In this chapter the current capabilities and potential of advanced single particle imaging techniques to study photodynamics in isolated molecules is reviewed. These so-called reaction microscopes are able to measure the full three-dimensional energy and angular distribution of (correlated) particles like electrons and molecular fragments ejected after photo-excitation of molecules. In particular the performance and capabilities of a novel photoelectron-photoion coincidence imaging spectrometer constructed at LaserLaB Amsterdam is discussed. This microscope was developed for the study of nonadiabatic effects in ultrafast time-resolved experiments. It is specifically targeted at optimal control studies of photodynamics to foster and advance our understanding of mechanisms in optimal control with shaped ultrafast laser pulses. A few recent experimental results are reviewed illustrating the wealth of detailed information that can be obtained in such imaging experiments about the interplay between (shaped) laser fields, molecular dynamics, ionization processes and competing multichannel pathways. Furthermore, the recently developed photoelectron-circular-dichroism imaging technique to detect enantiomers and to study chirality effects will be discussed, as a further illustration of the potential of modern reaction microscopes in stereochemistry.

d this chapter is adapted from:
The Reaction Microscope: Imaging and Pulse Shaping Control in Photodynamics
4.1 Introduction

The first chemist who proposed that molecules have a three-dimensional shape was Jacobus van ‘t Hoff in 1874\(^1\), the co-founder of the field of Physical Chemistry\(^2\). He proposed that the three-dimensional shape of molecules is responsible for many chemical and physical properties, like the optical rotation of light by molecules, and his novel ideas led to the development of stereochemistry.

Our present day understanding of the three-dimensional structure of molecules and their (photo)chemical dynamics has improved tremendously by a large variety of (gas phase) spectroscopic methods. One of those techniques uses the absorption of highly energetic photons by a molecule with the subsequent ejection of an electron from the molecule. This spectroscopic technique is known as photoelectron spectroscopy in which the kinetic energy of the resulting electron is determined after single photon absorption\(^3\)–\(^5\). The kinetic energy of the electron can be correlated to the energy of the electronic states of the molecule from which it originated.

The advances in ultrafast laser technology and time-resolved spectroscopic techniques led in the nineties of the previous century to the development of the field of Femtochemistry\(^6\)–\(^8\). Furthermore, the invention in 1987 of single particle imaging techniques by Chandler and Houston\(^9\), to measure the kinetic energy and angular distribution of photofragments, has led to the development of very advanced and powerful spectroscopic imaging techniques revealing many novel (fundamental) aspects of chemical dynamics\(^10\)–\(^13\). With the so-called ion imaging technique the initial three-dimensional distribution of recoiling ions is projected or imaged onto a two dimensional single particle detector. Subsequently, the three-dimensional distribution can be extracted by use of mathematical algorithms, like the inverse Abel transformation in case of cylindrical symmetry, or other more sophisticated inversion techniques\(^14,15\). Just as in time-of-flight (TOF) mass spectrometers, Chandler and Houston employed grids to create homogeneous electric fields. However, grids have several disadvantages, including some transmission loss of ions, and potential trajectory deflections with poorly constructed grids. Furthermore, the spatial extent of the ionization volume is determined by the size of the molecular beam and the laser focus. Because of the extended ionization region of several mm along the direction of the (laser) light propagation, a substantial blurring results that limited the achievable energy
resolution (about 10-15%) in the original ion imaging design\textsuperscript{9,16–18}.

The problem of limited resolution due to the extended source region was solved to a large extent by the invention of the velocity map imaging (VMI) technique in 1997 by Eppink and Parker\textsuperscript{19}. A three plate assembly, repeller, extractor and TOF-entrance, with two open grid-less electrodes (extractor, TOF-entrance) was used to image or map the velocity of the particles onto the detector. The two open electrodes introduce curved electric field lines, and act as ion lenses. The ions subsequently drift in a field-free tube towards the detector. With VMI particles are focused onto the same position of the detector (largely) independent of their initial position, and this leads to an improvement of the energy resolution down to typically 2-5%.

In principle, the three-dimensional distribution of the recoiling fragments is fully determined by the TOF and the two-dimensional position at the detector. Instead of projecting the full three-dimensional momentum distribution on a two-dimensional surface, time-slice imaging can be used to circumvent the cylindrical symmetry restriction used in many reconstruction (e.g. Abel inversion) techniques of the three-dimensional distribution. Kitsopoulos and coworkers \textit{et al.}\textsuperscript{20} introduced a method in which the extraction field is switched on after the ionization of molecules. The initial field free expansion of the ions will increase the width of the arrival time distribution at the detector. Subsequently, the particle detector is switched on for a short time period only, in order to slice out and measure the ions in the middle of the three-dimensional distribution. However, switched electric fields always have the risk of ringing effects that can distort the ion image. Suits and coworkers\textsuperscript{21} and Liu and coworkers\textsuperscript{22} introduced a time slicing method without the need of switching electric fields. A set of three or more lenses is used to lower the potential energy difference between the repeller and extractor, hence stretching the arrival time of the ions. The extraction field is lowered and therefore the TOF spread is increased. The additional lenses are used to focus the ions onto the detector like in VMI. This method is generally referred to as DC slice (velocity map) imaging. The strength of the imaging technique in all its variations is the capability of measuring the kinetic energy of the charged particles (ions or electrons) under investigation and this can presently be achieved with a very high resolution of about 0.2\%\textsuperscript{23,24}.

The combination of photoelectron spectroscopy with time-resolved femtosecond pump-probe spectroscopy resulted in the development of
time-resolved photoelectron spectroscopy, enabling the study of ultra-fast nuclear dynamics in a molecule\textsuperscript{25}. Furthermore, when integrating pump-probe spectroscopy with velocity map photoelectron imaging\textsuperscript{26–28}, the time-dependent photoelectron angular distribution (PAD) of the recoiling electron in a photo-ionization experiment can be determined\textsuperscript{29,30}. This PAD reflects the transition dipole moments of the initial bound state to the final state of the ion and the electron scattering dynamics and contains information about the initial charge distribution of the molecule under investigation.

In general, the study of molecular photodynamics and photoionization yields both an electron and an ion, and both particles contain valuable information about the dynamics. Therefore, the simultaneous and correlated measurement of both the electron and the ion yields the most complete information on the molecular dynamics. The coincidence (non-imaging) detection technique was introduced by Brehm and Von Puttkamer\textsuperscript{31}, Eland\textsuperscript{32} and Stockbauer\textsuperscript{33} during 1967-1973. The combination of the coincidence imaging technique with time-resolved (femtosecond) pump-probe spectroscopy was pioneered three decades later in 1999 by Hayden and coworkers\textsuperscript{34–36}. A similar technique, employing single photon synchrotron excitation, was invented almost simultaneously in the atomic physics community and called cold-target recoil-ion momentum spectroscopy (COLTRIMS)\textsuperscript{37}. In COLTRIMS, often delay-line detectors are used for the measurement of the full three-dimensional momentum distribution of the correlated particles, electrons and ions\textsuperscript{38}.

In this chapter the development and application of a novel coincidence imaging apparatus in Amsterdam\textsuperscript{39}, the reaction microscope, that employs coincidence imaging to study and control molecular photodynamics using time-resolved techniques and ultrafast pulse-shaping techniques is reviewed. Coincidence imaging\textsuperscript{34,36,40}, comprises of the coincident detection of the full three-dimensional momentum distribution of both the ion and electron ejected in a molecular dynamical process. Besides the measurement of the full three-dimensional laboratory frame momentum distribution of electron and correlated ion, this technique also allows for the measurement of the angular correlation of the momentum of the electron with respect to the direction of the recoiling ionic fragment\textsuperscript{41–43}. This correlated angular distribution is called the recoil-frame photoelectron angular distribution (RFPAD). In the fast axial recoil approximation, the recoil direction defines the orientation of the dissociated molecular bond in space and can be related directly to
the molecular frame photoelectron angular distribution (MFPAD)\textsuperscript{44-48}. In general, the final direction of the recoiling fragments depends on the detailed dynamics of the dissociation process and the parent ion may dissociate on the timescale of the rotation of the ion. In such a case, the MFPAD becomes smoothed and reduces to the RFPAD\textsuperscript{49}.

