

#### **MOLECULAR CHIRALITY UNDER THE REACTION MICROSCOPE**

mass-selective photoelectron circular dichroism of pure and multi-component enantiomeric mixture

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reaction

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#### VRIJE UNIVERSITEIT

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#### ACADEMISCH PROEFSCHRIFT

ter verkrijging van de graad Doctor aan de Vrije Universiteit Amsterdam, op gezag van de rector magnificus prof.dr. F.A. van der Duyn Schouten, in het openbaar te verdedigen ten overstaan van de promotiecommissie van de Faculteit der Exacte Wetenschappen op donderdag 22 oktober 2015 om 9.45 uur in de aula van de universiteit, De Boelelaan 1105

door

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geboren te Teheran, Iran

#### **Promotoren:**

prof.dr. W.M.G. Ubachs prof.dr. I. Powis

to my parents and my sister

The first essential in chemistry is that thou should perform practical work and conduct experiments, for he who performs not practical work nor makes experiments will never attain to the least degree of mastery.

Geber (Jabir ibn Hayyan), Persian polymath (c.721-c.815), Quoted in E. J. Holmyard, *Makers of Chemistry* (Clarendon Press, 1931), p.60. This thesis was approved by the members of the reviewing committee:

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The work described in this thesis was carried out in the Institute for Lasers, Life and Biophotonics and the Department of Physics and Astronomy at VU University Amsterdam and was financially supported by the Marie Curie Initial Training Network ICONIC.

The cover depicts the two enantiomers of limonene. Similar to a pair of hands, the molecules are non-superimposible mirror images of each other. The mass-selective three-dimensional photoelectron angular distributions show a forward-backward asymmetry along the laser propagation direction that reverses in sign when switching from one to another enantiomer.

ISBN:978-94-6259-852-2 Printed by: Ipskamp Drukkers B.V.

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#### INTRODUCTION

Molecular chirality has fascinated much of modern science in physics, chemistry and biology since its discovery in the 19<sup>th</sup> century. It appeared to be a fundamental property of life immediately after the discovery. Organic molecules are dominated by chiral molecules, e.g. only one out of twenty natural amino acids is achiral. Many of biochemical mechanisms in the human body involve chiral molecules and show a rigorous enantio-selectivity. Terrestrial life - as we know it - is homochiral and is based on L-amino acids and D-sugars (although some D-amino acids are found in the cell walls of bacteria, but not in bacterial proteins [1]). Chirality is very important in the pharmaceutical industry and crucial too, as the desired medicinal and therapeutic effects are found mostly in one enantiomer, while the other could be quite harmful.

Therefore, enantio-selective techniques for probing chirality are very much in demand, not only to discriminate between two pure enantiomers but also to have sensitivity to determine the enantiomeric excess ratio in a multi-component sample. Besides, investigation of electronic properties, molecular structure and conformation of chiral molecules can provide valuable information towards fundamental understanding of chirality. Chiroptical methods such as photoelectron circular dichroism (PECD) provides a robust probe for such studies.

This thesis explores chirality in molecules using the technique of PECD and a reaction microscope in single and multiphoton ionization regimes. The combination of PECD and electron-ion coincidence imaging shows the novel capability to measure mass-selective PECD of chiral molecules both for pure and multi-component mixtures.

#### **1.1** Historical introduction to molecular chirality

The first definition of chirality was given by *Lord William Thomson Kelvin* in 1884, during the Baltimore Lectures : "I call any geometrical figure, or group of points, chiral, and say it has chirality, if its image in a plane mirror, ideally realized, cannot be brought to coincide with itself." [2] This definition of chirality is still essentially accepted nowadays as it was re-phrased, by *Vladimir Prelog* in his Nobel Prize lecture almost a century after *Kelvin*'s speech, in 1975: "An object is chiral if it cannot be brought into congruence with its mirror image by translation and rotation." [3]

The word *chiral* is adopted from the Greek word, *cheir*, for *hand* as a common chiral object. Two non-superimposable mirror-imaged forms of a chiral molecule are called enantiomer (again from Greek words for *opposite* and *part*), see Fig. 1.1. The enantiomers are nowadays specified according to either their absolute configuration [4] with R (for Rectus) and S (for Sinister) letters or the direction of optical rotation [5] with (+) and (-) symbols. An older notation exists which labels enantiomers D- (for dextrorotatory) or L- (for levorotatory) based upon relating absolute configuration to that of chemical precursors, traceable back to glyceraldehyde as the absolute standard.



**Figure 1.1:** Example of the two enantiomers of limonene molecule. The gray and white spheres represent carbon and hydrogen respectively. The two enantiomeres are mirror-imaged but not superimposable.

Molecular chirality had been discovered a few decades before *Kelvin*'s speech. In the early 19<sup>th</sup> century, *Francois Arago* and later *Jean-Baptiste Biot* observed the fundamental phenomenon called *natural optical activity*. They observed that the plane of polarization of linearly polarized light was rotated when passing through a particular solid or liquid material. A few years later, *Augustin Jean Fresnel* studied the *optical rotation* in terms of differential refraction of right- and left- circularly polarized light and proposed that optical activity may have originated from "... helicoidal arrangement of the molecules of the medium, which would present inverse properties according to whether these helices were dextrogyrate or laevogyrate." [6].

In 1848, *Louis Pasteur* reported for the first time that an organic molecule could exist in two forms with opposite signs of optical rotation. He observed that crystallizing

of a sodium-ammonium tartrate solute (which is optically inactive) led into two forms of hemihedral crystals: "one asymmetric to the right, the other one asymmetric to the left" [7]. He manually separated these two forms and re-dissolved them. The new solutions, consequently, became optically active such that the rotation of polarization of these two was in opposite directions. The original solute was then an equi-molar mixture of these two forms that was called *racemic* mixture.

In 1874, *Jacobus Hendricus van 't Hoff* and *Joseph Achille LeBel* independently proposed a three-dimensional model for the structure of saturated carbon compounds where the four chemical bonds of the carbon atom were directed to the corners of a tetrahedron. The model explains how *optical rotation* is related to the three-dimensional structure of molecules [8]. The arrangement of atoms in three-dimensional space bonded in a molecule shows the existence possibility of two molecular forms which are mirror-imaged but not super-imposable.

Many physical properties of two enantiomers such as mass, melting point, boiling point, conductivity and so on are identical. Nevertheless, to distinguish between enantiomers, chiroptical methods using circularly polarized light (CPL) can be employed. Circular dichroism (CD) is a chiroptical method that has been widely used to determine and characterize enantiomers for many years. CD measures the differential absorption cross section of a chiral molecule for left- (LCP) and right circular polarized (RCP) light. However, this technique has some drawbacks. CD shows a weak signal in order of  $10^{-4}$  which is attributed to higher order electric quadrupole and magnetic dipole interaction. The small effect requires measurements to be made in dense samples, such as solutions. Recently, it was shown that the vibrational circular dichroism signal can be enhanced by an order of magnitude using electrochemical modulation of the energies of electronically excited states [9]. Yet, measurement in solution induces absorption cut-offs which limits the wavelength range available for the measurements. In addition, CD measurement typically requires a single chiral compound enantiomer and thus, it is not a reliable method for analysis of chiral isomer mixtures. Gas-phase approaches have been developed as alternative methods at higher sensitivity to overcome the limitations imposed by solvent. CD in ion yield generated by multiphoton laser ionization of chiral molecules in a TOF mass spectrometer has been reported recently to be capable of discriminating enantiomers in the gas phase [10–13].

An alternative powerful chiroptical method to probe isolated chiral molecules in the diluted gas phase sample with high sensitivity and selectivity is photoelectron circular dichroism (PECD) [14–16]. PECD records a forward-backward asymmetry in the photoelectron angular distributions (PAD) with respect to the propagation direction of the photon beam. The asymmetry effect was predicted to be stronger than CD since it originates purely from the first order electric dipole moment interaction.

*Ritchie*, in 1976, analytically demonstrated in his paper [17] that the PAD resulting from one-photon ionization of a randomly oriented chiral molecule by CPL behaved as

$$I_p(\theta) = \frac{I_{tot}}{4\pi} (1 + b_1^p P_1(\cos\theta) + b_2^p P_2(\cos\theta)), \qquad (1.1)$$
  
where  $I_{tot} = \int_0^\pi \int_0^{2\pi} I_p \sin\theta d\theta d\phi.$ 

Here,  $\theta$  is the angle between the velocity vector of the ejected electron and the propagation direction of the circular polarized light and  $P_n$  is the n<sup>th</sup> order Legendre polynomial.  $b_n^p$  coefficients depend on the polarization p as indicated by p = 0 for linear polarization, p = +1 for left circular polarization and p = -1 for right circular polarization. When either linear polarization or an achiral molecule is used, symmetry considerations determine that  $b_1 \equiv 0$  [17, 18]. Only in case CPL is used for photoionization of a chiral molecule, non-zero  $b_1^p$  is possible and consequently, the PAD shows a forward-backward asymmetry with respect to the light propagation direction because  $P_1$  evaluates as  $\cos\theta$ . Exchanging the enantiomer or handedness of the light results in a sign change of the  $b_1^p$  but not of the  $b_2^p$  parameter. In other words,

$$b_1^{+1} = -b_1^{-1} \text{ and } b_2^{+1} = b_2^{-1}.$$
 (1.2)

The PAD asymmetry can be expressed as a difference between the electron flux for leftand right- circular polarizations

$$I_{diff}(\theta) = I_{LCP}(\theta) - I_{RCP}(\theta) = I_{+1}(\theta) - I_{-1}(\theta) = 2b_1^{+1}P_1(\cos\theta).$$
(1.3)

Therefore, by considering the dichroism,  $I_{diff}(\theta)$  at  $\theta = 0^{\circ}$  or  $\theta = 180^{\circ}$ , PECD asymmetry is defined as  $2b_1$ .

In 2000, *Powis* calculated the quantitative estimation of PECD asymmetry to be in the order of  $10^{-1}$  [18] which is, three orders of magnitude higher than CD signal in absorption. The first PECD experiments were performed soon after and corroborated the capability of this technique [19, 20]. Moreover, performing experiments in a high vacuum apparatus facilitates electron imaging detection. The imaging PECD approach enables recording both the energy and angle of individual electrons with high efficiency.

Over the last decade, the PECD technique has been used to explore the photoionization dynamics, molecular conformation and structure of several chiral molecules using synchrotron radiation sources [21–25]. Recently, the first vibrational dynamics in photoionization of a chiral molecule has been studied where the high PECD sensitivity to the excited vibrational mode in the parent molecule was reported [26].

