accurately: the indirect pathways that involve the evolution of a vibrational wave packet on the ionic ground state \(V_1\) en route to the final ionic state upon which dissociation takes place.
and (500,700) meV. It is flat around 2.1 rad, but jumps to 4.1 rad at a KER of about 350 meV. While the absolute value of the Fourier transform is associated with the amount of population transfer for a particular ionization pathway, its phase (as a fraction of $2\pi$) can be translated to the time delay (as a fraction of the whole period of 351 fs) between pump and probe which leads to maximum re-excitation probability. For this reason one expects the phase value to be constant as a function of KER. If and only if, it is associated with only one pathway. Conversely, the double plateau in the phase lines implies that there are contributions from two different indirect pathways. They can be further disentangled using the assumption 5.1 described in the introduction. It yields, after applying the Fourier transform along the time domain (with $\omega_0 = 95$ cm$^{-1}$):

$$\tilde{Y}(E, \omega_0) = \tilde{P}_1(\omega_0) S_1(E) + \tilde{P}_2(\omega_0) S_2(E)$$ (5.2) $$= e^{i\phi_1} p_1 S_1(E) + e^{i\phi_2} p_2 S_2(E)$$ (5.3)

Here $\phi_{1,2}$ and $p_{1,2}$ refer to the absolute and the relative value of the Fourier transforms $\tilde{P}_{1,2}(\omega_0)$ of the functions $P_{1,2}(t)$. But the values of $\phi_{1,2}$ are known from plot 5.5 to be 2.1 and 4.1 rad, respectively. And one can use a projection to retrieve the original functions $S_{1,2}(E)$. Multiplying the last row with $e^{-i\phi_2}$ and taking the imaginary part yields:

$$\text{Im} \left[ \tilde{Y}(\omega_0, E) e^{-i\phi_2} \right] = \sin (\phi_1 - \phi_2) p_1 S_1(E) + \sin (\phi_2 - \phi_2) p_2 S_2(E)$$ (5.4) $$S_1(E) \sim \text{Im} \left[ \tilde{Y}(\omega_0, E) e^{-i\phi_2} \right]$$ (5.5)

The reconstructed $S_{1,2}(E)$ are shown in figure 5.6. The analysis has been performed independently for both sectors of the CH$_2$Br$^+$ distribution. This reconstruction required no a-priori knowledge about the studied system and was solely based on experimental observations: the time-dependence of the CH$_2$Br$^+$ distribution hinting at nuclear dynamics and two different plateaus in the phase value of its Fourier transform. A deeper insight can be gained with additional knowledge from ab-initial structure calculations. In figure 5.6 the two retrieved distributions are assigned to the indirect $V_{3,4}$ and the indirect $V_5$ excitation pathway. This is based on the following observations: (a) agreement of the cutoffs between experiment and theory, and (b) the reconstructed distributions can be used to extract $P_{1,2}(t)$, which agree qualitatively with the theoretical expectations from solving the time-dependent Schrödinger equation. The reconstructed cutoffs are 500 and $\approx 1000$ meV for the indirect $V_{3,4}$ and indirect $V_5$ population, respectively. This is in good agreement with
the predicted cutoffs (channel ind. V\textsubscript{3,4}-A and channel ind. V\textsubscript{5}-D), as listed in table 5.1 considering the additional uncertainties in the ab-initio structure calculations and additional internal thermal energies. As can be seen in figure 5.6 the signal due to both sectors is almost identical for the indirect V\textsubscript{3,4} population, but differs between sectors for the indirect V\textsubscript{5} population. The asymmetry parameters (integrated over the whole distribution) are \( \sim 0 \) and \( 0.38 \). This – together with the observed turn-ons and cutoffs – can be used to extract the associated populations \( P_{1,2}(E) \) from the raw data. For this reason one can estimate:

\[
P_{\text{ind.V}_{3,4}}(t) \sim \int_{0\text{meV}}^{440\text{meV}} dE \left( Y_p(E,t) + Y_o(E,t) \right) \tag{5.6}
\]

\[
P_{\text{ind.V}_{5}}(t) \sim \int_{440\text{meV}}^{1250\text{meV}} dE \left( Y_p(E,t) - Y_o(E,t) \right) \tag{5.7}
\]

This definition is motivated by the fact that the indirect V\textsubscript{5} population can be isolated from the indirect V\textsubscript{3,4} population, since the latter has almost no asymmetric contribution. The results are graphed in figure 5.7. According to simulations \cite{94} one expects the V\textsubscript{1} wavepacket to move through FC\textsubscript{2} twice per round trip with maxima at 50 fs and 250 fs. This is in good agreement with the reconstructed \( P_{\text{ind.V}_{3,4}}(t) \) line, since it shows maxima (i.e. effective transfer from V\textsubscript{1} to V\textsubscript{3,4} at FC\textsubscript{2}) at 57 fs and 254 fs. Since the Frank-Condon point FC\textsubscript{3} is close to the inner turning point, maximum indirect V\textsubscript{5} population is predicted for a time delay of 180 fs, which also matches well with the reconstructed line that exhibits maxima at 176 fs modulo the round trip time.