During the last decade the technique of coherent or optimal control has become a proliferating technique to study and manipulate molecular dynamics\textsuperscript{50,51}. The idea is to control the temporal and spectral shape of the interacting light pulses in such a way as to drive the outcome of a (chemical) process into the preferred direction. One of the most popular control techniques is adaptive femtosecond pulse shaping\textsuperscript{52} and for a recent overview of this rapidly evolving field see e.g. the special issues of J. Photochem. Photobiol. A\textsuperscript{53}, J. Phys. B: At. Mol. Opt. Phys.\textsuperscript{54}, New J. Phys.\textsuperscript{55}, Phys. Chem. Chem. Phys.\textsuperscript{56} and references therein. The application of adaptive pulse shaping to study the control of multichannel fragmentation in strong field excitation of polyatomic molecules was pioneered by the experimental groups of Gerber\textsuperscript{57} and Levis\textsuperscript{58}. Recently, the interpretation of some of the experimental observations in strong field control experiments of polyatomic molecules has become the focus of scientific debate\textsuperscript{59,60}.

Until now most experimental studies using adaptive pulse shaping on polyatomic molecules have used time-of-flight mass spectrometric detection. Mass spectrometry provides only information on the masses of the various ionic species produced and no or very limited information on the mechanism of the pulse shaping dynamics. With the novel Amsterdam reaction microscope we have combined for the first time the power of velocity map electron and ion coincidence imaging techniques with ultrafast pulse shaping.

This chapter is organized as follows. In section 4.2 we first review the performance and operation of the novel reaction microscope. In section 4.3 we will review some of the recent work in Amsterdam employing these sophisticated coincidence imaging techniques. The examples will range from the study of multichannel dynamics in polyatomic molecules to the study of mechanisms in the control of molecular photodynamics by shaped femtosecond laser pulses. Furthermore, in section 4.3 we will illustrate the power of angular-resolved photoelectron spectroscopy by discussing the recently developed technique of Photo-Electron-Circular-Dichroism (PECD) by Powis and coworkers\textsuperscript{61,62}. This novel application of photoelectron imaging is a state-of-the-art technique to study, under-
and employ chirality effects in molecules and weakly bound complexes. As such PECD provides a very timely and powerful demonstration of the enormous development in the field of physical chemistry and the advancement of our understanding of the three-dimensional structure and stereochemical aspects of molecules, a field that was pioneered by Jacobus 't Hoff in 1874, a scientist who is celebrated in this special issue. Finally, in section 4.4 we will provide a brief outlook and will summarize our conclusions.

4.2 Experimental: The reaction microscope

A new photoelectron-photoion coincidence imaging instrument, the reaction microscope, has been constructed at LaserLaB Amsterdam for femtosecond time-resolved experiments including full pulse shaping control of the excitation laser field. The apparatus was designed to have high temporal and energy resolution for the electrons and ions, using the latest developments in micro-channel-plate detector technology and state-of-the-art time-of-flight detection electronics. The particles are detected with delay-line detectors and some of the experimental aspects are reviewed briefly. The full details of design and performance are reported in Ref 39 and in chapter 2. In Fig. 4.1 a three-dimensional drawing of the apparatus is shown together with a photo of the vacuum machine with electronics and part of the laser equipment.

In this section we will review the major features of the novel apparatus and some of the experimental developments concerning velocity map ion optics and mass spectrometry are discussed. Furthermore, we will demonstrate the novel implementation in the reaction microscope of a fast cantilever piezo valve for the production of intense and cold pulsed molecular beams at repetition rates up to 5 kHz. This piezo valve was developed in our lab recently and reported on in detail in two publications in 2009. This high repetition rate valve is now incorporated into the coincidence apparatus and we will briefly discuss the improvement of molecular beam production with the pulsed valve, relative to the continuous molecular beam employed so far in the Amsterdam coincidence machine. The mass resolution of ions and the energy resolution of electrons are briefly illustrated by the TOF spectrum of various isotopes of (fragment) ions of CH$_2$BrCl and the electron TOF detection resolution from the ionization of Xenon atoms. The calibration of the
detector is described and an illustrative energy correlation diagram of NO$^+$ ions and coincident electrons from multi-photon ionization of NO$_2$ is discussed.

4.2.1 Photoelectron-photoion coincidence velocity map imaging with delay line detectors

The detection of the electrons and ions after laser interaction occurs on two separate detectors in a velocity map imaging geometry. The ionization volume is enclosed by velocity map imaging lenses, as shown in Fig. 4.1(a). The acceleration direction of the charged particles is indicated. First, the electrons are extracted with negative voltages on the lenses and subsequently the polarity is changed. The flight time of electrons to the detector is approximately 10-15 ns. The polarity and amplitude of the voltages on the ion lenses are switched in less than 100 ns after the arrival of the electron at the electron delay-line detector. The lenses remain positive for more than 20 µs to ensure a distortion free extraction and detection of all masses of interest. The homebuilt high-voltage switching electronics can operate at a repetition frequency of up to 5 kHz, which is the maximum repetition rate of the femtosecond amplified laser system.

The charged particles (electrons and ions) hit a micro-channel plate (MCP) and induce an avalanche of electrons with high efficiencies. At the back side of the MCP, an electron cloud leaves and is accelerated towards a commercial delay-line detector from Roentdek GmbH. The electron cloud leaving the MCP is collected on the delay-line wire and the induced signal will travel towards the ends. The delay-line detector consists of two wires, one for each dimension, with two endpoints for each wire. However, each wire itself is a pair of two wires in a so-called Lecher-line configuration. This configuration transmits high frequency signals with low damping and dispersion in a differential mode. The differential signal is generated by the application of a slightly higher potential on one of the wires. The charge is effectively collected on the wire with the highest potential, also called the signal wire and the other is the reference wire. The difference between the two channels gives an almost background free pulse corresponding to the electrons collected on the delay line. The signal and reference wires are connected to an impedance matched differential amplifier (ATR-19 from Roentdek GmbH). These pulses are converted to digital NIM pulses via so-called...
constant fraction discriminators (CFD). Subsequently, the arrival times of the NIM pulses are determined by a commercial 8-channel time-to-digital converter (HPTDC by Roentdek GmbH\textsuperscript{38}). The TDC measures the total time by measuring the number of clock cycles spaced by a time period of 25 ps.

\textbf{Figure 4.1:} (a) Side view of the photoelectron-photoion coincidence apparatus, consisting of three connected vacuum chambers: the source, buffer and imaging chamber\textsuperscript{39}. The molecular beam is formed in the source chamber by expansion through either a continuous nozzle or a high-repetition rate (1-5 kHz) pulsed cantilever nozzle\textsuperscript{63,64}. The molecular beam is skimmed first before it enters the differentially pumped buffer chamber, and then skimmed a second time before the beam enters the imaging chamber with imaging detectors. The second skimmer (200 µm diameter) is located at 12 cm from the nozzle and determines the size of the molecular beam in the interaction region with the femtosecond laser pulse. The total distance from nozzle to interaction region is about 45 cm. The laser excitation produces electrons and ions which are measured with opposite detectors in coincidence. The TOF and position of the particles at the imaging detectors are used to extract the initial momentum distribution of ion and electron. (b) Photo of the coincidence laboratory with the reaction microscope, electronics and gas handling manifold in the front. The optical tables with the regen-amplified femtosecond laser system, non-collinear opto-parametric amplifiers, pulse-shaper and various laser pulse shape diagnostics are partially visible behind the coincidence apparatus.
The time difference between the two signal pulses at both ends of the wire is proportional to the position on the detector. For example, in the case that the cloud hits the detector in the middle, both pulses appear at the same time at both ends of the wires and for such an event in the middle the time difference will thus be zero. The time difference together with the time-to-position conversion factor of 1.9 ns/mm can be used to determine the position in mm.