The PECD technique has been developed successfully in the multiphoton ionization regime using femtosecond laser systems [27–33]. This new approach enables a table-top experiment in the laboratory and also offers some new possibilities such as ionization via intermediate excited states. The PAD expected from a *n*-photon ionization of a chiral molecule with CPL can be expressed in the most general case as:

$$I_p(\theta) = \frac{I_{tot}}{4\pi} \left( 1 + \sum_{i=1}^{2 \cdot n} b_i^p P_i(\cos\theta) \right).$$
(1.4)

The multiphoton-PECD asymmetry can then be determined again from the difference between two polarizations as a single quantity in terms of the odd Legendre coefficients  $b_i^{+1}$ :

$$G = 2b_1^p - \frac{1}{2}b_3^p + \frac{1}{4}b_5^p - \frac{5}{32}b_7^p + \dots$$
(1.5)

#### **1.2** Summary and outline of the thesis

In this thesis, I investigate mass-selective PECD measurements on camphor, methyloxirane and limonene enantiomers measured by synchrotron radiation at SOLEIL synchrotron facility, in Paris and by a femtosecond laser system at LaserLaB Amsterdam. Moreover, I demonstrate that mass-selected PECD enhances the analytical application and enables enantiomeric differentiation detection in a multi-component mixture.

Several aspects of the experimental methods being used in the laboratory are discussed in **chapter 2**. The first part of this chapter comprises a detailed description of the electron-ion coincidence imaging spectrometer including a molecular beam setup to provide samples in gas-phase, electron and ion detection system, 3D velocity map imaging and calibration of the electron detector and ion time-of-flight spectrometer. I also give a statistical argument related to false coincidences in the measurements. The last part of this chapter introduces the experimental methods for multiphoton PECD measurements. In particular, it consists of data acquisition, data analysis and error estimation for PECD asymmetry determination.

The femtosecond laser system is described in **chapter 3**. Special attention is given to non-linear optical methods that were implemented and developed in the laboratory in the course of this research. These include the second and third harmonic generation of the fundamental output of the laser as well as an extensive description of a home-built non-collinear optical parametric amplifier (NOPA) used for production of tunable femtosecond pulses in the visible spectral region. The visible light is upconverted to the UV region by a home-built sum frequency mixing setup. Further attention is given to home-built ultrashort pulse characterization setups. A single-shot intensity autocorrelator is used to monitor pulse duration of fundamental outputs during the measurements. The visible pulses generated by the NOPA are characterized by an interferometric autocorrelator and the duration of UV pulses is determined by measuring the cross-correlation signal resulting from the multiphoton ionization of Xe inside the coincidence machine. Finally, the generation and characterization of circular polarized light is discussed.

**Chapter 4** presents the photoionization study of pure limonene enantiomers using VUV synchrotron radiation with a photon energy ranging from threshold to 18 eV performed with double imaging coincidence spectrometer DELICIOUS III. The assignment of the limonene slow photoelectron spectrum (SPES) is discussed. PECD are obtained across a range of photon energies for the HOMO/HOMO-1 band for mass-selected parent ion data. The VMI recordings made for photon energies below 10 eV reveal a very strongly structured PECD. The oscillations in PECD spectra are strongly correlated with the vibronic features in the photoelectron spectrum. At higher photon energies, due to a loss in VMI resolution, the VMI photoelectron spectra become featureless and PECD measurements will merely see an average value. More interestingly, it is also observed that the sign of PECD asymmetries changed by passing from ionization of the HOMO to HOMO-1 orbital.

Chapters 5-7 report mass-selective multiphoton PECD as an asymmetry in photo-

electron angular distribution after the ionization of pure enantiomers of two different types of chiral molecules using femtosecond multiphoton ionization and the electronion coincidence imaging spectrometer.

The small chiral molecule methyloxirane is studied in **chapter 5** using femtosecond laser pulses at 420 nm. The ionization at this wavelength requires at least four photons. The chiral (odd) terms in the photoelectron angular distribution expression are isolated by switching the laser between left- and right-circular polarization, and observing the differences in the full three-dimensional electron momentum distribution recorded in the electron-ion coincidence technique. Electron events additionally are filtered by coincident ion mass, providing mass-tagged electron distributions and quantitative measures of the multiphoton PECD asymmetry that help characterize the different ionization channels. For the production of the ground state parent cation, the magnitude of the mean chiral asymmetry is measured to be 4.7%, with the peak magnitude exceeding 10%.

In **chapter 6** both limonene enantiomers are investigated by circularly polarized 420 nm femtosecond laser pulses in the single-detector coincidence spectrometer. Ion mass and photoelectron energy spectra identify the dominant (2+1) multiphoton ionization mechanism. TDDFT calculations of the Rydberg excitations, considering the three lowest energy equatorial conformers of limonene, are used to help interpret the ionization pathway. PECD measurements on pure enantiomers reveal a chiral asymmetry of  $\pm 4\%$ .

Mass selected multiphoton PECD of limonene is discussed in **chapter 7** using three different wavelengths (420 nm, 412 nm and 392 nm) for excitation in combination with the double-detector coincidence spectrometer. The results are discussed and compared with experiments reported in the previous chapters on limonene. PECD asymmetry shows a mirroring between the dichroism of two enantiomers at all wavelengths. The 392 nm PECD shows a striking sign change across the photoelectron band with the maximum of about  $\pm 9\%$  for mass-tagged parent ion electrons. Moreover, we compare two different approaches for analysisng the experimental data to extract quantitative PECD.

**Chapter 8** presents a proof-of-principal demonstration of a direct method for simultaneous enantiomer specific identification of chiral molecules in multi-component mixtures. Enantiomers are differentiated by coincident mass-selected PECD using a laser-based imaging electron-ion spectrometer. Mixed vapors of two chiral monoterpene molecules, limonene and camphor, were irradiated by a circularly polarized femtosecond laser at 392 nm. The momentum of photoelectrons coincident with parent ion masses is determined by electron imaging. PECD asymmetries are observed in the mass-tagged electron distributions for camphor (4%) and limonene (2%) that switch sign according to the handedness (R- or S-) of the enantiomer in the mixture. When the camphor component was prepared with just 50% enantiomeric excess (e.e.) its observed PECD scaled proportionately. The results demonstrate that mass spectrometric identification of mixtures of chiral molecules and quantitative determination of e.e. can be achieved in a table-top instrument employing mass-selected PECD.

# 

### **EXPERIMENTAL METHODS**

#### 2.1 Introduction

Photoelectron circular dichroism (PECD) is used as an experimental technique to study chiral molecules in the gas phase where the complexities imposed by solvent-solute interaction can be eliminated. For such experiments, molecular beams are the tool of choice for preparing samples in the gas phase, and charged particle imaging provides energy and angular distribution information of photoelectrons emitted after ionization. Moreover, combination of mass-spectroscopic imaging and PECD in an electron-ion coincident imaging spectrometer offers the ability for mass-selective discrimination of chiral molecules.

In this chapter, several experimental aspects that I used for PECD experiments are discussed. The chapter is structured as follows. In section 2.2, sample preparation in gas phase and molecular beam generation are described. In section 2.3, the charged particle imaging technique is first reviewed and then the experimental setup is presented in detail. In section 2.4, the PECD experiment together with data acquisition and data treatment are explained.

# 2.2 Sample preparation and molecular beam generation

Supersonic atomic and molecular beams [34, 35] are used as an experimental approach to prepare isolated and cold molecules in many fields of physics and chemistry. The gas sample is seeded in a noble gas and the mixture expands through a nozzle into high vacuum. The high pressure gas inlet behind the nozzle (from < 1 bar up to few tens of bar) is essential to expand the molecular gas adiabatically into high vacuum chambers resulting in velocity distribution narrowing along the jet axis and cooling down the molecular samples. Cooling is achieved through collisions of gas samples with the carrier gas that decrease the internal energy. Translational temperatures as low as 1 K can be achieved easily in molecular beams. However, the rotational cooling is typically less efficient than the translational cooling and vibrational cooling is even less efficient than rotational cooling.

Many molecules of our interest to study are not available in the gas phase under normal conditions. Therefore, one can flow a carrier gas through liquid or solid samples with a convenient vapour pressure (few mbar at room temperature) to transfer the molecules via a nozzle expansion into the vacuum. For the samples with lower vapour pressure, slightly heating the reservoir containing the sample may help to get the sufficient density of molecules in the gas phase as long as decomposition is not a problem.

In experiments performed in Amsterdam, liquid and solid samples were held respectively in a stainless steel bubbler and a sample reservoir outside the vacuum chambers at room temperature. The reservoir is separated from the transfer lines by sintered steel filters to prevent clogging the nozzle by solid dust. A stream of pure neon gas (typically < 1 bar backing pressure) sweeps the vapour of samples through a stainless steel transfer line. The neon gas containing seeded sample molecules then expands through a 150  $\mu$ m diameter conical nozzle in the source chamber. The expanding gas mixture is doubly skimmed as it passes through the buffer chamber into the imaging spectrometer chamber. The first skimmer (500  $\mu$ m diameter) separates the source from the buffer chambers while the second skimmer (200  $\mu$ m diameter) separates the buffer from the imaging chambers. Skimmers are fixed in their positions and separated 12 cm from each other.

The nozzle is mounted on a three dimensional translational stage in the source chamber. The skimmer-to-nozzle distance is fixed (about 2.5 cm) while the position of the nozzle can be controlled horizontally (along laser beam direction) and vertically (along TOF direction) by two knobs from outside of the molecular machine. The nozzle is aligned, on a day-to-day basis, for the highest Xe ion signal and highest pressure inside the imaging chamber. Under this configuration, the translational temperature of about 9.4 K was reported for a seeded beam of 1.4% Xe in Ne at 1 bar backing pressure [36].

# 2.3 Velocity map electron-ion coincidence imaging spectrometer

The first realization of ion imaging technique to study a molecular photodissociation process was reported by Chandler and Houston in 1987 [37]. Such a technique revolutionized experimental studies in reaction dynamics by providing angular, speed and internal energy information. In the typical ion imaging technique, the initial 3D momentum distribution of a recoiling ion is projected onto a 2D micro-channel plate (MCP) [38] detector followed by a phosphor screen and (CCD) camera. Subsequently, a data recovery method (known as an inversion method [39]) is needed to reconstruct the initial 3D momentum distribution from the recorded 2D data. However, in this technique, the spatial resolution is still relatively low due to rather extended ionization source volume for charged particles. The next breakthrough in the ion imaging technique came in 1997 with the invention of velocity map imaging (VMI) technique [40]. Eppink and Parker employed a three electrostatic plate (repeller, extractor and ground TOF entrance) configuration and removed grids from electrodes separating extraction, acceleration and TOF region. The open electrodes caused curved electric field lines that act as ion lenses to focus charged particles with the same velocity (speed and direction) to the same spot in the detector irrespective of the initial position where they are formed. By that the spatial resolution was increased dramatically.

In conventional VMI method introduced by Eppink and Parker, the ion sphere is *crushed* into a disc with small width along the TOF direction by an inhomogeneous extraction field. Therefore, the entire ion sphere can be essentially recorded at the same time in 2D image. To extract the maximum information from the 2D images, the Abel inversion algorithm is still needed to reconstruct the 3D velocity distributions of the charged particles recorded in the image. Abel inversion requires an axis of cylindrical symmetry parallel to the imaging plane. In other words, the propagation direction for

circularly polarized light (CPL) or the polarization direction for linearly polarized light must be parallel to the detector surface.