### 5.6 Chirped Pulse Parameterization

This section studies the shape of the slow peak as a function of pump pulse duration. Simulations of the wavepacket propagation on V\textsubscript{1} show that parts of the population can be re-excited to V\textsubscript{3,4} via FC\textsubscript{2}, if the tail of the pump pulse is sufficiently long and intense. This is similar to the observation of the 130 cm\textsuperscript{-1} frequency component in CH\textsubscript{2}I\textsubscript{2} as described in the chapter \cite{4}. To test this directly, a single pulse experiment was performed, where the pump pulse duration was scanned by applying second order phase between -2500 fs\textsuperscript{2} and +2500 fs\textsuperscript{2}. This stretches the pulse duration up to 200 fs. The peak intensity increased by a factor of 1.6 between 0 and \( \pm 2500 \) fs\textsuperscript{2}. Two extreme KER distributions are shown in figure 5.8. They demonstrate that the total CH\textsubscript{2}Br\textsuperscript{+} distribution broadens with increasing chirp. This was to be expected, since the reconstructed indirect V\textsubscript{3,4} distribution has a much higher cutoff (\( \approx \)
Figure 5.6: This figure shows the reconstructed pure KER distributions for CH$_2$Br$^+$ associated with the indirect V$_{3,4}$ and indirect V$_5$ population. They were retrieved from the pump probe data as described in section 5.5. The analysis has been performed independently for both the orthogonal and the parallel sector. Further the total (i.e. sector O + sector P) KER distribution associated with direct V$_{3,4}$ has been plotted for comparison. The reconstructed lines have been normalized to one at their maximum yield in sector P.
Figure 5.7: This graph shows the estimate on the indirect \( V_{3,4} \) (dark blue line) and indirect \( V_5 \) (red line) population as a function of time delay. They are extracted from the total CH\(_2\)Br\(^+\) distributions \( Y_{p,o}(E, t) \) using the definitions stated above\( ^5.6 \). The green line refers to the total CH\(_2\)BrI\(^+\) yield versus time delay, the light blue line shows the integrated CH\(_2\)Br\(^+\) population, which is roughly \( pi \) out of phase with the parent ion yield. This reflects the population transfer between the bound \( V_1 \) and an unbound state (leading to CH\(_2\)Br\(^+\) formation), which can be modulated by the probe pulse timing. Further this graph shows that CH\(_2\)Br\(^+\) formation is dominated by the indirect \( V_{3,4} \) pathway.
500 meV) than the direct $V_{3,4}$ distribution (maximum at 50 meV, compared to figure 5.6).

Furthermore, the reconstructed distributions from section 5.4 can be used to extract the indirect $V_{3,4}$ contribution from the total yield. For this purpose, the total set of KER distributions $Y(E,\alpha)$ of this chirp data set was approximated by a vector basis formed out of the indirect $V_{3,4}$, the indirect $V_5$ distribution and the low intensity\footnote{As mentioned in section 5.4, the slow peak exhibits a shift of center of gravity at higher intensities. This can be explained by additional indirect transfer to $V_{3,4}$ in the tails of the pump pulse. At the lowest intensity - around ionization threshold - one expects ionization only to occur to the lowest dissociative state, which is $V_{3,4}$} KER distribution associated with mostly direct $V_{3,4}$. This basis set allows us to describe all observed KER distributions with a relative error of 5% or better. The result is summarized in figure 5.9. As expected from theoretical simulations\footnote{The population transfer from the molecular ground state to $V_1$, $V_2$, etc. was approximated as a single photon ionization, using a weak 20 fs XUV pump pulse, superimposed with a strong IR pulse as used in the experiment.} stretching the pump pulse does favour the indirect $V_{3,4}$ pathway. The calculations show that the ratio indirect/direct increases from near zero to above 0.3; further a second set of calculations with frozen nuclear coordinates was performed, that showed no change in the indirect/direct ratio, verifying that nuclear evolution on $V_1$ is indeed required for this excitation pathway.

The agreement between theory and simulation is not perfect. Most notably they exhibit a different asymmetry between positive and negative chirp. But it should be noted that the observed preference for positive chirp of the indirect $V_{3,4}$ wavepacket is consistent with an increase in the indirect $V_{3,4}$ population in CH$_2$I$_2$ by positive chirp - as can be seen in the inset of figure 4.3.

5.7 Conclusion

This experiment shows how ultrafast pulse shaping and velocity map imaging can be used to disentangle several ionization pathways occurring in SFI. They can be characterized by searching for variations of the fragmentation pattern with different pump pulse shapes (intensity, double pulses and chirped pulses). It should be stressed that the KER distributions as presented in figure 5.6 as well as the extracted populations as shown in figures 5.7 and 5.9 could be retrieved without any ab-initio knowledge of the system. Ab-inito structure calculations further could identify and interpret the various observed pathways, whose pulse shape dependence agrees qualitatively with theoretical predictions. Last but not least, once the KER distributions associated with each
Figure 5.8: This figure compares the KER distributions of CH$_2$Br$^+$ for two extreme cases: At zero chirp (i.e. when ionized with a transform-limited pulse), the distribution mostly consists of direct V$_{3,4}$ population. When the pump pulse is stretched in time by applying second order phase, parts of the V$_1$ wavepacket can be re-excited using FC$_2$ to V$_{3,4}$. Since the this indirect V$_{3,4}$ population is associated with faster fragments the total KER distribution slightly broadens and shifts to faster fragments. This is true for both sectors independently. In this graph, all lineouts have been normalized to their maximum.
Figure 5.9: This graph compares the theoretical prediction on the ratio $P_{\text{indirect} V_{3,4}} : P_{\text{direct} V_{3,4}}$ with the experimentally retrieved values. For this purpose, the raw chirp data was fitted by a basis set formed out of the KER distributions shown in figure 5.6.
pathway are identified they could further serve as a basis set to extract the
different populations from fragmentation patterns produced by pump pulses
with arbitrary shape.
Chapter 6

Application of Pulse Shaping to Interpreting Photoelectron Spectra

6.1 Motivation and Freeman Resonances

This chapter expands the method of the previous section to photoelectrons. Again, ionization with differently shaped pulses is used to acquire - this time - different photoelectron spectra. Their differences help to isolate multiple ionization pathways and connect them with specific features in the spectra.