The velocity map imaging technique projects particles with the same momentum onto the same position of the detector. The ions are accelerated towards the detector and the TOF depends on several factors. The TOF of a charged particle with mass \( m \) and charge \( q \) can easily be calculated when only a single homogeneous electric field is used to accelerate the particle towards the detector. In this case, the flight time of the charged particle is determined by the potential difference (\( V \)) between the ionization region and the (grounded) detector. This potential difference is converted into kinetic energy of the charged particles. Furthermore, the TOF depends on the length of the field free flight region in the spectrometer (\( L \)) and is then given by

\[
TOF = L \sqrt{\frac{m}{2qV}}
\]

The ion optics shown in Fig. 4.1(a) consist of three open lenses instead of one extraction field. For the detection of ions the typical voltages applied on the repeller (\( R_i \)), extractor (\( E_i \)) and lens (\( L_i \)) are typically +2000 V, +1550V and +750V respectively. The open lens structure causes a significant lowering of the electric fields experienced by the ions. The potential difference with respect to the grounded detector in the interaction region is 1710 V according to SIMION simulations\(^7\). Because of the open lens structure of the ion optics and the different regions of acceleration the TOF of ions can be reproduced quantitatively only by a more elaborate calculation taking the geometry of the optics into account.

The TOF of different ions can be compared to simulations for both conventional ion imaging and velocity map imaging (VMI). From these simulations also the positions of the ions at the detector can be obtained. The position of the ions is only dependent on the initial kinetic energy and not on the mass. The direction of the molecular beam velocity is parallel to the plane of the detector. Ions with zero recoil kinetic energy show a narrow flight time distribution (gaussian), with a FWHM
on the order of 2 ns\(^{39}\). This TOF distribution is solely determined by the spatial extent of the interaction region. However, for a large interaction region the position spread on the detector can be large as well. The particles along the laser propagation direction are projected on a proportional position of the detector. However, the extent of the projection of the interaction region at the detector can be much smaller. The best configuration is obtained with a small interaction region with a length below 1 mm\(^{39}\). Finally, the initial velocity or momentum of the charged particle can be obtained from the three-dimensional data after calibration, see also section 4.2.3.

### 4.2.2 Cold pulsed molecular beam expansion and spatial resolution

The coincidence apparatus, displayed in Fig. 4.1, has three different vacuum chambers, the source chamber with the molecular beam source, the buffer chamber and the detection chamber. The molecular beam is crossed with the laser beam at a distance of 45 cm from the nozzle. The size of the molecular beam along the laser propagation direction is solely determined by the opening of the second molecular beam skimmer which was reduced to 200 µm to achieve the best configuration for the coincidence imaging\(^{39}\). The ionization yield is determined by the cross section, the flux of photons and the number of molecules present in the interaction volume of the molecular beam and the laser beam. The laser beam is skimmed by light baffles close to the interaction region and the ion optics. This reduces the amount of scattered UV light significantly.

Although a large molecular beam skimmer gives in principle a larger signal because of the larger ionization volume, the drawback is that background molecules are imaged in the center of the detector with a broad distribution. The limited pumping speed of the buffer chamber results in a larger contribution of ions from background thermalized molecules. This is contrary to the ions from the molecular beam, which are displaced from the center with a narrow velocity distribution. This means that with a large second skimmer the number of molecules entering the detection chamber can be significant compared to the number of molecules extracted from the molecular beam with the laser. The situation is significantly improved by reducing the size of the second skimmer opening to 200 µm.

Recently, we have replaced the continuous molecular beam source
that we used originally, by a homebuild high-repetition rate cantilever piezo valve. A pulsed molecular beam source matches much better the duty cycle of the experiment because of the pulsed femtosecond laser source, in our case the repetition rate of the laser system is selectable between 1-5 kHz. This makes it possible to produce stronger beams and to use higher backing pressures. The piezo valve can operate both in pulsed mode and continuous mode and the gas was expanded through a nozzle with a diameter of 200 µm.

In Fig. 4.2 we compare the parent ion beam spot on the ion detector of Xe ions produced by multi-photon ionization with femtosecond laser pulses at 400 nm for a pulsed and a continuous beam. For the present results we used a gas mixture of 1.4% Xenon seeded in Neon. The displacement of the molecular beam ion spot of Xe is caused by the orthogonal extraction relative to the direction of the molecular beam. The velocity of the molecular beam and the TOF determines the displacement from the center. The velocity of the seeded Xe molecules in the Ne-carrier gas is equal to the speed of Neon as they are seeded in such a small amount (1.4%). From the image of the parent beam spot we can obtain the velocity distribution by analyzing the width of the spot along the molecular beam direction.

The speed ratio is proportional to the ratio between the forward velocity and the width of the distribution. The speed ratio for the continuous seeded molecular beam, with a pressure of 1 Bar behind the nozzle, is found to be about $S=8.6$, see Fig. 4.2(b). When we operate the piezo valve in pulsed mode (the laser system and valve were running at 1 kHz) we can operate at much higher backing pressure of about 7 Bar, and the width of the beam spot decreases substantially. The speed ratio increases to about $S=29$, see Fig. 4.2(a). This much lower velocity spread in the parent molecule will also, in principle, increase the velocity resolution of fragment ions, as they will have a much reduced spread from the reduced centre-of-mass velocity spread.

When seeding polyatomic molecules in a pulsed expansion of Neon at a backing pressure of 7 Bar, the rotational cooling will be substantial, and can be down to 0.9 Kelvin (see section 2.4 for more details). This provides a molecular beam with only few rotational quantum states populated. Vibrational cooling is usually (much) less efficient than rotational cooling, but still we expect that for polyatomic molecules the distribution of initial vibrational quantum states will be more narrow. The strong reduction in internal temperature in the pulsed expansion
also enables the formation of clusters, dimers, trimers and larger complexes. To prevent clustering we typically work with very diluted mixtures (about 1% or less). We can observe cluster formation very easily by analysis of the TOF mass spectrum, and the seeding ratio is reduced such that mass peaks of dimers are barely visible.

Figure 4.2: Comparison of the histogram of detected Xe$^+$ ions produced by multi-photon ionization with a femtosecond laser pulse at 400 nm and about 60 µJ pulse energy. The inserted images show the two-dimensional projected image of all detected $^{129}$Xe$^+$ ions along the horizontal direction of the molecular beam. The vertical direction in the inserts is along the propagation direction of the laser. The molecular beam was produced from a premixed gas of 1.4% Xe seeded in Neon. Panel (a) shows the image and distribution of Xe$^+$ ions produced by ionization of a pulsed molecular beam using the novel cantilever piezo valve$^{63,64}$, with 6.8 Bar backing pressure behind a 200 µm nozzle. Panel (b) shows the image and distribution, using the same gas mixture and the same nozzle, but now expanding a continuous molecular beam at a backing pressure of 1 Bar. The laser crosses the machine near the middle of the detector at a position of about 22.5 mm behind the second skimmer. Because of the supersonic velocity of the seeded molecular beam (forward velocity is about 770 m/s) the Xe$^+$ ions are displaced from the center of the imaging detector. It is very clear how the high pressure pulsed expansion, panel (a), produces a much more narrow velocity distribution along the molecular beam direction representing a much colder parallel translational temperature of the Xe beam. The speed distribution is well represented by a Gaussian distribution defined by $f(v) \propto \exp(- (v - v_0)^2 / 2\sigma_v^2)$, with $v_0$ the most probable forward flow velocity and $\sigma_v$ the standard deviation. The speed ratio S is defined as $S = 2\sqrt{(\ln 2) \frac{\Delta v_{FWHM}}{\Delta v_{FWHM}}}$, where $\Delta v_{FWHM}$ is the Full-Width-Half-Maximum of the distribution, $\Delta v_{FWHM} = 2.355\sigma_v$. 