To avoid the need for inversion techniques, methods such as slice imaging [41–43] and 3D-imaging [44] have been developed to measure the 3D momentum distribution directly. In slice imaging, the ion sphere arrival time spreads out sufficiently and homogeneously so that a simple gating of the MCP detector can slice a narrow part of the Newton ion sphere to obtain the full 3D information. In 3D imaging, all three components of a single particle are recorded simultaneously by a time and position sensitive detector (e.g. using delay-line anode). Another advantage of 3D imaging techniques is the capability to perform coincidence measurements.

Ionization of molecules produces electron(s) as well as ion(s). Determination of the correlated energetic and angular distributions of these particles gives complete kinematic information of photo-ionization and -dissociation process. This information can be obtained by so-called *photoelectron photoion coincidence* (PEPICO) techniques and have been utilized fruitfully for many years [45]. The first illustration of PEPICO experiment performed with a femtosecond laser system appeared in 1997 [46, 47]. The experimental setup contained a magnetic bottle electron spectrometer and a time-of-flight mass spectrometer. The first fully angle-resolved PEPICO studies was reported by Powis *et al.* in 1999 [48]. In the same year Hayden *et al.* [49] combined femtosecond time-resolved *imaging* with the PEPICO technique measuring 3D energy and angular distributions for electrons and ions. At the same time, the recoil-ion and cold target recoil-ion momentum spectroscopy (COLTRIMS) reaction microscope [50, 51] was invented using delay-line detectors to measure full correlated 3D momentum distributions of photoionization products. Very recently, PEPICO experiments with few cycle laser pulses at 400 kHz have been reported [52].

Apart from the applications of VMI setups in laser-based laboratories, several VMI coincidence apparatuses were developed successfully in synchrotron facilities over last few years [53–56]. In chapter 4, I will give a short review on the so-called DELICIOUS III electron-ion coincidence detector [56] that operates on the DESIRS VUV beam line at the SOLEIL synchrotron near Paris.

#### **2.3.1** Experimental setup

The experimental double VMI coincidence imaging apparatus, constructed in Amsterdam in 2008, is described in detail elsewhere [57, 58]. Apart from the results reported in chapter 4, all measurements were done with this coincidence spectrometer.

Figure 2.1 shows a schematic configuration of the apparatus and a photo of the vacuum machine with electronics. The coincidence imaging apparatus consists of three differentially pumped UHV chambers, a source chamber, a buffer chamber and the imaging spectrometer chamber. Oil-free pumps are used in the whole machine to avoid contamination from the vacuum system as much as possible. The source, buffer and imaging chambers are pumped by a 1250 l/s (Alcatel ATH 1300 MT), a 400 l/s (Alcatel, ATH 400 MT) and a 2100 l/s (Alchatel, ATH 2300 MT) magnetic levitated turbo pumps respectively. All turbo pumps are backed by a single oil-free roots pump





Schematic configuration of ion optics (Repeller (R), Extractor (E) and extra lens (L)) and TOF tubes for single- and double- detector coincident imaging mode. In Single-detector mode the coincident ion is extracted (dashed line) to the same detector as for electron detector while in double-detector mode it is extracted downward (solid line) to the opposing detector with a longer TOF tube for the ion. C) Photo of the coincidence laboratory with the coincidence spectrometer, electronics, turbo and roots pumps, gas handling station in front. The optical table with the femtosecond laser system, non-collinear optical parametric amplifier is partially visible behind the coincidence machine.

(Alcatel ACP28G). The continuous molecular beam is generated in the source and the buffer chambers as it is described in section 2.2. In the imaging chamber the molecular beam intersects the laser light at 90° about 45 cm from the nozzle. A lens with a focal length of 30 cm is used to focus the femtosecond laser waist down to about 100-150  $\mu$ m in diameter. To reduce scattered laser light reaching the detectors, light baffles are used at entrance and exit ports of the laser beam.

After the ionization of the molecule by a laser pulse, the electron and ion are extracted to two opposing time-of-flight (TOF) tubes by several charged particle lenses. Both TOF tubes and lenses are shielded by a 1mm thick  $\mu$ -metal tube. The length of electron and ion TOF tube are 5.25 cm and 29.5 cm respectively. To improve the particle's energy resolution in the setup, high voltage (HV) switches (Behlke HTS-51), operated at the repetition rate of the laser system, are employed to change the magnitude and polarity of the high voltages on the ion lenses. Due to the shorter TOF of the electron (~15 ns) than the ion (~ in  $\mu$ s order), the ion lenses are first set to image the electrons.

Our VMI setup consists of three electrostatic electrodes (repeller ( $\mathbf{R}$ ), extractor ( $\mathbf{E}$ ) and extra lens (L)). Extra lens, L, in our setup facilitates a lower extraction voltages (compared with the standard VMI configuration with repeller and extractor plate only) while preserving the VMI condition with a better time resolution. The VMI voltages for electron detection has been determined by a SIMION simulation [57]. They were also adjusted for optimum electron images before measurements. The typical acceleration voltages of  $R_e = -520$  V,  $E_e = -385$  V,  $L_e = -275$  V gives the ultimate electron energy resolution of  $\Delta E/E=3.5$  % for electrons near 2 eV [57, 59]. The voltages for ion detection were empirically optimized as  $R_i = 2000$  V,  $E_i = 1460$  V,  $L_i = 0$  V, for optimal mass resolution (and not necessarily optimal voltages for VMI of ions). Figure 2.1B shows schematic overview of the charged particle lens. The voltages are initially set for electron detection mode for 200 ns. Then, the voltages are switched to ion detection mode within about 50-70 ns. The lenses are maintained at positive voltages long enough (20  $\mu$ s) so that all desired ionic fragments can be detected. Finally, the voltages switch back to electron detection mode within about 10  $\mu$ s and are ready for next event.

The high voltages on the charged particle lenses could also be switched in such a way that both electron and the coincident ion are extracted to the same detector (see Fig.2.1 B). This single-detector coincidence imaging setup [60] can still measure the full three-dimensional velocity distribution of electron and ions by choosing the proper high voltages [61]. However, due to the shorter length of ion TOF tube the mass resolution is slightly reduced (see Fig.2.6). Only the measurement reported in chapter 6 was performed with the single-detector coincidence imaging mode. The voltages on the ion optics operated for detecting electron were similar to the double-detector mode while for ion detection were  $R_i = 2000$  V,  $E_i = 1610$  V,  $L_i = 0$  V.

#### 2.3.2 Detector and 3D-imaging

The detector in the coincidence apparatus consists of two parts, a MCP followed by a time and position sensitive delay-line detector (DLD) which are mounted at the end of each TOF tube. The MCPs are in chevron configuration with 40 mm active diameter and 5  $\mu$ m pore size. The DLDs (from Roentdek [62]) are located at the back of MCPs and consist of two different wires oriented orthogonal to each other, one for each dimension. The schematic and a photo of detector system are depicted in Fig. 2.2.



**Figure 2.2:** (left, top) A photo of a detector unit consisting of a MCP mounted in front of the delay line detector (DLD). (Left, bottom) A photo of the DLD. (Right) A schematic representation of the DLD. The DLD comprises two wires, one for each dimension. The electron cloud generated from the back of the MCP hits the DLD and pulses of electrons travel to four ends of wires. The time difference between two signals at both ends of each delay line wire provides the position information along *x* and *y* coordinates ( $x = X_1 - X_2$  and  $y = Y_1 - Y_2$ ). The time sum of the two ends of delay line wire ( $X_1 + X_2 = Y_1 + Y_2 = \text{const}$ ) is used for direct measurement of the ion TOF in our setup.

The full three dimensional momentum distributions of ions and electrons can be recorded by DLDs. A single hit of a charged particle (electron or ion) to front surface of the MCP induces an avalanche of electrons in the MCP pore and creates an electron cloud at the back side of the MCP. The electron cloud is accelerated toward the DLD by a potential difference between MCP and DLD. Subsequently, the electron cloud hits somewhere on the DLD wires and induces a signal in the wires. The induced signal propagates to both ends of each wire. The delay line signals are decoupled and processed by a differential amplifier (ATR-19 from Roentdek) followed by a high resolution Time-to-Digital (TDC) board (HPTDC form Roentdek). By measuring the signal arrival times at both ends of the wire, the signal origin along the delay line can be determined. In summary, one event on the MCP results in two pairs of time on delay line ( $X_1, X_2$ ) and ( $Y_1, Y_2$ ), see Fig. 2.2. The time difference between two signals at both ends of each delay line wire provides the position information along  $x (= X_1 - X_2)$  and y

 $(= Y_1 - Y_2)$  coordinates with the conversion factor of 1.9 ns/mm. On the other hands, the time sum of two signals of each delay line wire is constant  $(X_1 + X_2 = Y_1 + Y_2 = \text{const})$  and is used to determine the TOF of ions in our spectrometer. Consequently, the position and time (x, y, t) recorded by a DLD for each individual event can be directly mapped to the three momentum components  $(p_x, p_y, p_z)$ . Therefore, unlike the phosphor screen/CCD camera based imaging detector used for 2D projection image of (non-coincident) photoelectrons, no inversion routine (like Abel transformation) is needed to recover data and extract full 3D kinetic energy and angular distributions.



**Figure 2.3:** The projections of 3D-photoelectron images of Xe on three orthogonal surfaces. 4-photon ionization is induced by 150 fs laser pulses at 392 nm with LCP (left) horizontal (middle) and RCP (right) polarizations of laser pulses.

The TDC has a resolution of 25 ps. In order to have a better accuracy on the electron TOF, a pickup pulse from the back of the MCP plate is processed by a time-to-analogue converter (TAC, SPC-130 from Becker & Hickl) [63]. The TAC is operated in inverse start-stop mode. The start and stop trigger signals to TAC are respectively the electron pickup pulse and the laser pulse (collected by a fast photodiode). Under this mode of operation, the TAC is only triggered if an electron is recorded and thus, it works at the rates of electron events. In our spectrometer, an ultimate electron TOF resolution of about 16 ps [58] can be achieved.

Fig. 2.3 shows the projection of a measured 3D-electron image in three orthogonal planes. After calibration of the electron detector the full 3D momentum of the electron can be obtained.

#### 2.3.3 False coincidence

False coincidence events are electron-ion pairs that originate from two different molecules. It is essential to eliminate the false coincidence events as much as possible from the data in a coincidence measurement. There are some well-established false coincidence treatments in the literature for non-pulsed experiments [64–67] using a continuous light source e.g. synchrotron radiation. In such experiments, the false coincident ions are randomly distributed in time which appear as a constant background

in ion mass spectrum. Thus, the coincident events can be easily estimated from the baseline height between the peaks.

However, in the measurements with pulsed lasers, the source of ionization is as short as the pulse duration. Since the laser pulses are focused in the interaction region, many electrons and ions may be produced by each laser pulse and usually none of them can be correlated uniquely as corresponding ion-electron pairs. Both true and false coincident ions have a same temporal correlations and a distinct structure according to their mass. Hence, the estimation of false coincident ions is not straight forward in pulsed-based experiments. In order to separate two different events and reduce the probability of false coincidence events in this experiment, the ionization events per laser pulse must be kept very low.