In general, photoelectrons provide a qualitatively different view of SFI than photoions: (a) ionization to non-dissociative states creates only the parent ion without any substantial momentum recoil, resulting in a trivial ion momentum distribution. For this reason, different ionization pathways leading to bound states cannot be differentiated with the technique described in chapter 5. (b) After SFI removes the electron from the system it is only weakly coupled to the remaining ion core. In particular post-ionization excitation is expected not to alter the photoelectron kinetic energy distribution significantly\[113\]. Using the language of direct and indirect ionization pathways, introduced in section \[4.1\], one could describe that photoelectron spectra to be blind to the indirect part of the ionization step. Further (c), the final kinetic energy of photoions is only determined – to first order – by the difference in electronic potential energy between initial and asymptotic geometry; this is the assumption used in section \[5.3\] to make predictions on the cutoff energies for photoion distributions. On the other hand, the kinetic energy of photoelectrons depends on the potential energy of the involved states during the ionization step. Dynamic Stark shifts and ponderomotive shifts couple the potential energy of the various states to
the instantaneous field intensity, which makes them a function of ionization time [125]. For a CW laser field with an intensity $I$ and frequency $\omega$, the kinetic energy $E_{\text{kin}}$ of the photoelectron is determined by:

$$E_{\text{kin}} = n\hbar \omega - (\text{IP} + \Delta E_{\text{gf}}(I) + U_p(I))$$

(6.1)

Here $n$ refers to the net number of absorbed photons, IP refers to the ionization potential of the final ionic state (in the field free case), $\Delta E_{\text{gf}}$ stands for the intensity-dependent differential dynamic Stark shift (between initial and final state) and $U_p$ is the ponderomotive shift, given by $\frac{2e^2}{\varepsilon_0 m_e c \omega^2} \frac{I}{\omega}$. The ponderomotive shift is proportional to the field intensity per definition. The dynamic Stark shift term is also proportional to the intensity, if higher order Stark shifts can be neglected [21, 81]. Equation 6.1 is only exactly valid for a CW ionization field, but in the described experiments the laser pulse duration (about 40 fs) is much longer than one optical cycle (2.5 fs), and expression 6.1 is still applicable, if one interprets the intensity $I$ as the instantaneous intensity $I(t)$ at time $t$, when the ionization step occurs [108, 113]. This expression also provides an intuitive interpretation for the phenomenon of above threshold ionization: The net number of absorbed photons $n$ is not fixed, and can be higher than the minimum number required to make the right hand side of this equation energetically allowed. The molecule always can absorb extra photons, which leads to multiple copies of one structure in the photoelectron spectrum spaced by the energy of one photon.

Again, it is helpful to picture the theoretical treatment of the ionization event as a multi-photon absorption, which is described by a (very long) perturbative expansion and consider two extreme cases (as used in section 4.1): there are on-resonant terms and - the other extreme - far off-resonant terms contribution to ionization. In the former case, one of the intermediate molecular (electronic) states is in resonance with an integer number of photons, which boosts the ionization rate. Since all states experience an AC-Stark shift, an initially on-resonant state shifts out-of resonance with the onset of the laser pulse, and conversely another initially off-resonant state might move into resonance for a narrow window of intensities. These resonances are usually refereed to as Freeman resonances [108, 126]. This situation is illustrated in figure 6.1. The intensity window for which a particular state enhances the ionization depends on multiple parameters, e.g. the dynamic stark shifts of the involved states, their linewidth, Frank-Condon overlap or transition matrix elements. In the extreme case that resonant enhancement occurs only for a very narrow window of intensities, this process contributes only a single delta-like peak to the photoelectron spectrum. Its associated electron kinetic energy distribution is independent of the ionization pulse’s temporal and spatial distribution.
Figure 6.1: This cartoon illustrates the concept of Freeman resonances. It shows the electronic energy (the nuclear degrees of freedom are neglected) associated with the ground molecular state, an intermediate state and the final ionic state as a function of laser intensity. The measured kinetic energy of the photoelectron is determined by the energy difference between the net number of absorbed photons and AC-Stark shifted ionization potential, according to expression 6.1. All states experience a dynamic stark shift, the ionic state (including the free electron) additionally experiences a ponderomotive shift. For our laser central frequency the ponderomotive shift is given by \( U_p \, [\text{eV}] = 56.8 \, I \, [\text{PWcm}^{-2}] \) as a function of intensity \( I \). The ionization rate is greatly enhanced when one of the intermediate (neutral) states is on resonance with an integer number of photons, which typically happens only for one narrow window around a specific intensity, leading to relatively narrow features in the photoelectron spectra associated with Freeman resonances.
Examples for this can be seen in figure 6.2, which highlights four peaks associated with Freeman resonances, whose positions are unaffected by the pulse intensity. The dashed lines highlight four peaks created by enhanced ionization corresponding to a Freeman resonance. Their position is unaffected by the laser intensity, only their relative height changes. They are the focus of the following sections.

It should be stressed that most of the detected electrons are not associated with a particular Freeman resonance, e.g., the most dominant structure $F_2$ contains only about 7% of all electrons in figure 6.3. Most electrons are due to 'shifting' structures, whose shape and position in electron kinetic energy changes as a function of laser peak intensity. Those can be understood, as contributions from far off-resonant intermediate states. Since intermediate resonances play less of a role, the ionization rate is non-zero across a range of different intensities. In this case the AC-Stark shifts and the ponderomotive shift are not constant and lead to the emission of photoelectrons across a range of different kinetic energies, according to equation 6.1.

The rest of this chapter is divided into four sections. The following section 6.2 introduces the idea of pulse shape induced electron-ion-correlations. Section 6.3 describes the details of its implementation in CH$_2$BrCl. The results are discussed afterwards and compared with an alternative approach in section 6.4.

### 6.2 Correlating Freeman peaks with different fragmentation patterns

Traditionally a photoelectron-photoion-coincidence (PEPICO) measurement is performed to identify structures in the photoelectron spectrum with certain photoions [127]. In this case, the sample density is kept sufficiently low, such that statistically less than one (on average) ionization event takes place per laser pulse. The resulting photoelectron and -ions are then detected, with varying degrees of sophistication and complexity depending on how many of their properties (fragment type, absolute momentum, three dimensional momentum, etc.) can be measured. The main drawbacks are the low data acquisition rate, and the need for an extremely clean vacuum chamber, such that the data acquisition rate is not further slowed down by uninteresting background gas contributions.