60
4.2.3 Energy calibration, resolution and electron-ion energy correlation

The TOF-spectrum of ions observed in femtosecond laser excitation of a seeded beam of CH$_2$BrCl in Neon is shown in Fig. 4.3. The mass of the detected ions of the various isotopes of CH$_2$BrCl can be easily assigned using the TOF of the various peaks. The coincidence apparatus has a very good mass resolution which was illustrated before on the different isotopes of Xe$^{39}$. The average of the arrival times of one delay-line wire is a direct measure of the flight time of the particles and can be used to determine the TOF of the ions. The TOF of the isotopes of Xe was determined with a width of 2 ns FWHM$^{39}$. Typically the mass resolution obtained from the width of the TOF-spectrum is about 1:2000, using full coincidence mode with switching acceleration fields, and improves to about 1:4000 using non-switching ion imaging mode.

Figure 4.3: Time-of-flight mass spectrum of ions produced in the multi-photon excitation of CH$_2$BrCl using a short (about 30-35 fs) femtosecond pulse near 520 nm from by a non-collinear opto-parametric amplifier. The ion optics of the velocity map ion lenses were operated in switched high-voltage mode for full coincidence detection. The TOF-mass spectrum (only the part with 4-10 $\mu$s arrival time is displayed) clearly shows the well separated arrival time of the various isotopomers of the parent CH$_2$BrCl$^+$ ion and the fragment ions. The mass resolution is about 1:2000 in this mass region of m=130 atomic mass units.
A special effort was made to obtain the TOF of the electrons with very high temporal resolution, see Fig. 4.4. The signal induced on the MCP by the electron cloud leaving the MCP can be picked up by a small capacitor connected to the MCP. This MCP pickup signal is shown in Fig. 4.4. The best time resolution is obtained by measuring the arrival time of the MCP pick-up pulse with a Time-to-Amplitude Converter (TAC, SPC-130 by Becker & Hickl). We operate the TAC in an inverse start-stop configuration, where the TAC is started with the detection of an electron event, and stopped by the laser pulse, see Fig. 4.4.

**Figure 4.4:** Detail of the velocity map optics and MCP-delay line detector for measuring the full 3D momentum of electrons. The TOF arrival time, under our typical voltages used for electron imaging, is about 15 ns. The position of the electron is obtained from the time-difference of the four delay line signals, as obtained from the 8-channel Time-Digital-Converter (not shown here). The insert graph shows our best TOF distribution of electrons, in coincidence with Xe ions, measured by taking the pickup signal from the back MCP plate which is pre-amplified and processed by the Time-Amplitude-Converter (B&H SPC-130). The polarization of the 400 nm femtosecond laser was oriented along the TOF axis, resulting in a forward ejected electron and a backward ejected electron peak. With the applied lens voltages (acceleration field between extractor and repeller is about 19 Volt/mm) the forward and backward electrons arrive at a time separated by about 188 ps. The colored solid lines (red for forward and green for backward electron distribution) are Gaussian curves with a fitted resolution of \( \sigma \approx 16 \) ps, representing the temporal uncertainty of a single electron hit on the electron detector. The uncertainty is mostly caused by the intrinsic transit-time-spread of the 5\( \mu \)m MCPs. (Adapted and reproduced with permission from Ref. 39).
We have been able to determine the ultimate arrival time resolution of the electrons in our microscope to be about $\sigma=16$ ps, see the insert graph in Fig. 4.4. Our present electron arrival time detection resolution is limited by the intrinsic residual transit-time-spread (TTS) of the 5 $\mu$m pore MCP$^{39}$. The calibration of the position on the electron detector to the kinetic energy of the electron has been discussed extensively in Ref. 39 and is checked routinely on a day-by-day basis using the ionization of NO molecules or Xe atoms.

Finally, the flight time spread of the ions is determined by several factors. The dominant factor is the magnitude of the extraction field with respect to the distance between the laser interaction region and the detector. The higher the extraction field, the smaller the time spread. Other factors are the extent of the molecular beam along the laser propagation direction and the initial kinetic energy distributions of the recoiling fragments. These effects are all taken into account in SIMION simulations of the ion trajectories$^{71}$.

To further calibrate the ion detector, the energy correlation plot is employed showing the correlation between the kinetic energy of the electron and the total kinetic energy of the fragments, see Fig. 4.5. More details are given in section 2.3. In short, the conservation of energy gives a constraint to the maximum value for the sum of the kinetic energy of the electron and atomic fragments, according to

$$E(\text{photons}) - E(\text{appearance}) = E_k(\text{ion}) + E_k(\text{neutral}) + E_k(\text{electron})$$

(4.2)

The internal energy of the parent molecule has been neglected as the beam is internally cold. The calibration of the ion detector is exemplified on the single-color 400 nm photodissociation of NO$_2$. The dominant product in the single color 400 nm multi-photon excitation of NO$_2$ is NO$^+$, which accounts for 95% of the events originating from NO$_2$. The energy correlation plot for the NO$^+$ fragment is given in Fig. 4.5. The vertical axis of the correlation plot shows the kinetic energy of the electron and the horizontal axis the total kinetic energy of NO$^+$ + O. The diagonal line indicates the maximum available energy for a five photon absorption process. The correlation plot shows that the electrons obtain well defined kinetic energies according to the three photoelectron bands. On the other hand, the kinetic energy distribution of the fragments ranges from zero to the maximum available energy. This multi-photon process is assigned to instantaneous electron ejection, i.e. within the
temporal width of the laser pulse. Subsequently, the NO$_2^+$ is produced in three dissociative states giving rise to fast NO$^+$ + O fragments. The total kinetic energy of the atomic fragments can be determined from the correlation plot and thus the ion detector can be calibrated.

The delay-line detector enables the determination of the full three-dimensional momentum distribution of the observed ion. The acquired data for a single ion consists of the position in the plane of the detector (x and y directions) and the time-of-flight of the ion, perpendicular to this plane, all measured by the TDC with 25 ps bins.

Figure 4.5: The energy correlation plot of electrons and NO$^+$ formed in the single color multi-photon ionization of NO$_2$ at 400 nm. The diagonal line near 3.0 eV gives the total available energy for electron and (NO$^+$,O) fragments for excitation with five photons at 400 nm.
4.3 Examples of Imaging and Control in Photodynamics

4.3.1 Disentangling Multichannel Multi-photon Dynamics

Over many years NO\textsubscript{2} has served as a benchmark molecule for both frequency and time domain studies of photophysical processes like dissociative ionization, unimolecular reaction dynamics, cluster dynamics, vibrational autoionization, state-to-state photoionization dynamics, and non-Born-Oppenheimer dynamics. Even though at first sight NO\textsubscript{2} looks like a simple triatomic molecule, absorption and fluorescence spectra in the visible energy range proved to be extremely complex and congested\textsuperscript{75–77}. For a recent overview of the electronic structure, spectroscopy and dynamics of NO\textsubscript{2} see the review by Wilkinson and Whitaker and references therein\textsuperscript{78}.

In recent years several ultrafast experiments studying the photodynamics of NO\textsubscript{2} were reported using femtosecond laser pulses in either single color or two-color pump-probe configurations. Especially, in a series of velocity map imaging experiments using femtosecond pump-probe spectroscopy at 400 nm and 266 nm an oscillatory component in the pump-probe transient of NO\textsuperscript{+} fragments and electrons was observed\textsuperscript{79–82}.

The first extensive study performed with the novel coincidence imaging machine described above was the time-resolved dynamics in NO\textsubscript{2} in a two-color pump (400 nm) - probe (267 nm) scheme with laser pulses of about 120 fs duration\textsuperscript{65}. Time dependent photoelectron images in coincidence with NO\textsubscript{2}\textsuperscript{+} or NO\textsuperscript{+} were measured and the (NO\textsuperscript{+},e) photoelectron versus fragment ion kinetic energy correlations were reported. The correlated information provided very clear explanations and assignments of the different competing multi-photon channels leading to the formation of NO\textsubscript{2}\textsuperscript{+} or NO\textsuperscript{+} cations and the various observed photoelectron channels.