False coincidences may arise from the situation when multiple events, created from a single laser shot, arrive at the detector but with a greater separation than detector dead-time. The detector dead-time in our apparatus is about 30 ns. Thus, on the electron side, it is very unlikely that two electrons can be recognized by the detector. On top of that, because TAC is not a multiple hit device, we have a complete paralysis in the TAC channel so that only the first hit on the electron detector is recorded. At the end of measurements, the signals from the TDC and TAC channels are synchronized. It means that only when the four TDC channels and the single TAC channel receive a signal, the electron event is saved into the data file.

On the ion side, because ions have greater range of flight time than electrons, it is possible that two ions with different masses exceed detector dead-time. Therefore, the probability of recognizing more than one ion per laser shot by the ion detector is higher than detecting of two or more electrons by the electron detector. Our acquisition program only records and analyses the first hit registered by TDC. In other words, if two ions were generated by a laser pulse the second hit is disregarded. Again, the program only saves an event into the data file when the four TDC channels record a signal.

The time windows to resolve electrons and ions in our data acquisition program are 100 ns and 17000 ns respectively. Under this condition, a valid coincidence event is saved when all the eight TDC channels and the single TAC channel have a recorded event.

In order to work out the coincidence counting statistics and false coincidence treatments in our experiments we need to deal with the detector efficiency. In the case the efficiency of either detectors is unity and no multiple particle events per laser pulse is registered, there is no false coincidence and we can store the data with count rate of 1. However, the finite detection efficiency for electrons and ions requires a very low count rate (<<1). Following the analysis given by Stert *et al.* [68], the detected electron, ion events are

$$w_i = \xi_i \bar{n} \quad , \quad w_e = \xi_e \bar{n} \tag{2.1}$$

where  $\xi_i$  and  $\xi_e$  are the detection efficiencies of electron and ion respectively,  $\bar{n}$  is the average number of electron-ion pairs produced per laser pulse. Assuming Poisson



**Figure 2.4:** (Top) total  $(w_{11})$ , true  $(w_{11}^t)$  and false  $(w_{11}^f)$  coincidence counts versus average number of ion-electron pairs per laser shot. The electron and ion detection efficiencies are 0.18 and 0.13 respectively. (Bottom) the ratio of the number of true coincidences to the total number of coincidences versus electron count rate.

distribution, the detection of exactly one electron and one ion simultaneously per laser shot (total coincidence events) is given by

$$w_{11} = \xi_i \xi_e \bar{n} [1 + \bar{n} (1 - \xi_e) (1 - \xi_i)] \times \exp\left[-\bar{n} + \bar{n} (1 - \xi_e) (1 - \xi_i)\right].$$
(2.2)

Subsequently, true and false coincidences can then be determined as

$$w_{11}^t = \xi_i \xi_e \bar{n} \times \exp\left[-\bar{n} + \bar{n}(1 - \xi_e)(1 - \xi_i)\right], \qquad (2.3)$$

$$w_{11}^f = \xi_i \xi_e \bar{n}^2 (1 - \xi_i) (1 - \xi_e) \times \exp\left[-\bar{n} + \bar{n}(1 - \xi_e)(1 - \xi_i)\right], \qquad (2.4)$$

where  $w_{11}=w_{11}^t+w_{11}^f$ . The experimental values of  $w_e$ ,  $w_i$  and  $w_{11}$  are obtained from each measurement and  $\xi_i$ ,  $\xi_e$  and  $\bar{n}$  can be determined by Eq. 2.1 and Eq. 2.2. Table 2.1 shows the number of counts recorded for several experiments on different days. The typical values for the detection efficiency are  $\xi_i = 0.13$  and  $\xi_e = 0.18$ .

**Table 2.1:** Detected electron, ion, coincidence and TAC counts and their corresponding  $\xi_i$ ,  $\xi_e$  and  $\bar{n}$  values for different experiments.

detected events							
laser shots	electron	ion	coin	TAC	$\xi_e$	$\xi_i$	n
1500000	121710	88717	18138	148405	0.17	0.13	0.47
1500000	137198	93409	21064	171649	0.20	0.13	0.47
1500000	137127	89714	20544	168049	0.20	0.13	0.46
1500000	121973	85952	18395	146098	0.19	0.13	0.44
1500000	102104	81007	14176	125462	0.14	0.11	0.47
1500000	195603	119391	35790	218895	0.28	0.17	0.46

The total  $(w_{11})$ , true  $(w_{11}^t)$  and false  $(w_{11}^f)$  coincidence rates as a function of  $\bar{n}$  are plotted in Fig. 2.4(top). It is clear that for small  $\bar{n}$  the true coincidence rate is much larger than the false coincidence rate. However, under this circumstance, the number of detected coincidence events becomes small. Thus, it is a matter of compromise how low the count rate should be. Fig. 2.4(bottom) shows the ratio of true to total coincidence rate as a function of electron count rate. According to this plot, if we keep the electron count rate  $(w_e)$  around 0.08, we achieve about <20% false coincidences.

## **2.3.4** Energy calibration of the electron detector and ion mass resolution

The energy scale and the origin of the 3D electron velocity distribution are usually calibrated by multiphoton ionization of a seeded beam of 5% Xe in Ne.

In Fig. 2.5, typical photoelectron spectra measured for Xe are shown for different laser wavelength excitation. These calibration images on Xe photoionization are taken under the same conditions, using the same position and polarization settings of the



**Figure 2.5:** The photoelectron VMI (left) and corresponding kinetic energy distribution (right) measured in coincidence with Xe ions at 392 nm (top) and 420 nm (bottom). With the ionization energy of xenon ( IE  $({}^{2}P_{3/2}) = 12.13$  eV and IE  $({}^{2}P_{1/2}) = 13.44$  eV) and measured wavelength of femtosecond laser, it can be concluded that the electrons result from 4 (top) and 5 (bottom) photon ionization. The electron kinetic energy can then be calibrated using energy conservation: nhv - IE = photoelectron energy. n is the number of photons needed to ionize Xe.



**Figure 2.6:** TOF spectrum of Xe isotopes recorded in coincidence with electrons with (A) double-detector mode and (B) single-detector mode. The TOF of Xe isotopes was determined with FWHM of 1 ns and 2 ns respective. The mass resolutions of about  $\Delta m/m = 4300$  (A) and  $\Delta m/m = 950$  (B) for masses around 136 amu are obtained for these two modes of coincidence detection.

laser beam, within the same experimental runs. This allows for a careful analysis of the calibration of the photoelectron images.

Figure 2.6 shows typical TOF spectra of Xe isotopes recorded by 4-photon ionization at 392 nm using the double-detector and the single-detector coincidence imaging modes. In both modes of operation, the high voltages for ion detection are optimized to achieve the best mass resolution and thus the ion optics is not necessarily operated under a VMI condition. Moreover, using the HV switches in the setup ,which is improved the ion extraction condition very much, results in a an excellent ion mass resolution, see Fig. 2.6. The shorter length of the TOF tube in the single detector mode with respect to the double-detector mode reduces the arrival time resolution and achievable mass resolution of ions. Nevertheless, the single detector mode is still perfectly usable as long as a few fragments or fragments with enough mass difference are detected.

The TOF mass spectrum can be calibrated with respect to the TOF of different Xe isotopes since the TOF of a charged particle is proportional to square root of its mass  $(TOF \propto \sqrt{m})$ .

# 2.4 PECD experiment, data acquisition and data analysis

The PECD can be extended to the multi-photon ionization regime. Multiphoton PECD and experiments using a femtosecond laser system are described in detail elsewhere [28, 29, 36]. Here, I give a brief description of the multiphoton PECD, data acquisition and analysis.

The photoelectron angular distribution (PAD),  $I_p(\theta)$ , arising from *n*-photon ionization of a chiral molecule with circularly polarized light is given by [28],

$$I_p(\theta) = \frac{I_{tot}}{4\pi} \left( 1 + \sum_{i=1}^{2 \cdot n} b_i^p P_i(\cos\theta) \right),$$
(2.5)

where p is the polarization of the light,  $P_i(cos\theta)$  are Legendre polynomials,  $b_i^p$  are the corresponding expansion coefficients. For CPL,  $\theta$  is the angle between the electron momentum and the propagation direction of the laser beam.

Figure 2.7 shows the experimental PAD data of S-methyloxirane obtained by LCP and RCP. The data are fitted by Eq. 2.5 and show a permanent forward-backward instrumental asymmetry that may be attributed to detector gain inhomogeneity. Nevertheless, in fact, the sign of odd  $b_i^p$  coefficients are changed by switching the polarization (or exchanging enantiomers) while the even coefficients are unaltered. Therefore, one can isolate the chiral (odd) coefficients by examining the dichroism between two polarizations (or two enantiomers):

$$I_{LCP}(\theta) - I_{RCP}(\theta) = \frac{I_{tot}}{4\pi} \left( \sum_{i=1}^{n} 2b_{2i-1}^{+1} P_{2i-1}(\cos\theta) \right).$$
(2.6)



**Figure 2.7:** Experimental (symbols) and best-fit (line) angular distributions of masstagged m/z=58 and energy selected coincident electrons for both LCP (left) and RCP (right) for S-methyloxirane. The distributions were fitted using the expression  $I(\theta) =$  $(1 + b_1P_1 + b_2P_2 + b_3P_3 + b_4P_4 + b_5P_5 + b_6P_6 + b_7P_7 + b_8P_8)$ , see Eq. 2.5. The experimental data shows a permanent forward-backward instrumental asymmetry which is expected to be polarization independent.

The multiphoton PECD asymmetry can then be expressed as a single value by (expanded here for the case of a 4-photon ionization process) [28, 36]:

$$G = 2b_1^p - \frac{1}{2}b_3^p + \frac{1}{4}b_5^p - \frac{5}{32}b_7^p, \qquad (2.7)$$

where  $b_i^p$  coefficients are obtained by fitting the measured difference PAD with Eq. 2.6. Using the difference PAD expression (Eq. 2.6) has the experimental advantage respect to the direct observation of PAD (Eq. 2.5) since it can cancel any instrumental asymmetry.

Alternatively, a fully equivalent G value (Eq. 2.7) can be obtained, directly, as it is shown in the appendix, from the integrated electron counts in the forward,  $N_{p,f}$ , and backward,  $N_{p,b}$ , hemispheres for each polarization, p:

$$G = 4 \times \frac{F - B}{F + B}, \tag{2.8}$$

where,  $F = N_{LCP,f} + N_{RCP,b}$  and  $B = N_{LCP,b} + N_{RCP,f}$ . To ensure optimum cancellation of instrumental asymmetry, the same total count for each polarization is required  $(N_{LCP,f} + N_{LCP,b} = N_{RCP,f} + N_{RCP,b})$ . In the appendix the evaluation of instrumental asymmetry cancellation is discussed.