The ion-electron correlation technique described in this section, differs from other setups reported in the literature. It is rather an extension of the approach used in chapter 5 to electrons: The electron kinetic energy spectra are
Figure 6.2: This graph shows three typical photoelectron spectra created by the ionization of CH$_2$BrCl with a transform limited IR pulse ($\approx$ 40 fs) with different intensities. The electron yield is integrated overall angles after inverse Abel transforming the raw image (such as shown in figure 6.3). The used peak pulse intensity is given in the legend. All graphs are rescaled to fit. The four vertical dotted lines highlight the Freeman resonances, which are discussed in this chapter. They can be easily distinguished from off-resonant contributions, since their position remains constant independently of the used ionization pulse intensity. They are named F$_1$, F$_2$, F$_3$ and F$_4$, starting from the left and correspond to a photoelectron kinetic energy of 750, 1070, 1285 and 1465 meV respectively.
Figure 6.3: This graph shows a full two dimensional photoelectron velocity distribution corresponding to the ionization of CH$_2$BrCl with a transform-limited pulse ($\approx 40 \text{ fs}$) and a peak intensity of $3.8 \cdot 10^{13} \text{ Wcm}^{-1}$. The image is not inverse Abel transformed, and thus the x and y axes refer only to the transverse part of the electron velocity. The laser polarization is along the x-axis. The color axis is proportional to the local density of the electron wave function, normalized to its maximum. Some prominent structures are highlighted with arrows: on the right hand side, they point to the Freeman resonances $F_2$ and $F_3$ (following the same naming convention as introduced in figure 6.2). The big 'blobs' on the left and right edge corresponds to the second above-threshold-ionization (ATI) order of the structures around $F_1$. The asymmetry of the shown distribution is due to an imperfect flat-field correction of the detector signal (see section 2.5). A perfect detector would yield images that are mirror-symmetric along the x- and y-axis. The inset in the lower left corner, illustrates the division of the two dimensional distribution into eight sectors, labeled by roman numerals I, II,... VIII. They are chosen to be equal in size, i.e. each covering a total area of $\frac{2\pi}{8}$. But each sector is broken up into four (or two for sectors I and VII) parts, which form a 'butterfly' pattern, such that each part contains the same kind of information (considering the x/y symmetry of the acquired distributions). The total electron yield measured in sector $s$ with kinetic energy $E$ is refereed to as $Y^{-}(E, s)$. 

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measured as function of ionization pulse shape. Afterwards, the same measurement, using exactly same pulse shapes, is repeated on ions. Ionization with different pump pulse shapes exhibits some control on the relative importance of different ionization pathways (e.g. as demonstrated in chapter 1). In this case, systematic variations – induced by different ionization pulse shapes – in the photoelectron spectra should be mirrored by systematic variations in the photoion spectra and thus can be associated with each other. The difference to the traditional coincidence approach is that these variations in the electron and ion spectra are not due to statistical fluctuations in the yields of the various ionization pathways, but are rather artificially introduced by actively changing the individual transition rates.

Generally, two photoelectron spectra (and their associated ion spectra) resulting from ionization with two different pulse shapes differ vastly. In this case, features in the ion and electron signal cannot easily be associated with each other. But if a sufficiently large space of pulse shapes is explored, it is possible that two photoelectron spectra are almost identical except for a narrow region of kinetic energies. This kind of control is termed ‘isolated’ control. The difference in the ion fragment pattern then can be directly identified with this particular class. One such example is illustrated in figure 6.4. Here the photoelectron spectrum of CH$_2$BrCl is shown, after ionization with two different pulses A and B. They widely overlap, besides in the two regions (0, 100) meV and (1050, 1500) meV. The inset shows the corresponding difference in the photoion yields, which then can be attributed to those energy classes, where the photoelectron spectra differ. This comparison is repeated for all pairs of the studied pulse shape space. Even though, there might not be a ‘perfect’ pair of ionization pulse shapes, which only differ exactly for the studied feature, it is still possible to perform a correlation type analysis that searches for changes in both photoions and a particular feature of photoelectron spectra, with the same systematic pulse shape dependence. In this approach, by contrast to traditional methods, the photoelectron and -ion distributions do not need to be acquired simultaneously. The only requirement is that experimental environment is reproducible for both the ion and electron data sets, including all applied pulse shapes.

Figure 6.3 shows a full two dimensional velocity distribution as measured when ionizing CH$_2$BrCl with an intense transform-limited pulse. As indicated in the inset in the lower left corner, it is convenient to divide the complete two dimensional electron kinetic energy distribution into sectors (‘slices’, in an analogous way to the ion momentum distributions in section 5.2). The total electron yield in sector $s$ with kinetic energy $E$ is abbreviated as $Y^{-}(E,s)$, with sector I referring to the most parallel sector. By contrast figure 6.2

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Figure 6.4: This figure shows two photoelectron spectra of CH$_2$BrCl, associated with two different pulse shapes, referred to as A and B. The graph differentiates between the total electron yields (integrated over all eight sectors, $\sum_{s=1}^{VIII} Y(E, s)$) shown in the solid lines. And represented by the dashed lines, the yield which only takes electrons into account that are ejected within $\pm 11.15$ deg of the laser polarization, i.e. sector I, $Y(E, I)$. Note that the electron distributions are almost identical over a wide range of energies, and differ mostly around the Freeman peaks $F_2$, $F_3$ and $F_4$ and also in the region of $(0, 100)$ meV. The inset shows the difference of the associated ion signal (normalized to its maximum), which then can be attributed to the regions where the two electron spectra differ. In this case the degree of isolated control over $F_3$, defined as ratio of difference in electron yield in $F_3$ divided over total absolute difference in electron signal is 2.6%. By contrast, the total difference in electron yield between both distributions is 0.37% (relative to yield of distribution A). The phase mask applied by the pulse shaper to generate pulse shapes A and B is part of data set A, as stated in table 6.1 with $\beta_1$ being 75 fs and 125 fs, respectively. The slope towards 0 meV (compared to lineouts shown in figure 6.2) is due to the presentation of this data in the raw, not inverse Abel transformed form, i.e. fast electron structures extend into slower regions and they are overrepresented in this graph.
shows a radially integrated lineout, as retrieved when the two dimensional
distribution is inverse Abel transformed and then integrated over all angles
corresponding to one constant kinetic energy $E$.