Two ions, the parent NO\textsubscript{2}\textsuperscript{+} and the fragment NO\textsuperscript{+}, are observed in the mass spectrum of the photo-products of NO\textsubscript{2} after excitation with 400 nm pump and 267 nm probe photons. The pump-probe transients for both ions are shown in Fig. 4.6(a) and the number of NO\textsuperscript{+} fragment ions per laser shot is about a factor of 10 larger than the number of NO\textsubscript{2}\textsuperscript{+}. 
parent ions. In these coincidence experiments, the count rate is rather limited, to avoid false coincidences\textsuperscript{83}. In our experiments the typical coincidence rate is 1-5\%, i.e. we need about 100 laser shots to have 1-5 (ion,e) coincidence events. Therefore, the transients have limited signal-to-noise and no dedicated effort was done to observe the oscillations with sufficient contrast. In Fig. 4.6(a) one can see that the pump-probe transients are rather featureless.

**Figure 4.6:** (a) Pump-probe transients of \(\text{NO}_2^+\) and \(\text{NO}^+\) in a two-color excitation of \(\text{NO}_2\)\textsuperscript{65}. A positive delay time means that the 267 nm probe pulse crosses the molecular beam after the 400 nm pump pulse. (b) Energy correlation plots of the (\(\text{NO}^+,\text{e}\)) events at three different delay times, 0 fs, 500 fs and 1750 fs. The diagonal dark green line near 1.55 eV gives the total available energy for electron and fragments for excitation with three photons at 400 nm plus one photon at 267 nm, a (3+1') process. The red diagonal line at 60 meV gives the upper boundary of the available energy for excitation with one photon at 400 nm plus two photons at 267 nm, a (1+2') process. A diagonal line at 1.3 eV shows the upper boundary of the available energy for the channel leading to vibrationally excited \(\text{NO}^+\) (v=1) after excitation with three photons at 400 nm plus one photon at 267 nm. The energy correlation plots display complex competing multi-photon dynamics that cannot be extracted from the rather featureless transients shown in panel (a). (Adapted and reproduced with permission from Ref. 65).
However, the photoelectron-photoion coincidence images show a complex time varying dynamics with various competing multi-photon excitation pathways. The coincidence photoelectron spectra and the correlated energy distributions make it possible to assign the different dissociation pathways involved. In Fig. 4.6(b) the energy correlation plots for (e, NO$^+$ fragments) are shown at three different pump-probe delay times, 0 fs, 500 fs and 1750 fs. The vertical axis of the correlation plots shows the kinetic energy of the electron and the horizontal axis the total kinetic energy of all fragments. The diagonal lines indicate upper bounds for the available energy of a specific multi-photon process. It is directly observed from such energy correlation plots that both (1+2') multi-photon processes as well as (3+1') processes are competing and leading to different dynamics and energy distributions of coincident (e, NO$^+$). The labels (1)-(6) correspond to various channels. For instance, peak (6) at 0 fs, is a channel producing very fast electrons at 1.4 eV and very slow NO$^+$($1\Sigma$). This suggests a slow statistical dissociation of NO$_2^+$ after prompt ejection of a fast electron when both lasers have time-overlap. It leaves the NO$_2^+$ parent system at an energy just above the thermodynamic threshold for the formation of NO$^+$(1$\Sigma$) + O(3P). The excitation pathway (3+1') apparently accesses configurations that can slowly dissociate on the ionic NO$_2^+$ ground state surface at an energy just above the thermodynamic threshold. At a long pump-probe delay time of 1750 fs there are only two electron peaks remaining in the correlated (e,NO$^+$) events. Photoelectrons of zero eV, peak (1), and photoelectrons of about 0.9 eV, peak (4).

Peak (4) is assigned to a (3+1') photon pathway, and using the total excitation energetics a maximum kinetic energy expected for the NO$^+$(v=0) + O(3P) channel, created by this (3+1') photon pathway, is 0.7 eV. The correlation plot in Fig. 4.6(b) shows that the total kinetic energy of peak (4) is (mostly) limited to 0.4 eV. This must mean that the ionization takes place towards NO$^+$(v=1) in the first vibrational excited state, and this accounts for 0.3 eV of available energy. The free neutral NO(A) in the first vibrational state is ionized by one 267 nm photon towards NO$^+$ in the first vibrational state.

In a different (non-coincidence) imaging spectrometer we have recently studied in extensive polarization experiments and much more detail the distinctive oscillatory patterns (not shown here)$^{81}$. The time scale of the oscillations and the polarization experiments exclude rotational wavepackets in NO$_2$ or NO as the origin of the oscillations. New
*ab initio* calculations show that there are avoided crossings or conical intersections between bound and dissociative excited states of different Rydberg and valence character near 9 eV. Supported by the results from the coincidence experiments we discussed the origin of the oscillatory mechanism in relation to *ab initio* calculations of relevant Rydberg and valence type excited states of NO₂ near 9.3 eV. It was proposed that an oscillating and predissociating wavepacket of mixed Rydberg and valence character is responsible for the observed oscillations in the transients of the fast (0.88 eV) photoelectron. Recently, Whitaker, Blanchet and coworkers further discussed NO₂ imaging experiments and the origin of the oscillations.

The energy correlation plots reveal the complex multi-photon multichannel pathways in the ultrafast photodynamics of a small molecule like NO₂. In addition insight about the photoionization dynamics in NO₂ was obtained from the RFPAD, which will not be reviewed here.

### 4.3.2 Fixed in Space Molecules: Molecular Frame Photoelectron Angular Correlation

In this section we present some results obtained with the novel coincidence microscope on the single color multi-photon excitation dynamics in nitromethane, CH₂NO₂. Previously, the single photon ionization spectrum was determined in a study by Rabalais and later by Mok et al. The vertical ionization energy of the first two photoelectron bands are 11.32 eV and 11.73 eV. These bands display vibrational structure, which was assigned to the NO₂ bending mode (565 cm⁻¹) and originates from a large difference of the bond angle of the NO₂ group in the parent ion compared to the neutral molecule. The three highest occupied molecular orbitals are calculated to be the two lone pair orbitals and one π-bonding orbital of the NO₂ moiety of nitromethane. The two lone pair orbitals are nearly degenerate and their symmetry was revealed by angular resolved photoelectron spectroscopy and the change of the angular distribution with photoelectron energy by Katsumata et al. Furthermore, at higher energy two broad bands at 14.73 eV and 15.75 eV vertical ionization energy were also observed. At lower excitation energy, the UV absorption spectrum consists of two bands. One weak band in the energy range of 3.5-5 eV and a strong band centered at 6.26 eV extending over a range of 5.5-7.5 eV. Absorption of a photon in these energy ranges leads to the cleavage of the C-N bond and the
formation of the CH$_3$ and NO$_2$ fragments. Electronically excited NO$_2$ fragments were found in theoretical and experimental studies, while the CH$_3$ fragment has almost no internal energy.$^{91}$

Here we show experimental results of the RFPAD of nitromethane after femtosecond single-color multi-photon excitation at 400 nm and an intensity of about $1 \times 10^{12}$ W/cm$^2$. The TOF-mass spectrum of nitromethane is shown in Fig. 4.7(a). Single color 400 nm excitation of nitromethane results in the formation of the parent ion as well as several fragment ions. Only the formation of the parent ion, representing up to 44% of the events and the formation of the fragment NO$_2^+$ (8%) and CH$_3^+$ (18%) ions will be discussed. The NO$^+$ fragment represents 30% of the coincidence events.

![TOF-mass spectrum](image1)

**Figure 4.7:** (a) TOF-mass spectrum of nitromethane after femtosecond excitation at 400 nm. The dominant product is the parent ion, but several fragments are observed as well. (b) The Recoil-Frame-Photoelectron-Angular-Distribution (RFPAD) of electrons in coincidence with CH$_3^+$, the recoil direction of the fragments are indicated. (c) (RFPAD) of electrons in coincidence with NO$_2^+$. In both RFPADs, the recoiling fragment are within a slice of $\pm$20 degrees with respect to the laser polarization.
The velocity map images of the parent ion, CH$_3$NO$_2^+$, and both the CH$_3^+$ and NO$_2^+$ ionic fragments, together with their coincident electron images were measured (not shown here). The parent ion image shows no recoil (as expected) but the CH$_3^+$ and NO$_2^+$ ionic fragments have significant kinetic energy from the dynamics after excitation.