Assuming Poisson counting statistics, there is an uncertainty  $\sqrt{N}$  in each count and

so the error in PECD is obtained by standard error propagation:

$$Error_{absolute} = \left| G \times \frac{2FB}{F^2 - B^2} \sqrt{\frac{F+B}{FB}} \right|.$$
(2.9)

Equation 2.7 shows how higher-order odd  $b_i$  coefficients contribute to determine multiphoton PECD asymmetry. The absolute PECD value is increased when the odd coefficients in the alternating sum change sign. This has been seen in the camphor measurement [28] where the PECD was calculated around 7.9% from  $b_1$ =+0.28,  $b_3$ =-0.48 and  $b_5$ =+0.002.

In general, there might be a case where the odd  $b_i$  coefficients cancel each other in Eq. 2.7 so that the total *G* value leads to zero. Thus, under such a condition, the above mentioned approach may not be a good criterion for quantifying chiral effect. Baumert *et al.* [31] recently proposed a method to overcome this cancellation effect. They derive a quadratic PECD (QPECD) measure as:

$$QPECD \approx \sqrt{12} \times \sqrt{\sum_{i_{odd}} \frac{b_i^2}{2i+1}},$$
(2.10)

However, multiphoton PECD asymmetries reported in this thesis, for methyloxirane and limonene, strongly depend on  $b_1$  while  $b_3$ ,  $b_5$  and  $b_7$  contributions are almost negligible, see Table 5.3 and 7.2. Therefore, *G* and QPECD values are very close to each other for these systems. Table 2.2 shows the comparison of these two values from methyloxirane data, reported in chapter 5.

**Table 2.2:** Calculated *G* and QPECD values of methyloxirane enantiomers for  $1.3\pm0.2$  eV electrons coincident with m/z=58 parent ions.

	$G^{\mathrm{a}}$	QPECD <sup>b</sup>
S- methyloxirane	0.047±0.012	0.050±0.011
R- methyloxirane	-0.048±0.011	0.049±0.009

<sup>a</sup> Obtained from Legendre polynomial (LP) fitting coefficients, given in Table 5.3, using Eq. 2.7. Error estimates are derived from the LP coefficient fitting uncertainty.

<sup>b</sup> Obtained from Legendre polynomial (LP) fitting coefficients, given in Table 5.3, using Eq. 2.10. Error estimates are derived from the LP coefficient fitting uncertainty.

In multi-photon PECD measurements reported in this thesis, the circular polarization (LCP/RCP) is altered every 500 s (1.5 million laser shots) in order to reduce the effect of any experimental drift in, for instance, laser intensity, molecular beam stability, or laser/molecular beam crossing position. At the end of the measurement, after careful checks that the center of the electron data are the same (by checking the xenon data files taken during the measurements), all files with the same polarization are combined together for data analysis.

## **APPENDIX: MULTIPHOTON PECD EVALUATIONS**

In a *n*-photon ionization process, the number of electrons emitted into forward  $(N_{p,f})$  and backward  $(N_{p,b})$  hemispheres along the light propagation direction for a given laser polarization, *p*, can be obtained from following integrals:

$$\begin{split} N_{p,f} &= \int_{0}^{\frac{\pi}{2}} \int_{0}^{2\pi} I_{p}(\theta) \sin\theta d\theta d\phi \\ &= \frac{N_{p,tot}}{4\pi} \cdot 2\pi \int_{0}^{\frac{\pi}{2}} \left( 1 + \sum_{i=1}^{2n} b_{i}^{p} P_{i}(\theta) \right) \sin\theta d\theta, \end{split}$$

$$N_{p,b} = \int_{\frac{\pi}{2}}^{\pi} \int_{0}^{2\pi} I_{p}(\theta) \sin\theta d\theta d\phi$$
$$= \frac{N_{p,tot}}{4\pi} \cdot 2\pi \int_{\frac{\pi}{2}}^{\pi} \left(1 + \sum_{i=1}^{2n} b_{i}^{p} P_{i}(\theta)\right) \sin\theta d\theta,$$

where,  $N_{p,tot} = N_{p,f} + N_{p,b}$ . Therefore, one can calculate these integrals for a 4-photon process (taking into the account that  $b_i^{LCP} = -b_i^{RCP}$ ) as:

$$\begin{split} N_{LCP,f} &= \frac{N_{LCP,tot}}{2} \left[ 1 + \frac{1}{2} b_1 - \frac{1}{8} b_3 + \frac{1}{16} b_5 - \frac{5}{128} b_7 \right], \\ N_{LCP,b} &= \frac{N_{LCP,tot}}{2} \left[ 1 - \frac{1}{2} b_1 + \frac{1}{8} b_3 - \frac{1}{16} b_5 + \frac{5}{128} b_7 \right], \\ N_{RCP,f} &= \frac{N_{RCP,tot}}{2} \left[ 1 - \frac{1}{2} b_1 + \frac{1}{8} b_3 - \frac{1}{16} b_5 + \frac{5}{128} b_7 \right], \\ N_{RCP,b} &= \frac{N_{RCP,tot}}{2} \left[ 1 + \frac{1}{2} b_1 - \frac{1}{8} b_3 + \frac{1}{16} b_5 - \frac{5}{128} b_7 \right], \end{split}$$

If we consider multiphoton-PECD (MP-PECD) asymmetry as the relative difference in forward and backward hemispheres to the average counts per hemisphere, we have:

$$G_{LCP} = \frac{N_{LCP,f} - N_{LCP,b}}{\frac{N_{LCP,f} + N_{LCP,b}}{2}},$$

$$G_{RCP} = \frac{N_{RCP,f} - N_{RCP,b}}{\frac{N_{RCP,f} + N_{RCP,b}}{2}},$$

$$MP - PECD = G_{LCP} - G_{RCP}.$$

Thus, with no explicit instrumental asymmetry and equal counts in both polarizations:

$$MP - PECD = 2b_1 - \frac{1}{2}b_3 + \frac{1}{4}b_5 - \frac{5}{32}b_7.$$

However, if one introduces an explicit instrumental forward-backward asymmetry likes:

$$N_{LCP,f} \equiv aN_{LCP,f},$$

$$N_{LCP,b} \equiv (1-a)N_{LCP,b},$$

$$N_{RCP,f} \equiv aN_{RCP,f},$$

$$N_{RCP,b} \equiv (1-a)N_{RCP,b}.$$

The number of counts for a given polarization in forward and backward hemispheres are:

$$\begin{split} N_{LCP,f} &= a \frac{N_{LCP,tot}}{2} \left[ 1 + \frac{1}{2} b_1 - \frac{1}{8} b_3 + \frac{1}{16} b_5 - \frac{5}{128} b_7 \right], \\ N_{LCP,b} &= (1-a) \frac{N_{LCP,tot}}{2} \left[ 1 - \frac{1}{2} b_1 + \frac{1}{8} b_3 - \frac{1}{16} b_5 + \frac{5}{128} b_7 \right], \\ N_{RCP,f} &= a \frac{N_{RCP,tot}}{2} \left[ 1 - \frac{1}{2} b_1 + \frac{1}{8} b_3 - \frac{1}{16} b_5 + \frac{5}{128} b_7 \right], \\ N_{RCP,b} &= (1-a) \frac{N_{RCP,tot}}{2} \left[ 1 + \frac{1}{2} b_1 - \frac{1}{8} b_3 + \frac{1}{16} b_5 - \frac{5}{128} b_7 \right], \end{split}$$

In the case of  $a = \frac{1}{3}$ , the forward-backward asymmetry is:

$$\begin{split} MP - PECD &= \\ \frac{2 \times (64b_1 - 16b_3 + 8b_5 - 5b_7 - \frac{128}{3})}{-\frac{64}{3}b_1 + \frac{16}{3}b_3 - \frac{8}{3}b_5 + \frac{5}{3}b_7 + 128} - \frac{2 \times (64b_1 - 16b_3 + 8b_5 - 5b_7 + \frac{128}{3})}{-\frac{64}{3}b_1 + \frac{16}{3}b_3 - \frac{8}{3}b_5 + \frac{5}{3}b_7 - 128}. \end{split}$$

Therefore, forming the forward-backward asymmetry for each polarization separately, and then "averaging" produces the same results equivalent to Eq. 2.7 for ideal case, but does not provide cancellation of an instrumental error.

Let us now consider the MP-PECD asymmetry proposed as Eq. 2.8:

$$G_{FB} = 4 \times \left(\frac{F-B}{F+B}\right),$$

where,  $F = N_{LCP,f} + N_{RCP,b}$  and  $B = N_{LCP,b} + N_{RCP,f}$ . Thus:

$$G_{FB} = \frac{1}{N_{LCP,tot} + N_{RCP,tot}} [4 \times (\frac{1}{2}N_{tot,LCP}b_1 - \frac{1}{8}N_{tot,LCP}b_3 + \frac{1}{16}N_{tot,LCP}b_5 - \frac{5}{128}N_{tot,LCP}b_7 + \frac{1}{2}N_{tot,RCP}b_1 - \frac{1}{8}N_{tot,RCP}b_3 + \frac{1}{16}N_{tot,RCP}b_5 - \frac{5}{128}b_7)].$$

Assuming equalized counts in both polarization (i.e.  $N_{LCP,tot} = N_{RCP,tot}$ ) this gives:

$$G_{FB} = 2b_1 - \frac{1}{2}b_3 + \frac{1}{4}b_5 - \frac{5}{32}b_7,$$

In the case of explicit instrumental asymmetry as suggested above, the forwardbackward asymmetry is calculated as:

$$\begin{aligned} G_{FB} &= 4 \times \left(\frac{F-B}{F+B}\right) \\ &= 4 \times \left[\frac{1}{2}N_{LCP,tot}b_{1} - \frac{1}{8}N_{LCP,tot}b_{3} + \frac{1}{16}N_{LCP,tot}b_{5} - \frac{5}{128}N_{LCP,tot}b_{7}\right. \\ &+ \frac{1}{2}N_{RCP,tot}b_{1} - \frac{1}{8}N_{RCP,tot}b_{3} + \frac{1}{16}N_{RCP,tot}b_{5} - \frac{5}{128}N_{RCP,tot}b_{7} \\ &- 2aN_{RCP,tot} + 2aN_{LCP,tot} - N_{LCP,tot} + N_{RCP,tot}\right] \\ &/ \left[aN_{LCP,tot}b_{1} - \frac{a}{4}N_{LCP,tot}b_{3} + \frac{a}{8}N_{LCP,tot}b_{5} - \frac{5a}{64}N_{LCP,tot}b_{7} \\ &- aN_{RCP,tot}b_{1} + \frac{a}{4}N_{RCP,tot}b_{3} - \frac{a}{8}N_{RCP,tot}b_{5} + \frac{5a}{64}N_{RCP,tot}b_{7} \\ &- \frac{1}{2}N_{LCP,tot}b_{1} + \frac{1}{8}N_{LCP,tot}b_{3} - \frac{1}{16}N_{LCP,tot}b_{5} + \frac{5}{128}N_{LCP,tot}b_{7} \\ &+ \frac{1}{2}N_{RCP,tot}b_{1} - \frac{1}{8}N_{RCP,tot}b_{3} + \frac{1}{16}N_{RCP,tot}b_{5} - \frac{5}{128}N_{RCP,tot}b_{7} \\ &+ N_{LCP,tot} + N_{RCP,tot}\right]. \end{aligned}$$

Again, by assuming equalized counts in both polarizations, the asymmetry is:

$$G_{FB} = 2b_1 - \frac{1}{2}b_3 + \frac{1}{4}b_5 - \frac{5}{32}b_7.$$

Therefore, with equal count in both polarizations, it is essential to combine LCP and RCP data set as suggested in Eq. 2.8 in order to cancel any residual instrumental forward-backward asymmetry.