Let $Y^-(E, s, \alpha)$ denote the photoelectron distribution versus kinetic energy
$E$ in sector $s$, associated with a pulse shape $\alpha$ (again this parameter serves as
a collective label for all pulse parameters varied in the experiment). Similarly
let $Y^+(f, \alpha)$ denote the total yield of photoion type $f$ associated with the same
pulse shape $\alpha$. Then the correlation coefficient $K$ between photoions of type
$f$ and photoelectrons with energy $E$, detected in sector $s$ is defined as follows:

$$K(E, s, f) = \sum_{i \neq j} W_{ij}^+(f)^m \cdot W_{ij}^-(E, s)^n$$

(6.2)

Here the sum stretches over all (non-identical) possible pairs $(i, j)$ of pulse
shapes $\alpha_{i,j}$. $n$ and $m$ are odd integers. The weight functions $W^\pm$ are defined
as:

$$W_{ij}^-(E, s) = \frac{Y^-(E, s, \alpha_i) - Y^-(E, s, \alpha_j)}{\sum_{E, s} |Y^-(E, s, \alpha_i) - Y^-(E, s, \alpha_j)|}$$

$$W_{ij}^+(f) = \frac{Y^+(f, \alpha_i) - Y^+(f, \alpha_j)}{\sum_{f} |Y^+(f, \alpha_i) - Y^+(f, \alpha_j)|}$$

(6.3)

The weight functions are a formal criterion for isolated control: They can
vary in the interval $\pm 1$, with the extrema being assumed, if and only if, all
differences between two ion/electron distributions are concentrated in on single
fragment type/electron kinetic energy class. Usually two distributions differ
at multiple locations, which increases the denominator of equation 6.3 but
not necessarily their numerator. In those cases the value of $W^\pm$ is closer to
zero.

Equation 6.2 can be understood as a modified correlation coefficient between
the ion and electron signals. But instead of the normalized standard
deviation $\frac{X-\mu(X)}{\sigma(X)}$ (i.e. the difference of the signal $X$ its mean, divided over
its standard deviation), the weight factors $W^\pm$ are used in the product. If a
given pulse shape pair $(i, j)$ exhibits a degree of isolated control in both the
electron and the ion distributions, then both weight factors are large (in absolute values), and increase the (absolute) value of $K$. By contrast, if there
is isolated control in only one distribution, either electrons or the ions, or in
neither of them, at least one of the weight factors is close to zero and this pulse
shape does not contribute to the correlation function. The exponents $m$ and
$n$ in equation 6.2 are parameters that adjust the sensitivity of $K$ to the degree
of isolated control in the ion and electron spectra. Since $W_{ij}^\pm$ varies between
-1 and 1, a larger exponent biases the sum towards those pulse shapes with the most isolated control. While a larger exponent $n$ enhances the contrast, it also reduces the number of pulse shape pairs effectively contributing to $K$ and thus worsens the signal to noise ratio. A larger exponent $m$ biases the analysis towards ionic states that are not associated with a complicated branching pattern, i.e. bound ionic states (being only visible in the parent ion) or dissociative states forming predominantly only one particular fragment ion.

Altogether $K$ can be interpreted as a measure of to which extent a feature in the electron spectrum at $(E,s)$ and fragment ion types $f$ can be controlled and are correlated. It should be stressed that this approach provides only a sufficient, but not a necessary criterion for correlation. It is always possible that two different ionization channels respond to the applied pulse shapes in a a similar way and cannot be distinguished; or the sampled pulse shape parameter space is not large enough to exercise isolated control on a particular feature.

### 6.3 Implementation in CH$_2$BrCl

The described procedure was implemented for CH$_2$BrCl. Its photoelectron $Y^-(E,s,\alpha)$ spectrum and fragment ion $Y^+(f,\alpha)$ distribution were recorded with the velocity map imaging setup as described in section 2.3 as a function of various ionization pulse shapes $\alpha$. The angular part of the photoelectron spectra was discretized into eight sectors.

The different pulse shape sets were created using the IR pulse shaper by applying a series of specific phase masks. The applied phase as a function of laser frequency $\phi(\omega)$ were:

$$\phi(\omega) = \omega \beta_1 \text{sgn} (\omega - \omega_0)$$

$$\phi(\omega) = \frac{\pi}{2} \text{sgn} (\omega - (\beta_2 + \omega_0))$$

Here $\omega_0$ is a constant, picked close to the central frequency of the laser pulse of $2.41 \cdot 10^{15}$ radHz. The laser spectral bandwidth supported a minimum pulse duration of $\approx 40$ fs. Four different sets of correlation data were acquired, their parameters are summarized in table 6.1.

In addition to these ion-electron correlation measurements, two other data sets were acquired. The photoelectron spectra of CH$_2$BrCl and CS$_2$ after ionization by a single transform limited pulse were measured. Here the intensity was scanned between 0 and a maximum of $4.0 \cdot 10^{13}$ W cm$^{-2}$. Latter data set was used to experimentally estimate the peak field intensity. The spectrum
Table 6.1: This table summarizes the chosen intervals for the parameters of the applied pulse shapes in the correlation data sets. The first column refers to the used functional form of the applied phase mask in the pulse shaper. The third column gives the total used pulse energy. The last column lists the parameter $\beta_{1,2}$ as states in formulas 6.4 and 6.5. Pulse shape series 6.4 splits the incoming broadband pulse into two pulses according to their color, i.e. the reddish and the blueish half of the pulse spectrum. Both pulses are then separated in time by $2\beta_1$. Phase mask 6.5 introduces what is commonly referred to as a $\pi$-phase flip pulse, since it exhibits a phase that is flat across the whole spectrum, but has an artificial sign switch from $-\pi/2$ to $+\pi/2$ at frequency $(\beta_2 + \omega_0)$.