The direction of the electron with respect to the correlated recoiling fragment gives the RFPAD and these are shown in Fig. 4.7 for both the CH$_3^+$ (panel b) and NO$_2^+$ (panel c) fragments. Fragments recoiling within an angle of 20 degrees with respect to the laser polarization direction are selected. The RFPAD shown in Fig. 4.7(b) corresponds to the CH$_3^+$ ionic fragment with the CN bond aligned parallel to the 0-180 degree vertical axis. Fig. 4.7(c) corresponds to the RFPAD of the NO$_2^+$ ionic fragment. As can be seen the RFPADs are very asymmetric along the dissociating bond with a preference for the electron ejection either along the direction of the CH$_3^+$ fragment or opposite to the NO$_2^+$ fragment. Also, the RFPADs are very similar, the RFPADs in Fig. 4.7(b),(c) are only rotated by 180 degrees with respect to each other as they are correlated to the velocity direction of either the CH$_3^+$ or the NO$_2^+$ ionic fragment.

The RFPADs can be expanded in terms of Legendre polynomials, $P_n(\cos \theta)$ and the angular distribution is expressed as $I(\theta) = 1 + \sum_n a_n \cdot P_n(\cos \theta)$, where the $a_n$ parameters describe the contribution to the recoil frame angular distribution. In the analysis presented here, the expansion is truncated at $n=6$ and only the coefficients that have a significant contribution are shown. The $a_n$ parameters are given in Table 4.1. The relatively strong and significant $a_1$ parameter reflects the asymmetry along the dissociating C-N bond and is of oppositive sign for the two RFPADs of CH$_3^+$ and NO$_2^+$.

<table>
<thead>
<tr>
<th>RF-PAD</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_4$</th>
<th>$a_6$</th>
</tr>
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<tbody>
<tr>
<td>CH$_3^+$</td>
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<td>0.96</td>
<td>0.63</td>
<td>0.37</td>
</tr>
<tr>
<td>NO$_2^+$</td>
<td>-0.46</td>
<td>1.02</td>
<td>0.73</td>
<td>0.34</td>
</tr>
</tbody>
</table>

Table 4.1: The coefficients of the expansion in Legendre polynomials of the Recoil-Frame-Photoelectron-Angular-Distribution of the electron correlated with either the recoil direction of CH$_3^+$ or NO$_2^+$, as shown in Fig. 4.7.

The formation of CH$_3^+$ or NO$_2^+$ fragment ions requires a total excitation energy exceeding the dissociation energy of the parent plus the ionization energy of the fragments. Femtosecond laser pulses enable the absorp-
tion of multiple photons due to the high peak power of the laser pulse. Furthermore, because of the short pulse duration, multiple photons are easily absorbed and ionization is likely to occur before the dissociation can take place. The ionization process is fast and can occur during the laser pulse, while the dissociation process is much slower and cannot be completed during the excitation process. However, the temporal width of the pulse allows for some geometry changes and the Franck-Condon constraint is somewhat relaxed. Kilic et al.\textsuperscript{92} have observed single-color multi-photon ionization of nitromethane at 375 nm. Their experiment (with a slightly shorter pulse of 90 fs) showed a TOF-mass spectrum comparable to our TOF spectrum shown in Fig. 4.7, although in Ref. 92 the intensity of the NO\textsuperscript{+} peak was comparable to the intensity of the CH\textsubscript{3}NO\textsubscript{2}\textsuperscript{+} parent ion peak.

The reported appearance energy (AE), or minimum energy needed to produce CH\textsubscript{3}\textsuperscript{+} and NO\textsubscript{2}\textsuperscript{+} fragments are 12.6 eV and 12.1 eV, respectively.\textsuperscript{93,94} The total excitation energy of four 400 nm photons is 12.4 eV, which would allow only the NO\textsubscript{2}\textsuperscript{+} ion and CH\textsubscript{3} neutral fragments to be formed. Ionization in this four-photon process at 12.4 eV is above the second experimental photoelectron peak at 11.72 eV. In single-photon photoelectron spectroscopy, a large vibrational progression of the vibrational bending mode of the NO\textsubscript{2} moiety is observed.\textsuperscript{86} Therefore, the parent ion is highly vibrationally excited and could thus dissociate to NO\textsubscript{2}\textsuperscript{+} and CH\textsubscript{3}.

From the analysis of the relative contribution of correlated (e,NO\textsubscript{2}\textsuperscript{+}) events at low photoelectron energy we concluded that not much NO\textsubscript{2}\textsuperscript{+} is formed after four-photon absorption. We find from our coincidence data that this four-photon channel contributes only 0.5\% of the total coincidence events, whereas the total number of (e,NO\textsubscript{2}\textsuperscript{+}) coincidence events (independent of photoelectron energy) represent 8\% of all coincidence events. The low four photon contribution to the dynamics is attributed to the fact that large geometrical changes are required for the formation of the fragments. While the CH\textsubscript{3} is planar and the NO\textsubscript{2}\textsuperscript{+} fragment is linear, the CH\textsubscript{3} moiety has a pyramidal geometry and the NO\textsubscript{2} moiety is bend in the nitromethane molecule. The limited available total energy after four-photon excitation appears to limit the probability of this process to the dissociation dynamics, relative to a competing five-photon excitation and dissociation process.

Most of the NO\textsubscript{2}\textsuperscript{+} fragments that we observe obtain significant kinetic energy, the total kinetic energy observed in this channel is approximately...
1.6 eV. For the CH$_3^+$ fragment, a similar kinetic energy distribution is obtained. Both channels are attributed to result from dynamics after a five-photon absorption that gives a total excitation energy of 15.5 eV. Using the total measured kinetic energy of 1.6 eV an upper bound of the appearance energy, AE, of 13.9 eV is obtained for both the CH$_3^+$ and NO$_2^+$ fragments, when the electron has zero kinetic energy. This value is larger than the reported AE values of 12.6 eV and 12.1 eV$^{93,94}$. We attribute the difference to significant internal energy, which can amount up to 1.3 eV and 1.8 eV, respectively. Taking a total excitation energy of 15.5 eV and a photoelectron kinetic energy of 0.56 eV, where the peak in the correlated photoelectron spectrum is observed in both ion channels, we can calculate a vertical ionization energy of about 15 eV. From comparison with the assignment of the photoelectron peaks observed after one-photon XUV excitation$^{86}$ we propose that excitation of the 9a’ orbital is involved in the five photon ionization process. Photoionization of the 9a’ orbital was assigned at an experimental vertical ionization energy of 14.70 eV$^{86}$.

The experimental RFPAD and first calculations$^{84}$ of the angular distribution of photoejection of the molecular 9a’ orbital from single photon ionization do not appear to be very similar yet. In first calculations (in collaboration with dr. Lucchese and dr. Carey), the electron kinetic energy and total excitation energy were taken to be similar to the values in the experiment. The calculated RFPADs do not show a maximum in the distribution of the emitted photoelectron in the direction of the recoiling fragment. However, these first calculations were performed for single-photon dissociative ionization, while in the experiment the dynamics results from multi-photon ionization with femtosecond laser pulses with a duration of 120 fs. The multi-photon excitation allows for a contribution and (some) fast dynamics on intermediate excited states, within the 120 fs pulse duration, and such processes have not been taken into account in the calculations. The difference between experiment and calculation could also be attributed to the geometric and electronic configurations of the parent ion used in the calculation of the final state wavefunctions. The parent ion can have larger geometrical changes compared to the neutral molecule. It is clear that more realistic multi-photon photoionization excitation modelling, in combination with dynamical calculations, need to be performed in order to compare more quantitatively the observed experimental RFPAD in nitromethane.
4.3.3 Mechanism of Femtosecond Pulse Shaping by Coincidence Imaging

One of the objectives of the field of molecular dynamics is to understand in full detail the processes leading to the breaking and formation of a chemical bond. As explained in section 4.1 multidimensional particle imaging techniques are able to reveal molecular dynamics at unprecedented detail. Especially, photoelectron-photoion coincidence imaging in combination with femtosecond time-resolved pump-probe spectroscopy is extremely powerful to provide insightful information on multi-photon multichannel dynamics.