## LASER SYSTEM AND APPLICATIONS
## **3.1 Introduction**

The advent of ultrafast laser technology has had a great impact in chemical physics. Ultrashort laser pulses have provided an opportunity of observing and studying extremely fast dynamics in atoms and molecules [69–72]. Almost all experiments reported in this thesis (except chapter 4) were performed by use of the second harmonic of a femtosecond laser system output at a 3 kHz repetition rate. The development of high repetition rate (1-10 kHz) femtosecond lasers makes large data collection at a fast rate feasible. High repetition rate lasers are essential, in particular, for coincidence imaging experiments where single event detection schemes are required. The recent developments in fiber-doped lasers are also making high pulse energy available with repetition rates from 10 kHz to 10 MHz [73]. The increase in repetition rate of ultrafast lasers enables the higher data acquisition rates up to 100 k-events/s with coincidence imaging. However, fundamental as well as second and third harmonic pulses have a limited tunability. Extending the availability of ultrashort pulses to the shorter wavelengths in the visible and UV spectral regions is essential for molecular photodynamics studies. Many chemical and biological samples have absorption features in the visible and UV spectral region. In order to excite these molecules resonantly in photodynamics experiments, a tunable laser pulse is necessary. Furthermore, many of physical, chemical or biological processes occur rapidly, dissociating on timescales of a few tens of femtosecond. Resolving such fast processes requires a better time resolution. Hence, the demand for pulses of shorter duration than the fundamental laser pulses (120-150 fs) is obvious. Ultrashort pulses need a very large amplification bandwidth which can be achieved in a non-collinear optical parametric amplifier (NOPA) [74, 75].

In this chapter, I firstly describe the commercial femtosecond laser system and several non-linear optical methods and devices which extend the applicability of the laser system. Particular attention is paid to NOPA and sum-frequency-mixing setups built by me in the early stage of my PhD studies. Moreover, I discuss the measurement techniques using to determine the pulse duration in our lab. Finally, the generation and characterization of circularly polarized light is explained.

## **3.2** The laser system

The commercial femtosecond (fs) laser system used for most of the experiments described in this thesis was manufactured by Spectra Physics. It consists of a Titanium:Sapphire oscillator (Mai Tai), regenerative amplifier (Spitfire Ace) and pump laser (Empower 45). The output of the laser system can be tuned in the range of 750-850 nm wavelength with 4-5.2 W power at 3 kHz repetition rate and pulse duration of around 120-150 fs. The pulse duration of the Spitfire is determined by a home-built second harmonic single-shot autocorrelator and monitored online during the measurement. The pulse duration is optimized on the efficiency of frequency doubling or tripling in a thin non-linear crystal. The fundamental laser output is used to generate either second/third harmonic pulses by nonlinear crystals or tunable pulses in the visible spectral range employing a NOPA. The spectrum of these pulses is monitored by a fiber spectrometer (Ocean Optics USB 4000) during the measurement.

## **3.3** Second and third harmonic generation

Second and third harmonic generations are two of the most straightforward and commonly used nonlinear optical processes to generate laser pulses at shorter wavelengths. For different experiments reported in this thesis, fundamental wavelengths of 840 nm, 825 nm and 784 nm are used. Fig. 3.1 shows second harmonic (SH) spectra of above mentioned pulses at 420 nm, 412.5 nm and 392 nm respectively.



**Figure 3.1:** Several second harmonic spectra of femtosecond laser output pulse with a central wavelength of 392.3 nm, 412.5 nm and 420.3 nm. Full-Width-Half-Maximums are 2.3 nm 2.5 nm and 2.5 nm respectively.

The SH pulse is generated in a Beta Barium Borate (BBO) crystal (d = 1 mm,  $\theta = 29.2^{\circ}$ ) for all measurements; the crystal is slightly tilted for different wavelengths to fulfill the phase-matching condition. The achieved conversion efficiency is about 25-35%. Since a collinear SH setup is used, the fundamental and SH pulses have a spatial overlap after the doubling stage. To obtain *pure* SH pulses for measurements, the SH and fundamental pulses are separated by two or more dichroic mirrors.

For generating the third harmonic of the fundamental output of the laser, a collinear geometry setup is used in our lab. The SH pulse is mixed with the remaining fundamental pulse in a third harmonic BBO crystal (d = 1 mm,  $\theta = 44.3^{\circ}$ ) with appropriate group delay compensation. After the doubling crystal the generated SH pulse is delayed in time and orthogonally polarized to the fundamental pulse. In order to maximize the third harmonic generation efficiency it is essential to compensate these

differences. A dual wave plate rotates the polarization of the SH pulse by 90 degrees - to be the same as the fundamental - while it does not affect the fundamental pulse. The temporal delay introduced to these two pulses due to their different group velocities inside the nonlinear crystal can be compensated by a time-plate for which, a 1-mm calcite crystal is used in the setup. The calcite crystal is a negative uniaxial material, like BBO crystal, that introduces an adjustable delay (depends on the tilting angle) to the ordinary ray (fundamental pulse) with respect to the extraordinary ray (SH pulse). The total conversion efficiency of the third harmonic generation (with respect to the fundamental) is about 7-8%.

## **3.4** Non-collinear optical parametric amplifier

A NOPA is nowadays a common source of tunable femtosecond pulses in the near IR and visible spectral region. Due to the broad amplification bandwidth of the noncollinear arrangement, pulses with very broad bandwidth can be generated. This larger bandwidth leads to shorter pulses after compensating the chirp using a prism or grating compressor. The shortest NOPA pulses were reported to be 4 fs using a micro-machined flexible mirror [76].

A NOPA consists of two main parts: white light continuum generation and parametric amplification. White-light continuum is used as a seed pulse in the first stage of the NOPA. Tight focusing of 100 fs pulses at 800 nm with energy of  $1\mu$ J into transparent material such as a sapphire plate results in self-focusing and generation of a stable filament continuum [77]. The continuum spectrum extends across the visible and NIR as shown in Fig. 3.2 B. Generating a single filament of spatially circular Gaussian and stable white-light (see the inset in Fig. 3.2 B) is essential to have a very stable NOPA output beam. SH of the laser output is used as pump pulse and interacts non-collinearly with seed pulse in a BBO crystal.

Phase matching is achieved for a broad range of wavelengths from 500 to 750 nm by a crystal cut at an angle of  $31.3^{\circ}$  and pump-signal angle of  $3.7^{\circ}$  [78]. The NOPA signal can be tuned through the most part of the visible spectral region from 500 to 660 nm, while pumping the system with the second harmonic of the laser output around 400 nm. Finally, the output power of the NOPA is determined by number of the stages and pulse energy of pump pulses in each stage. In the following, I describe the detailed instrumentation and optical components of the two-stage NOPA built by me (based on the design of [74, 78]) in the lab.

The schematic layout of the two-stage NOPA is shown in Fig. 3.2 A. The NOPA system is pumped by part of the fundamental laser output (150 fs, 780  $\mu$ J). The laser spot size is reduced by a factor of two using a telescope arrangement in front of the NOPA. In the NOPA, the fundamental pulses are split into two beams by a beam splitter (BS1). A small fraction (5%) is focused tightly into a sapphire plate (1-mm thickness) by a 30-mm (focal length) lens to generate a white-light continuum. A variable neutral density filter together with an iris are used to control the energy of the 800 nm light focused into the sapphire plate. The seed beam is then focused by another 30-mm lens



**Figure 3.2:** A) Schematic layout of the home-built two-stage NOPA and prism compressor setup. BS, SP and CM stand for beam splitter, sapphire plate and concave mirror, respectively. B) Typical white light spectrum. The image of white light produced by focusing of 800 nm light in the sapphire plate is captured by a CCD camera and shown in the inset. C) Schematic representation of the SFM setup using to up-convert the tunable visible pulses to UV pulses.

a few mm in front of the BBO crystal (BBO2, d=2 mm,  $\theta = 32^{\circ}$ ). Another fraction of the 800 nm beam is frequency doubled to 400 nm by a BBO crystal (BBO1, d=0.5 mm,  $\theta = 29.2^{\circ}$ ) and used as a pump. Pump pulses are split in two by a beam splitter (BS1, 15% reflection). The reflected and transmitted pulses are used respectively for the first and second stages of amplification. The reflected beam is steered down in height to a

concave mirror (CM1, f= 150 mm) and reflected toward the BBO2 crystal. To avoid any damages in the crystal, BBO2 is positioned a few mm away from the focus in the diverging beam. The seed and the pump beams interact non-collinearly inside the BBO2 crystal and the first stage of parametric amplification is achieved. CM1 is lower than BBO2 and BS2 in height. The white light is chirped, therefore; by fine-tuning the temporal delay between pump and seed beams (by moving BS2 a few mm forward and backward on stage line) and a slight tilting of the crystal, the desired frequency of white light is overlapped with pump beam and amplified. For the optimum amplification the angle between pump and seed pulses has to be set as well. The signal from the first stage is used as the seed beam for the second stage and amplified further in another BBO crystal (BBO3, d=2 mm,  $\theta = 32^{\circ}$ ). Consequently, pulses at energies of 30-40  $\mu$ J in the range of 500-660 nm can be obtained from our two-stage NOPA. Fig. 3.3A shows The typical spectra generated by the NOPA.

# 3.5 Prism compressor

The broad bandwidth output pulses of the NOPA are not transform-limited. They are mainly chirped by initial chirp of the white light continuum and dispersion induced by optics and BBO crystals. These chirped pulses are compressed by a double-pass prism pair compressor. The prism compressor [79] provides negative group velocity dispersion (GVD) with about 70-80% energy throughput and it is very easy to handle. The prism compressor can also be used to pre-compensate extra GVD introduced by optics on the way to the experiments.

Our home-built prism compressor is made of two prisms (N-SSk8) with typical separation of 45 cm and an end mirror, see Fig. 3.2 A. Pulses as short as 25-40 fs can be obtained in our setup. A home-built interferometric autocorrelator is used to characterize the output pulse of NOPA.