<table>
<thead>
<tr>
<th>Mask $\phi(\omega)$</th>
<th>Set</th>
<th>Pulse Energy</th>
<th>$\beta_{1,2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Function [6.4]</td>
<td>A</td>
<td>61...68 (\mu J)</td>
<td>75...125 (fs)</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>68...75 (\mu J)</td>
<td>175...225 (fs)</td>
</tr>
<tr>
<td>Function [6.5]</td>
<td>C</td>
<td>56...73 (\mu J)</td>
<td>$+0.01...+0.05 \times 10^{15}$ radHz</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>50...61 (\mu J)</td>
<td>$-0.06...+0.00 \times 10^{15}$ radHz</td>
</tr>
</tbody>
</table>

The number of net absorbed photons $n$ can be guessed from the observed energies. Since this intensity calibration is based on determining the electron kinetic energy $E_{kin}(I)$, any error in the kinetic energy calibration carries over to the intensity calibration. According to section 2.6, this procedure leads to an uncertainty in the laser pulse of at least 8%.
Table 6.2: This table summarizes the theoretical and experimental values given in literature on the lowest ionization potentials \cite{128, 129} and appearance energies AP of the two lowest lying fragmentation channels \cite{96} of CH$_2$BrCl. All values are given in eV, referenced to the neutral ground state equilibrium. The error associated with the calculated IPs is estimated to be about 100 meV. The ionic states are labelled $V_1$, $V_2$ etc. with increasing electronic potential energy. The third column indicates the expected electron kinetic energy, associated with each ionic state. The value is determined by formula 6.1, neglecting ponderomotive and AC-Stark shifts, but assuming the absorption of the minimum number of photons to make this process energetically allowed. Further, the fragmentation channels are written next to the lowest ionic state from which they are energetically allowed. This implies, that direct ionization to $V_1$ and $V_2$ leaves a stable CH$_2$BrCl$^+$ ion. Ionization to $V_3$ and $V_4$ leads to fragmentation into CH$_2$Cl$^+$. Higher lying states can also decay into CH$_2$Br$^+$.

<table>
<thead>
<tr>
<th>state</th>
<th>IP (exp.)</th>
<th>IP (theo.)</th>
<th>$E_{kin}$</th>
<th>fragments</th>
<th>AP</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_1$</td>
<td>10.77</td>
<td>10.77</td>
<td>0.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$V_2$</td>
<td>11.06</td>
<td>11.05</td>
<td>0.03</td>
<td>CH$_2$Cl$^+$ + Br</td>
<td>11.496</td>
</tr>
<tr>
<td>$V_3$ (not resolved)</td>
<td>11.72</td>
<td>0.92</td>
<td>CH$_2$Br$^+$ + Cl</td>
<td>11.982</td>
<td></td>
</tr>
<tr>
<td>$V_4$</td>
<td>11.81</td>
<td>11.82</td>
<td>0.83</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$V_5$</td>
<td>14.64</td>
<td>14.70</td>
<td>1.10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

6.4 Results and Discussion

The ionization potentials associated with the lowest ionic states of CH$_2$BrCl have been determined experimentally \cite{128} and are also reproduced by \textit{ab-initio} structure calculations \cite{129}. Further, the appearance energies of the easiest to form fragments, when ionized from the equilibrium of the neutral ground state, are known experimentally \cite{96}. These values are summarized in table 6.2. As in the previous chapters, the ionic states are referred to as $V_1$, $V_2$, etc. with increasing order of potential energy at the geometry of the ground state equilibrium. In particular, table 6.2 implies that the two lowest ionic states $V_1$ and $V_2$ are bound and result in CH$_2$BrCl$^+$ parent ion formation. By contrast, $V_3$ and $V_4$ are above the appearance energy for CH$_2$Cl$^+$, but below the appearance energy of the second easiest fragment to form CH$_2$Br$^+$.

As shown in figure 6.2 by the vertical dashed lines four distinct Freeman resonances have been identified; they can be distinguished from other off-resonant contributions by the fact that these features do not shift with increasing laser pulse intensity. They are located at 750, 1070, 1285 and 1465 meV and are referred to as $F_1$, $F_2$, $F_3$ and $F_4$ respectively. As already indicated in the two-dimensional distribution shown in figure 6.3 all four peaks are concentrated in
the sector most parallel to the laser polarization, i.e. sector I and the correlation analysis for sector I provides the highest contrast. The results are plotted in figure 6.5, which shows the correlation coefficient $K(E, I, f)$ of the electron yield in sector I, as a function of electron kinetic energy $E$ and fragment ion type $f$. The correlation function has been calculated three times with different choices of the parameter $n$, as used in the definition 6.2. The three panels (a), (b) and (c) represent an $n$ of 1, 3 and 5 respectively, while $m$ is fixed at 1.* The dashed lines again highlight the position of the four identified Freeman resonances. The progression from $n$ equals 1 to 5 illustrates how this parameter controls the selectivity of which pulse shape pair effectively contributes to sum 6.2. Panel (a) is generated with $n = 1$ and suffers from trivial, intensity induced correlations: both the yield of fast electrons (e.g. the second ATI order) and the absolute yield of any fragment monotonically increases with laser intensity. This explains the qualitative similar behaviour of most fragments and the overall tilted correlation graph towards higher kinetic energy. This linear background contribution is successively reduced with higher $n$, as can be seen in panels (b) and (c). Furthermore, the structures progressively become sharper towards panel (c). Last but not least, the correlation results shown in panel (b) and (c) qualitatively agree, i.e. the four Freeman resonances are positively/negatively correlated with the various fragment types in a similar way. For this reason the following analysis is based on panel (c). For $n = 5$ the best 50 pulse shape pairs out of all $1/2 \cdot 199 \cdot 198 \approx 20000$ pulse shape pairs considered in sum 6.2 contribute about 31% to the total weight of electrons ($\sum_{i \neq j} |W_{ij}^{-}(E,s)|^n$).