In this example we review first experimental results, that were reported recently, combining velocity map (non-coincidence) electron and ion imaging techniques with ultrafast pulse shaping to study the detailed mechanism of control of molecular ionization and fragmentation processes in polyatomic molecules. The system under study was CH$_2$BrCl, well suited for our imaging techniques, and also selected to make (future) comparison with theoretical calculations more tractable. The absorption of single UV photons by CH$_2$XY molecules leads to the promotion of an electron from a lone pair orbital of the halogen atom to a carbon-halogen antibonding molecular orbital. The resulting molecular dynamics on electronically excited potential energy surfaces results in dissociation to a halogen atom and halomethyl radicals CH$_2$X. Halomethanes like CH$_2$BrCl have even more complex UV absorption spectra and a greater number of dissociation channels in photodissociation compared with monohalogen molecules like CH$_3$Br or CH$_2$Br$_2$. This is due to the symmetry lowering because of the different halogens.

We performed pulse shaping control experiments by chirping a short (∼30-35 fs) femtosecond laser pulse in the visible region near 520 nm. Multiphoton excitation with visible pulses leads to the formation of mainly CH$_2$BrCl$^+$ parent ions and CH$_2$Cl$^+$ fragment ions, a very small mass peak is observed assigned to CH$_2$Br$^+$. Chirping the excitation pulse leads to strong changes in the CH$_2$Cl$^+/CH_2$BrCl$^+$ mass ratio. This ratio was observed to change by almost 500% when an upchirped pulse was used. In Fig. 4.8(a), the photoelectron spectra obtained from the electron images after multi-photon excitation at 521 nm are shown for differently chirped pulses. Near zero and negative chirp values, the electron distribution is dominated by a somewhat broadened peak between 0.7-0.9 eV. At positive chirp three more clearly separated peaks appear.
Figure 4.8: In the top panel (a) the total photoelectron spectra obtained from Abel-inverted photoelectron images after excitation of CH$_2$BrCl for femtosecond pulses centred at 521 nm are shown for varying linear chirp$^{99}$. In the bottom panel (b) the energy level scheme and proposed mechanism. The location of the relevant energy levels of the parent ion CH$_2$BrCl$^+$ and the CH$_2$Cl$^+$ + Br channels are indicated. We show the schematic of the proposed mechanism of either wavepacket following or time-delay resonance at the two-to-three photon transition between the two-photon excited repulsive (2 A') red-wing of the A-band and the A' Rydberg level at three-photon excitation. The up-chirped pulses will enhance the excitation of the $n_a$(Br, 22a') orbital in the five photon excitation resulting in an enhanced ejection of a low (0.1-0.2 eV) energy photoelectron and fragmentation to CH$_2$Cl$^+$ + Br ($^2P_{3/2}$). (Adapted and reproduced with permission from Ref. 99)
in the spectrum with energies at about 0.15 eV, 0.9 eV and 1.2 eV. Furthermore, the ion images of the CH$_2$Cl$^+$ fragment ion revealed that very little kinetic energy is released in the fragmentation dynamics. Having the total energetics of electron and ions we were able to assign the various peaks in the photoelectron spectrum. The photoelectron peak at low energy was assigned to five-photon excitation with subsequent fragmentation to CH$_2$Cl$^+$ + Br.

To interpret the observed data we used high-level ab initio calculations by Gonzalez and coworkers$^{100}$ that provide information on the principal configuration of the various lowest valence and Rydberg states of CH$_2$BrCl. The lowest electronically excited valence states result from the $n_x$(Br) $\rightarrow$ $\sigma^*$ (C-Br) (2 $A'$) and $n_y$(Br) $\rightarrow$ $\sigma^*$ (C-Br) (1 $A''$) excitations. The lowest states of Rydberg character, $n_x$(Br) $\rightarrow$ Rydberg (A') and $n_y$(Br) $\rightarrow$ Rydberg (A')$, are located near 7.4 eV. This is very close to three-photon excitation of 521 nm (7.2 eV). The ground state electronic surface of CH$_2$BrCl$^+$ has A' symmetry, and correlates to the lowest fragmentation channel CH$_2$Cl$^+$ + Br ($^2P_{3/2}$). In Fig. 4.8(b) a schematic of the various electronic states and fragmentation channels is shown.

The total energy of 11.9 eV after five-photon absorption at 521 nm and the ejection of a 0.1-0.2 eV electron brings the parent ion at an energy of 11.7-11.8 eV just above the energetic threshold of the spin-orbit ground state CH$_2$Cl$^+$ + Br ($^2P_{3/2}$) channel at 11.509 eV, but below the threshold of the spin-orbit excited state CH$_2$Cl$^+$ + Br ($^2P_{1/2}$) channel at 11.966 eV, see Fig. 4.8(b). The intensity of the photoelectron peak at high energy in Fig. 4.8(a) grows with increasing upchirp relative to the intensity of the lower photoelectron peak. This high energy photoelectron peak was assigned to ejection of the 22a' symmetric in plane $n_x$(Br, 22a') CH$_2$BrCl molecular lone-pair orbital, the middle electron peak to the 8 a'' anti symmetric $n_y$(Br, 22a') CH$_2$BrCl molecular lone-pair orbital.

Up-chirped pulses at 521 nm enhance the CH$_2$Cl$^+$ + Br ($^2P_{3/2}$) fragmentation channel, and favor the ejection of the in plane $n_x$(Br, 22a') electron orbital relative to the anti-symmetric $n_y$(Br, 8a'') electron orbital. Considering presently available theoretical calculations on potential energy surfaces $^{100-104}$ we therefore proposed that the up-chirp enhancement of the ejection of the in plane $n_x$(Br, 22a') electron orbital in the five-photon process is a manifestation of either wavepacket following or a time-delay resonance between the dissociative (2 A') surface,
Chapter 4

reached via two-photon excitation, and the Rydberg (A’) surface located at three-photon excitation. Because the (2 A’) surface is strongly repulsive in the C-Br coordinate an up-chirped pulse may provide a more enhanced coupling with the higher-lying n_x(Br) Rydberg (A’) state. The Rydberg (A’) state serves as the stepping stone for further two-photon excitation into the CH_2BrCl^+ (X A’) continuum. Furthermore, the dynamics on the (2 A’) repulsive surface after two-photon excitation may also lead to a more favorable geometric configuration of the CH_2BrCl molecule such that subsequent excitation via the Rydberg (A’) state to the five-photon excited CH_2BrCl molecule leads to a specific electron channel near low energy (0.1-0.2 eV) and the formation of the CH_2Cl^+ + Br (2P_{3/2}) fragmentation channel just above threshold, see Fig. 4.8(b). It is highly desirable to have more advanced theoretical calculations on the proposed mechanism for the control of the fragmentation dynamics with chirp and such calculations are in progress in collaboration with Gonzalez and Rozgonyi.

Chirped pulse shaping experiments on CF_3I have performed in the novel coincidence imaging reaction microscope with full LCD-pulse shaping control and are presented in chapter 6. The LCD-shaper enables the generation of arbitrarily shaped pulses, see section 3.3.

In conclusion, photoelectron and ion imaging experiments provide unprecedented detailed information on energy and angular distributions of (correlated) ions and electrons in pulse shaping experiments. We believe that these experiments will advance our understanding of the mechanism in (optimal) control studies of multichannel multi-photon dynamics in polyatomic molecules.

4.3.4 Chiral Recognition and van ‘t Hoff: Photo-Electron Circular Dichroism

Chirality is one of the most fundamental concepts of life, yet, experimental and theoretical characterization of stereoisomers by chiro-optical methods is still in its infancy compared to the level that has been reached for their non-chirality sensitive counterparts. Furthermore, many fundamental aspects of chirality in nature are poorly understood. It is known that chiral molecules in general have different absorption cross sections for left and right circularly polarized light. This phenomenon is called circular dichroism and is used to selectively detect enantiomers. However, this difference in the total absorption cross section between enantiomers
Reaction Microscope

is in general very small, typically of the order of $10^{-4}$.