# **3.6 UV pulse generation**

A simple method to generate UV pulses is third harmonic generation of the fundamental Ti:sapphire laser pulses but the main drawback is the very limited tunability of this method. However, since the NOPA provides a wide range of tunable visible pulses, one can generate ultrashort tunable UV pulses by up-conversion of NOPA pulses [80–83]. Second harmonic of NOPA pulse provides pulses in the range of 250-330 nm with efficiency up to 33% for pulses as short as 50 fs [80]. Sum-frequency-mixing (SFM) is an alternative method where the generation of tunable UV pulses with efficiency up to about 50% respect to the weaker beam can be achieved [82]. The advantages of the SFM scheme with respect to SH pulses are twofold; first, the generated UV pulses are more stable since only the fluctuations of the laser pump add to overall response and energy fluctuations of parametrically generated pulse are not increased [83]. Second, as was already mentioned, a larger conversion efficiency can be obtained with the SFM scheme.



**Figure 3.3:** A) Some broadband spectra of the NOPA output. B) Several UV spectra generated by the SFM setup. C) The typical auto-correlation trace of the NOPA output, where the upper envelope function corresponds to a pulse width of 26 fs. D) The pump-probe transient for Xe ions measured by 540 nm (33 fs) and 322 nm light beams. The pulse duration of 322 nm light is calculated at about 48-53 fs for the FWHM cross-correlation width (88.7 fs) of Xe ions (see the text).

I have built and optimized a SFM setup in our lab to generate tunable UV pulses. The schematic overview of the SFM setup is shown in Fig. 3.2 C. NOPA output (500-660 nm, 20-30  $\mu$ J, 25-40 fs) and IR light (800 nm, 355  $\mu$ J, 150 fs) are crossed by a small angle inside a BBO crystal (d=500  $\mu$ m,  $\theta$  = 35°). They are separately focused just in front of the crystal. By temporal and spatial overlapping of the two beams inside the crystal and tilting the crystal angle the highest conversion efficiency is achieved. The generated tunable UV pulses are in the range of the 307-362 nm with energies of 9-15  $\mu$ J. Figure 3.3B shows typical spectra of UV pulses. The UV pulse duration is measured by a collinear cross-correlation of UV and visible beams on Xe in the coincidence machine.

## **3.7** Ultrashort pulse characterization

To measure pulse duration or resolve the amplitude and phase modulation of the ultrashort laser pulses, there exist a vast variety of pulse diagnostic methods [84, 85]. These methods include simplistic and incomplete as well as complex and complete characterization of pulses. For our experimental approach, there is a need for a method

being quick and reliable.

In our lab, I use different setups and methods to measure pulse duration of fundamental output, NOPA and UV pulses. I discuss the instrumentation and application of these methods in the following.

#### **3.7.1** Single-shot intensity autocorrelator

The pulse duration of our fundamental laser output is measured and monitored on-line by a home-built single-shot intensity autocorrelator [86]. The fundamental pulses are firstly split in two replicas and then overlapped non-collinearly both in time and space inside a BBO crystal (d=0.5 mm,  $\theta = 29.2^{\circ}$ ). The intensity of the generated SH signal is recorded subsequently as a function of spatial coordinate by a CCD camera. The FWHM of the spatial function,  $\delta_0$ , is converted to pulse duration,  $\eta_0$ , by following formula:

$$\eta_0 = K \delta_0 \frac{\Delta t_0}{\Delta x_0},\tag{3.1}$$

where  $\frac{\Delta t_0}{\Delta x_0}$  is the calibration factor and *K* is a form factor depending on the incident pulse shape, e.g.  $K = (1.41)^{-1}$  for Gaussian pulse. Calibration of such a device is very easy, it only needs to introduce a delay  $\Delta t_0$  into one of the replicas, then counting the number of pixels,  $\Delta x_0$ , that the central SH spatial spectrum is shifted.

In comparison with the other diagnostic methods, this technique is far more simple and faster considering the fact that is not necessary to introduce a range of the delay between two optical beam paths and record the signal intensity as a function of these delays.

#### 3.7.2 Interferometric autocorrelator

A home-built interferometric autocorrelator [87] is used to optimize the compression of the NOPA output close to the Fourier-transform limit pulse and also measure NOPA pulse duration.

NOPA pulses are divided in two pulse replicas in a Michelson-type interferometer by a beam splitter. Each pulse is reflected by a mirror and recombined collinearly by the same beam-splitter. One of the end mirrors is mounted on the piezoelectric translator (PZT) that can scan an optical delay using a small step size (sub  $\mu$ m). An aluminum coated off-axis parabolic mirror (50.8 mm focal length and 90° reflection angle) focuses the recombined pulses into a BBO crystal ( $d=25 \mu$ m,  $\theta = 48.5^{\circ}$ ) in which SH signal is generated. With the help of a frequency filter placed just before the photodiode, the fundamental pulse can be filtered out. The intensity of the SH signal is recorded by a photodiode detector as a function of the delay between two replicas. A typical interferometric autocorrelation trace of a pulse as short as 27 fs is shown in Fig. 3.3 C. The pulse duration can be obtained by fitting a Gaussian on the upper envelope function of autocorrelation trace. The FWHM of this fit is 1.53 times larger than the pulse duration (assuming a transform limited pulse). This method can also provide some indication for spectral phase information.

#### Calibration

The piezo drive voltage of 0-5 V is nonlinearly coupled with the full scanning range (~ 100 $\mu$ m correspond to 330 fs). Therefore, it is necessary to calibrate the device. The calibration curve is then used to convert the drive voltage to time delay. I checked and calibrated PZT in the laboratory on the same interferometer setup as used for the pulse duration measurement. A continuous wave (CW) HeNe laser, operating at  $\lambda_c = 632.8$  nm, was employed as an optical source. The off-axis parabolic mirror was replaced by a flat mirror, and a pinhole (d= 80  $\mu$ m) was placed in front of the photodiode. While the PZT scans its whole range (about 100  $\mu$ m), the interference pattern is recorded by the photodiode as function of data points (Fig. 3.4 A and 3.4 B). We can determine the differences between the data points in  $\mu$ m since the peak-to-peak distance is as the same as the HeNe wavelength (*i.e.* 632.8 nm). Eventually, the calibration curve in which all 4096 data points are coupled to their positions (*i.e.* time delay value) is plotted (Fig. 3.4 C) and used for our measurement program. This calibration scheme shows the dynamics of PZT behavior under measurement conditions.



**Figure 3.4:** A) The typical interference pattern of a HeNe laser light source in autocorrelation setup. It is recorded as function of data points on a photodiode by scanning the PZT. B) Zoom-in on the same trace. The data points are shown as dots. C) The calibration curve of the PZT shows the displacement of the PTZ as a function of the data points.

## 3.7.3 UV Pulse characterization

The UV pulse characterization is not straightforward. There are no nonlinear crystals available that are transparent to and can frequency double the UV pulses. Therefore,

using the SH autocorrelation method used for IR and visible light is not feasible. Other approaches are needed to measure UV pulses. One such method is an autocorrelator based on two-photon absorption in a solar blind photomultiplier [88, 89]. The photomultiplier tube is one-photon insensitive below 310 nm and is therefore perfectly suitable to detect two-photon absorption signal of the UV pulses. This autocorrelator is simple and easy to operate, but a bit costly.

As an alternative method, I use a cross-correlation signal resulting from the multiphoton ionization of Xe in the coincidence machine to measure the UV pulse duration. Therefore, I employ the common pump-probe setup and two NOPAs output pulses, where one output is characterized by the SH autocorrelator. This pulse is acting as the pump pulse and the other NOPA pulse is up-converted to a UV pulse and serves as the probe pulse. Both pump and probe pulses are focused separately and recombined on the molecular beam. In the case that ionization occurs non-resonantly, the cross-correlation function has a FWHM equal to:

$$\sqrt{n_{pu} \cdot (\Delta t_{pu})^2 + n_{pr} \cdot (\Delta t_{pr})^2},\tag{3.2}$$

where  $\Delta t_{pu}$  and  $\Delta t_{pr}$  are the temporal widths of pump and probe pules,  $n_{pu}$  and  $n_{pr}$  are the number of pump and probe photons required for the ionization process.

Fig. 3.3D shows the pump-probe transient for Xe ionization (IE= 12.13 eV) by 540 nm (2.30 eV, 33 fs) and 322 nm (3.85 eV) pulses. The Xe ion can be formed by two different multiphoton ionization pathways: 3+1' and 2+2' where the number of 540 nm photons is labeled by the prime. The resulting cross-correlation FWHM is 88.7 fs. Therefore the pulse duration of the 322 nm pulse is about 48-53 fs (*i.e.* for 2+2':  $\Delta t_{pr} = \sqrt{(88.7^2 - 2 \times 33^2)/2} = 53$  fs and for 3+1':  $\Delta t_{pr} = \sqrt{(88.7^2 - 33^2)/3} = 48$ ).

## **3.8** Circularly polarized light

The fundamental laser pulse, second harmonic, third harmonic, NOPA and UV pulses are all linearly polarized. For the photoelectron circular dichroism (PECD) measurements, circularly polarized light (CPL) is required. Recently, the effect of ellipticity of ionizing photons on PECD asymmetry has been studied by Baumert *et al.* [31] where they reported a monotonic increase of the measured PECD with respect to the ellipticity. In addition, they showed that even for a weak elliptical polarization, PECD effect is still maintained.

The polarization of the optical field can be described in terms of intensity by four Stokes [90–92] parameters as:

$$S_0^2 = S_1^2 + S_2^2 + S_3^2, (3.3)$$

where, the parameter  $S_0$  describes the total intensity of the optical field,  $S_1$  and  $S_2$  describe the degrees of linear polarization and  $S_3$  describes the degree of left- (LCP) and right-circularly polarized (RCP) light. LCP (RCP) is assigned to the state of

polarization where the electric field at a fixed position, is rotating counter-clock wise (clock-wise) as a function of time as seen by an observer facing the light source.

The Stokes vector is given by:

$$S = \begin{pmatrix} S_0 &= & E_x^2 + E_y^2 \\ S_1 &= & E_x^2 - E_y^2 \\ S_2 &= & 2E_x E_y \cos\delta \\ S_3 &= & 2E_x E_y \sin\delta \end{pmatrix}$$
(3.4)

where  $E_x$  and  $E_y$  are the amplitudes of the electric field on the horizontal and vertical axis,  $\delta = \delta_x - \delta_y$  is the phase shift between the horizontal and vertical component.

The normalized Stokes vectors for horizontal, vertical, left circular and right circular polarizations are:

$$S_{hor} = \begin{pmatrix} 1 \\ 1 \\ 0 \\ 0 \end{pmatrix} \qquad S_{vert} = \begin{pmatrix} 1 \\ -1 \\ 0 \\ 0 \end{pmatrix} \qquad S_{LCP} = \begin{pmatrix} 1 \\ 0 \\ 0 \\ -1 \end{pmatrix} \qquad S_{RCP} = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 1 \end{pmatrix}$$
(3.5)

Linearly polarized light can be converted to CPL with the help of a quarter wave plate (QWP). A QWP is a birefringent material with two orthogonal axes: one fast and one slow axis. After a linearly polarized light propagates through a QWP the electric field of the light splits into two components along axes of the QWP where one of them is retarded in phase with respect to the other. In the case the optical axes of the QWP, and the polarization of the incident light make a 45° angle, the phase shift is 90° and CPL is generated.