Figure 6.5, panel (c) yields several conclusions: First, it demonstrates the capability of the introduced correlation analysis to extract single features and associate them with individual fragmentation patterns. Variations in the electron spectra help to isolate out its various components. This is further enhanced by the fact that different ionic states associated with different features are expected to exhibit a different fragmentation pattern. For example, as can be seen in figure 6.2, the peaks of $F_1$ and $F_4$ are only barely separable from the total electron distribution at the lowest used intensities. By contrast, they are not only clearly separable from their neighbours $F_2$ and $F_3$ in panel (c), but are also distinguishable by a different behaviour of the correlation graphs at their position. This is not surprising, since the definition of the weight factors $W_{ij}^{\pm}$ is geared towards narrow structures in the photoelectron spectrum (e.g. as the discussed Freeman resonances), which can be controlled independently.

*As mentioned above higher $m$ biases the analysis towards states decaying into only one fragment type. In the studied case the number of contributing pulse shapes is quickly reduced for $m > 1$ and turns out to be dominated by CH$_2$Cl$^+$ only, since this is by far the dominant fragment.
Figure 6.5: This plot summarizes the ion-electron correlation result as obtained by the procedure in section 6.2. More precisely speaking it graphs the function $K(E, I, f)$ as a function of electron kinetic energy $E$, separately for all studied fragments $f$. The three panels represent different choices for the parameter $n$ as introduced in definition 6.2, while $m$ is chosen as 1 in all three cases. All results are normalized to the interval (-1,1). The four vertical dashed lines highlight the four Freeman resonances as shown in figure 6.2.
In principle this procedure could also be applied to peaks that are not associated with Freeman resonances. But as described in section 6.1, their position in the photoelectron spectra depends on the ionization pulse intensity, and thus their contribution to the sum (6.2) is expected to be diluted over a range of kinetic energies.

Second, the correlation patterns associated with each of the first three Freeman peaks are qualitatively different, with only the patterns of F_3 and F_4 being qualitatively similar. This implies that at least the first three peaks are associated with ionization to different ionic states. Unfortunately, the fragmentation pattern associated with the individual peaks cannot be unambiguously assigned to any particular ionic state: Based on table (6.2) it is to be expected that peaks associated with V_1 and V_2 are only correlated with the parent ion, while V_3 and V_4 are predominantly correlated with CH_2Cl^+. By contrast, all Freeman peaks F_2, F_3 and F_4 are correlated with both the parent ion and fragment ions, which implies strong influence of post-ionization excitation or indirect ionization pathways.

### 6.5 Conclusion and Outlook

A new type of electron-ion correlation technique was introduced. It relies on modifying the relative importance of individual ionization pathways by exciting the molecule with differently shaped laser pulses. The benefits, compared to traditional measurements, are that electrons and ions do not need to be recorded in coincidence and not even simultaneously. This simplifies the technical challenge, since only one detector is needed and it also speeds up the data acquisition rate, which is not limited by the coincidence restriction (less than one event per laser shot) anymore. The technique has been applied to CH_2BrCl and demonstrated its capability to extract fragmentation patterns for even relatively small features associated with Freeman resonances. As a positive side effect, using pulse shaping to isolate out independent structures in the photoelectron spectrum directly yields which and how different ionization pathways can be controlled. Further, since a whole pulse shape space is explored, it is expected to detect more ionization pathways than correlation experiments utilizing only a transform-limited pulse. It has been shown that several direct ionization pathways play a role and leave the molecule in a superposition of several low lying ionic states. In addition, the analysis implies the contribution of several indirect ionization pathways.

Reference [108] suggests a procedure to assign ionic states to Freeman peaks, which offers the possibility to test the results of the correlation analysis: For this, the molecule’s photoelectron spectrum is recorded as a function of
ionization pulse intensity. The observed threshold intensity $I_m$ of a particular peak (located at an electron kinetic energy of $E_k$), i.e. the lowest intensity at which a the Freeman peak becomes visible, corresponds to the 'magic' intensity associated with the intermediate state shifting exactly into resonance. Rearranging formula 6.1 yields the ionization potential IP:

$$IP = n\hbar\omega - (\Delta E_{gf}(I_m) + U_p(I_m) + E_k)$$  \hspace{1cm} (6.7)$$

The net number of absorbed photons $n$ can be guessed. Once the IP associated with a structure is known, table 6.2 can be used to identify the corresponding ionic state. The only remaining unknown in this expression is the dynamic AC-Stark shift. Because of the high density of low lying ionic states, they can be expected to be a significant contribution, e.g. for the related molecules CH$_2$BrI and CH$_2$I$_2$ (as discussed in the previous chapters) AC-Stark shifts are up to 500 meV at around $I_m$. If all uncertainties for the energy axis calibration, intensity calibration, peak position and AC-Stark shifts, are included this procedure is not accurate enough to provide an exact assignment. But once \textit{ab-initio} values for the dynamic Stark shifts are available, this procedure can serve as an independent test for results of the correlation analysis.
Chapter 7

Conclusions

This thesis explored applications of ultrafast pulse shaping and velocity map imaging to gain insights into molecular dynamics and strong field ionization. The apparatus was described and characterized in chapter 2. The first experimental chapter focussed on controlling neutral molecular dynamics. It built on results of ab-initio structure calculations and demonstrated that it is possible to reshape a vibrational wavepacket with tailored pulse sequences. In particular two different control schemes, photon-locking and hole-burning, were observed.