In 1976, about a century after the first publication (in Dutch) by van 't Hoff\textsuperscript{1} in which he proposes that molecules have a three-dimensional structure, Ritchie\textsuperscript{105} reported theoretical calculations on a novel chiral phenomenon in the angular resolved photoionization cross section of enantiomers. In general, the laboratory angular distribution of photoelectrons ejected from a non-chiral molecule after one-photon ionization with linearly polarized light can be written as,

$$I(\theta) = 1 + b_2 \cos^2(\theta).$$

Here, $\theta$ is the polar angle between the velocity of the ejected electron and the polarization vector of the of the laser light. Ritchie showed that ionization with circular polarized light of chiral molecules results in an angular distribution of electrons that will show a (strong) linear term in $\cos(\theta)$,

$$I(\theta) = 1 + b_1 \cos(\theta) + b_2 \cos^2(\theta).$$

Here, $\theta$ is the angle between the velocity of the ejected electron and the propagation direction of the circular polarized light or the polarization of the linear polarized light. Furthermore, Ritchie showed that the $b_1$ coefficient changes sign for the left and right handed enantiomers, or changes sign when a single stereo-isomer is ionized with either left or right circularly polarized light. Subsequent calculations by Powis\textsuperscript{61} predicted that such effects in the electron angular cross section could be of the order of $10^{-1}$, three orders of magnitude larger than the differences measured in conventional circular dichroism experiments. Therefore, this strong linear term makes angular resolved photoionization studies of enantiomers very promising with regard to sensitivity and selectivity.

During the last few years Powis and coworkers have reported the first groundbreaking experiments employing angular resolved electron detection. They applied this novel photo-electron-circular-dichroism (PECD) effect to characterize and study several chiral molecules and even chiral dimers\textsuperscript{106–109}. Because PECD uses photoelectron spectroscopy it is a universally applicable spectroscopic technique and can be applied, in principle, to any chiral species. The ionization energy of most molecules is of the order of 8-12 eV. Therefore, quite energetic photons are needed to accomplish one photon ionization and these experiments were performed at synchrotron facilities. Furthermore, because advanced single particle imaging detectors are used, the molecules under study need to be available in the gas phase. For an extended overview of the present status of PECD experiments we like to refer to the recent review by Nahon and Powis\textsuperscript{62}.
Chapter 4

Here we illustrate the sensitivity of the effect showing two representative results reported by Powis and coworkers on enantiomers of camphor\textsuperscript{108} and fenchone\textsuperscript{110}, two closely related chiral molecules that have been studied extensively in benchmark studies of normal CD experiments. In Fig. 4.9(a),(b) the three-dimensional reconstruction of the PECD spectrum of the R (a) and S (b) enantiomers of camphor is shown as a surface-contour plot. The propagation direction of the circularly polarized light is indicated by the arrow and the photon energy was 10.3 eV. These panels offer an intuitive understanding of the experimental observable of the photoionization angular distribution of a chiral molecule subjected to circular polarized light. The angular distribution has the predicted\textsuperscript{105} cosine dependence about the propagation direction of the synchrotron light, leading to the asymmetric peaks in electron intensity along the forward and backward direction near $\theta=0$ or $180^{\circ}$. Furthermore, this forward-backward asymmetry in intensity reverses when the enantiomer is switched from R to S. In the region of photoionization of the HOMO-orbital with a photon of 10.3 eV the magnitude of the PECD effect is about 7\%, but it can reach an even higher value of almost 20\% at a photon energy of 20 eV\textsuperscript{108}. These effects are orders of magnitude larger than what is observed in conventional CD of camphor\textsuperscript{111}.

A closely related chiral molecule is fenchone that differs only in the attachment site of two methyl groups, and is otherwise very similar to camphor. In the bottom panel of Fig. 4.9 the PECD magnitude is shown for photoionization of 1S-fenchone at 19.3 eV\textsuperscript{110}. The upper thick solid line is the total photoelectron spectrum measured with the DELICIOUS Velocity Map Imaging instrument at SOLEIL\textsuperscript{112,113}. The thin solid line is a photoelectron spectrum recorded at higher resolution with 95 eV photon energy. The squares with error bars show the PECD effect from a difference image obtained with left circular polarized light and right circular polarized light at 19.3 eV photon energy.

At this particular photon energy, it is also clear that the sign of the PECD switches between the HOMO and adjacent orbitals in fenchone. While, as before for camphor, the HOMO (carbonyl oxygen lone pair) orbital is well separated given the size of the molecule, the remainder of the orbital bands are partially overlapped, even in the higher-resolution spectrum. However, although obtained simultaneously, and thus with identical energy resolution, the PECD spectrum is more obviously structured with features that can be correlated with the expected positions of unresolved bands. The authors attribute the more pronounced contrast
Reaction Microscope

Figure 4.9: Panels (a),(b). Three-dimensional reconstruction of the Photo-Electron-Circular-Dichroism (PECD) laboratory angular distribution observed on the R (a) and S (b) enantiomers of camphor photoionized at 10.3 eV. The arrows indicate the photon propagation axis of the circularly polarized light. (Adapted and reproduced with permission from Ref. 108). (c) PECD measurement for 1S-fenchone with photons from a synchrotron with an energy of 19.3 eV. The upper panel (solid dark line) shows the photoelectron spectrum extracted from the same 2D VMI data set, while the lower panel (thin gray line) shows a higher-resolution valence PES recorded at a photon energy of 95 eV. Also included are vertical markers indicating calculated vertical IPs. The PECD effect (symbols with error bars) is about 5% in the HOMO region. (Adapted and reproduced with permission from Ref. 110).

in the PECD spectrum from the larger variation in the magnitude of the linear $b_1$-coefficient for ionization of adjacent orbitals as compared to changes in the total ionization cross sections of adjacent orbitals.

The theoretical understanding and modeling of PECD is progressing rapidly providing quantitative comparison of PECD experiment and theory. It is understood now that PECD strongly probes molecular conformation and chemical substitution even, in larger species, at sites that
are somewhat remote from an initially localized ionizing orbital or from a chiral center. PECD can be viewed as a kind of electron diffraction study using electrons generated \textit{in situ} at various locations and with varying energies. The chiral nature of the diffraction process lends a much enhanced sensitivity to the detailed molecular structure, and as such the three-dimensional imaging of photoelectrons provides a novel and ultra sensitive (analytical) detection technique for enantiomers and even complexes\textsuperscript{109}.

The combination of multi-photon PECD with the photoelectron-photoion coincidence detection for the mass-selective discrimination on the chiral molecules Camphor and Methylloxirane is reported in chapter 8 and chapter 9 of this thesis. These measurements show that the one-photon PECD effect can be enhanced using multi-photon ionization.

## 4.4 Conclusions

Van \textquoteleft t Hoff proposed in 1874 that molecules have three-dimensional structures. The three-dimensional structure of molecules leads to three-dimensional patterns of ejected electrons and ions after excitation by photons of sufficient energy. In this contribution we have discussed the application of advanced photoelectron and photoion imaging techniques to make pictures of these three-dimensional photon-induced patterns to foster our insight into molecular photodynamics and chemical structure. The multichannel photodynamics in polyatomic molecules can be very complex with many competing pathways, especially when multi-photon ultrafast excitation schemes are employed. We reviewed the performance features of a novel reaction microscope that was developed recently in Amsterdam for the study of pulse shaping control of ultrafast photodynamics. The combination of various state-of-the-art technologies in single particle detection makes it possible to study the interplay between photons, electrons and molecules and the ultrafast dynamics in unprecedented detail and resolution. We have illustrated this with some recent studies from our laboratory in disentangling multichannel dynamics and mechanisms in pulse shaping control. Furthermore, an exciting novel application of reaction microscopes was reviewed that measures the photoelectron angular distribution to provide an extremely sensitive and selective fingerprint of chirality in stereo isomers.
References