The following chapters investigated strong field ionization of halogenated methanes. Chapter 4 described a proof-of-principle experiment that implies that SFI usually leaves the molecule in a superposition of various ionic states. In this study traditional pump-probe scans were employed. Their features could be linked to multiple vibrational wave packets on several ionic states. This approach was generalized in chapter 5, which aimed at characterizing the relative importance of various ionization pathways. It built on two concepts: (a) Measuring the fragment ion yield momentum resolved, which provides additional information and different vibrational wavepackets are represented by substructures in the observed momentum distributions. And (b), pulse shaping can manipulate the relative contributions of the various ionization pathways, which aided in identifying independent substructures. Once the different substructures were identified, they could be used as a basis set to approximate the raw acquired momentum distributions and quantify the contributions of different ionization pathways. The last chapter 6 expanded these two ideas to photoelectron spectra. In particular features associated with Freeman resonances were studied. It was demonstrated that ionization with shaped pulses, can modify the yield of these features to some degree. This systematic dependence was exploited to establish correlations between photoions and photoelectrons.
The described approaches to identify direct and indirect pathways in SFI via pulse shaping and velocity map imaging could be improved in multiple ways. In particular, the correlation between ions and electrons could benefit from measuring also the ion distributions momentum resolved. In this case a combination of both techniques \cite{5} and \cite{6} could circumvent the problem of reduced correlations due to post-ionization excitations and the contributions from direct and indirect pathways could readily be distinguished.
Appendix A

Retrieval of full three-dimensional Velocity Distribution

As mentioned in section 2.4 the detector can only measure the components of the particle velocity that is parallel to the detector surface. In this section the coordinate \( x \) refers to the polarization of laser pulse, which is usually parallel to the detector surface. \( y \) refers to the direction perpendicular to \( x \), which is also parallel to the detector surface. \( z \) is chosen to be perpendicular to \( x \) and \( y \), and thus parallel to the time-of-flight axis. Each position on the detector screen can be converted to a particular transversal velocity (i.e. velocity along \( x \) and \( y \)), but is the sum over all longitudinal velocities. Mathematically the measured two-dimensional \( Y(v_x, v_y) \) distribution is linked to the ‘real’ three-dimensional velocity distribution \( R(u_x, u_y, u_z) \) by a projection along the \( z \) coordinate. Let us assume that \( R \) is cylindrically symmetric around the laser polarization direction \( (x) \), then one can write:

\[
R(u_x, u_y, u_z) = R(u_x, u_{\perp}) \tag{A.1}
\]

And this is related to the measured distribution by the Abel transform \( A \):

\[
Y(v_x, v_y) = 2 \int_{v_y}^{\infty} \frac{R(v_x, u_{\perp}) u_{\perp} \, du_{\perp}}{\sqrt{u_{\perp}^2 - v_y^2}} \tag{A.2}
\]
The original distribution can be retrieved exactly using the inverse Abel transform:

\[ R(u_x, u_\perp) = -\frac{1}{\pi} \int_{u_\perp}^{\infty} \frac{dY(u_x, u_y)}{du_y} \frac{du_y}{\sqrt{u_y^2 - u_\perp^2}} \]  

(A.3)

This is also the way the data was reconstructed in this thesis. The used MATLAB algorithm is shown below (for one frozen \( u_x \) coordinate). Care needs to be taken to reduce numerical errors due to the finite pixel size of the camera images and to avoid the singularity at the lower bound of the integral.

```matlab
function [rho, f0] = invAbel5(x, F0, N)

% 1D Abel inversion algorithm based on direct evaluation of the inversion
% integral (see [http://mathworld.wolfram.com/AbelTransform.html] and [http://en.wikipedia.org/wiki/Abel_transform])

% Input Arguments:
% x    -- abscissa vector for the input vector F0
%       (x and F0 has to be the same length)
% F0   -- function to be inverted
% N    -- desired length for the output vectors rho and f0

% Output Arguments:
% rho  -- abscissa vector for the output vector f0
% f0   -- result of the Abel-inversion

Nx=length(x);
N_samp=10*Nx;
x_min=min(x);
x_max=max(x);
x_step=(x_max-x_min)/(Nx);

param1=3.5; % Sets offset between abscissa vectors x and rho; Magic number: 3.5

% generate new x-axis with higher sampling to reduce numerical errors
x2=func((x_min:(x_max-x_min)/(N_samp-1):x_max))'(func(
```
\[
\text{x\_max}) \times \text{x\_max};
\]
\[
\text{rhol=x2};
\]
% avoid singularity on lower bound of integral by slightly shifting lower bound
\[
x2=x2+(x2(2)-x2(1))/\text{param1};
\]
\[
\text{eps}=(x2(2)-x2(1))/\text{param1}/20;
\]
\[
x2=x2(\text{abs}(x2)\leq \text{x\_max});
\]
%
improve sampling density of input distribution
\[
\text{F1} = \text{interp1}(x, \text{F0}, x2, 'linear');
\]
\[
\text{rhol} = \text{rhol}(\text{rhol}<\text{max}(x2));
\]
\[
\text{Nrhol} = \text{length}(\text{rhol});
\]
%
generate new x-axis
\[
\text{rho\_min} = \text{min}(\text{rhol});
\]
\[
\text{rho\_max} = \text{max}(\text{rhol});
\]
\[
\text{rho\_step} = (\text{rho\_max}-\text{rho\_min})/(\text{N}-1);
\]
\[
\text{rho} = (\text{rho\_min}: \text{rho\_step}: \text{rho\_max})';
\]
%
calculate derivative of input function
\[
\text{dF} = \text{gradient}(\text{F1}, x2);
\]
%
implementation of inversion formula
\[
\text{func\_invtld2} = \text{zeros}([\text{Nrhol}, 1]);
\]
\[
\text{for} \ k=1: \text{Nrhol}
\]
\[
\quad \text{func\_invtld2}(k) = -1/\text{pi} \times \text{sum}(\text{dF}((x2-\text{rho}(k)) \geq \text{eps}).*1./\text{sqrt}(x2((x2-\text{rho}(k)) \geq \text{eps}).^2-(\text{rho}(k))^2).*\text{gradient}(x2((x2-\text{rho}(k)) \geq \text{eps})))\);
\]
\end{verbatim}
end
\[
\text{f0} = \text{interp1}(\text{rhol}, \text{func\_invtld2}, \text{rho}, 'linear');
\]
end
Bibliography


[106] Xibin Zhou, Robynne Lock, Nick Wagner, Wen Li, Henry C. Kapteyn, and Margaret M. Murnane. Elliptically polarized high-order harmonic