**Figure 3.5:** The retardance plot for the achromatic QWP made of MgF<sub>2</sub> and quartz in the range 300-470 nm, adopted from [93]. The retardance at 390 nm±1.2 nm is  $0.2606\lambda\pm0.0002\lambda$ . The calculated  $|S_3|$  for this range is 1.00.

Femtosecond pulses have a broad spectrum and it is important that the phase shift

is 90° for all frequencies within the laser pulse bandwidth. An achromatic QWP is used in our measurement to generate CPL. Figure 3.5 shows the retardance plot of such a plate as a function of wavelength [93]. The retardance at 390 nm±1.2 nm is  $0.2606\lambda\pm0.0002\lambda$ . Therefore,  $|S_3|$  is calculated to be 1.00 in this range.

All Stokes parameters can be measured in the laboratory since they are described in terms of intensity. The rotating QWP method [36, 92] is employed to determine the Stokes parameters. The experimental configuration consists of (I) a rotating QWP that can be rotated 360<sup>o</sup> throughly, (II) a fixed linear polarizer that transmits horizontally polarized light and (III) a power-meter to measure the light intensity. The measured intensity is given by,

$$I(\theta) = \frac{1}{2} \left( S_0 + S_1 \cos^2(2\theta) + S_2 \cos(2\theta) \sin(2\theta) + S_3 \sin(2\theta) \right),$$
(3.6)

where  $\theta$  is the angle of rotating QWP. At  $\theta = 0$  the fast axis of the QWP and horizontal axis are parallel and the QWP is rotated counter-clockwise during the measurement. The measured intensity curves for both LCP and RCP light for the pulses at 392 nm



**Figure 3.6:** Typical measured graph for the analysis of the Stokes parameters of the circularly polarized laser pulses near 392 nm using the rotating quarter wave plate method. The green curve (data points are green squares, best fit is line) was measured for LCP, the dark red (data points are solid dots, best fit is line) curve for RCP. The Stokes parameters obtained from the best fit are given in the text.

are shown in Fig. 3.6 and the Stokes vectors obtained from the curves are: RCP: S=(1, -0.01, 0.03, 0.99) and LCP: S=(1, -0.11, 0.08, -0.99). The results show a nearly perfect circular polarization of the laser light source ( $S_3 \approx \pm 1$ ).

4

# PHOTOIONIZATION STUDY OF PURE LIMONENE ENANTIOMERS USING CIRCULARLY POLARIZED VUV LIGHT AND ELECTRON-ION COINCIDENCE IMAGING

# 4.1 Introduction

Photoelectron circular dichroism (PECD) using synchrotron radiation has been developed as an experimental technique to probe molecular chirality over the last decade [14, 15]. A very recent development has been using a table-top femtosecond laser system to provide the required circularly polarized light source [27, 28]. Multiphoton PECD (MP-PECD) studies on pure and multi-component mixtures of limonene enantiomers are demonstrated in chapters 6, 7 and 8 of this thesis. However, the understanding of MP-PECD in intense laser fields is currently limited. One can develop such understanding by comparison with single-photon vacuum ultraviolet (VUV) PECD measurements and theoretical calculations [29]. In VUV one-photon PECD, the initial molecular orientation is purely random while in multiphoton experiments, the initial alignments should be worked out by introducing several assumptions which adds uncertainty to the modeling of the pure ionization dynamics. Another advantage of synchrotron based measurement is that, potentially, we could cover a much wider range of electron kinetic energies which makes more meaningful and easier comparison between theory and experiment. On the other hand, multiphoton ionization cases provide more parameters  $(b_3, b_5, b_7,...)$  to examine the theory.

In this chapter, I present the photoionization study of limonene using VUV PECD and electron-ion coincidence imaging. Single-photon PECD study is of significant and timely interest *per se*. Recent PECD investigations have shown that along with a strong sensitivity to static structural form (conformation) [23, 94, 95] there is a surprising sensitivity to dynamic (vibrational) structure [26]. The limonene HOMO orbital photoelectron spectrum (PES) [96, 97] shows well resolved vibronic structure with minimal dissociation of the corresponding ground state ion [96], making it a good candidate for vibrational resolved studies.

The chapter is structured as follows. In section 4.2, I explain the experimental method and setup. In section 4.3, I present and discuss the experimental results. My conclusion are in section 4.4.

## 4.2 Experimental and methodology

## 4.2.1 Samples

The liquid samples of both limonene enantiomers (purchased from Sigma-Aldrich with a stated purity of 96% (S) and 97% (R)) were held in a reservoir (at room temperature) just behind a 50  $\mu$ m diameter nozzle. A stream of He gas with backing pressure of 0.5 bar flows across the top of the reservoir, allowing vapor to be seeded in the flow. The gas mixture expands through the nozzle into the SAPHIRS molecular beam chamber. The molecular beam is doubly skimmed downstream of the nozzle before it enters the spectrometer chamber where it is crossed at right angle with a circular polarized light beam at selected photon energies.

## 4.2.2 Light source

All experiments reported in this chapter were performed at SOLEIL synchrotron, on the DESIRS VUV beamline [98]. This is an undulator-based beamline that can deliver left- (LCP) and right-circularly polarized light (RCP) with Stokes parameter values of  $|S_3| \ge 93\%$  [99]. The polarization of light is measured accurately with a dedicated VUV polarimeter [100]. The higher harmonic light generated by the undulator can be eliminated by a gas filter [101] filled with 0.25 mbar of Ar for photon energies below 15.76 eV (argon's ionization energy). A photodiode (AXUV, IRD Inc.), located right after spectrometer is used to measure the intensity of the light beam for normalization of all wavelength scans.

## 4.2.3 Electron-ion coincident spectrometer

The double imaging coincidence spectrometer DELICIOUS III used in the present work has been described in detail elsewhere [56]. In short, after the ionization of molecules, electrons and ions are extracted in opposite directions (up and down respectively), perpendicular to the molecular and photon beams. In the spectrometer, a velocity map imaging (VMI) analyzer [40] and a modified Wiley-MacLaren (WM) [102] spectrometer are used for electron and ion detections respectively. Electrons and ions can be recorded in a coincidence mode. Due to the quasi-continuous operational mode of the SOLEIL synchrotron, ion optics are operated with constant DC voltages. A delay line detector (Roentdek DLD80) and a custom-made position sensitive detector [103] are used respectively on the electron and ion sides. By such a design the ultimate electron kinetic energy resolution of 4% for fast electrons and constant energy resolution of about 1 meV in the threshold electron mode can be obtained. However, in slow photoelectron measurement, since we compromise between adequate resolution and count rate the effective resolution is reduced accordingly (see section 4.3.2). The ion spectrometer provides a spatial resolution down to 10%, a 3D kinetic resolution of about 15% (without comprising of mass resolution) and the typical mass resolving power,  $m/\Delta m$ , of 1600.

## 4.2.4 Photoelectron circular dichroism experiment

PECD is observed as a forward-backward asymmetry in the photoelectron angular distribution (PAD) along the light propagation direction. The normalized PAD for single photon ionization should be written as [17, 104]:

$$I_{p}(\theta) = 1 + b_{1}^{p} P_{1}(\cos\theta) + b_{2}^{p} P_{2}(\cos\theta), \qquad (4.0)$$

where  $P_n$  are Legendre polynomials,  $\theta$  is the angle between the velocity vector of ejected electron and the propagation direction of circular polarized light. p is a polarization index, p=0 for linear polarization, p=+1 for LCP and p=-1 for RCP. The  $b_n^p$  coefficient depends on the photoionization dynamics as well as the light polarization.  $b_1^p$  is zero when either linear polarization or an achiral molecule is used. Switching the

helicity of the circularly polarized light (or exchanging enantiomers) changes the sign of the odd Legendre coefficients while leaving the even Legendre coefficients unaltered. Thus, the odd Legendre terms containing the chiral information can be isolated and extracted by examining the difference between two polarizations (LCP and RCP) for a single enantiomer [29]:

$$I_{diff}(\theta) = I_{+1}(\theta) - I_{-1}(\theta) = 2b_1 \cos\theta.$$
(4.0)

Determination of chiral asymmetry from the difference signal (Eq. 4.2.4) has some advantages with respect to the direct observation of PAD (Eq. 4.2.4). In fact, any instrumental asymmetries such as detector efficiency in forward and backward scattering directions is canceled and consequently results in a higher chiral recognition sensitivity. Empirically, PECD asymmetry for a given enantiomer at a selected photon energy is obtained by taking the difference between two accumulated photoelectron images recorded by LCP and RCP light. The polarization is altered roughly every 15 min. The size of the monochrometer slit is used to control the photon flux and thence the ionization rate. Controlling of count rate is important, firstly to prevent MCP being saturated and degraded. Secondly, too high a count rate can lead to coincidence data loss because of limitations on the hardware data transfer bandwidth. Thirdly, a higher count rate does not necessary improve the signal to noise ratio due to increasing of false coincidence. At the end of the experiment, all images recorded with the same polarization are combined and normalized to the total electron count. Difference (LCP-RCP) and sum (LCP+RCP) data files are obtained for further analysis. The pBasex inversion algorithm [105] is used to treat the data and extract PECD asymmetry as well as PES. The measured Stokes parameter,  $S_3$ , is used to correct the PECD data for each photon energy. The experimental error bars are estimated by using standard error propagation formulae assuming Poisson statistics in each data bin. A detailed description of data recording and treatment for a PECD measurement can be found in Ref. [21].

# 4.3 **Results and discussions**

### 4.3.1 Time-of-Flight spectrum

TOF spectra of limonene obtained at different photon energies are shown in Fig. 4.1. No sign of cluster formation is observed in any of the spectra (see the insets). Fragmentation appears in the spectra with photon energies above 10 eV (panel B) and the parent ion ( $C_{10}H_{16}^+$ ; m/z=136) remains a dominant ionic channel in ionization with photon energies up to 14 eV. The peaks at m/z=137 in TOF spectra correspond to the parent molecule isotopomer with <sup>13</sup>C. An ion breakdown diagram of limonene has been published previously by Garcia *et al.* [96]. The appearance energies of the  $m/z \ge 79$  fragment ions were all reported around 9 eV. This overall fragmentation onset is obviously lower than the results shown here. This can be explained due to different molecular beam expansion and experimental conditions used for these two



**Figure 4.1:** Time-of-flight mass spectra of a seeded limonene sample (in 0.5 bar He) recorded at different photon energies. Insets on the back panel show the extended mass spectra up to m/z=280 for two exemplified spectra recorded by hv=9.5 eV and hv=18 eV. No sign of cluster formation in TOF spectra is seen.

experiments. In Garcia's experiment the sample was heated up to 110  $^{o}$ C and 1.3 bar Ar was used as a carrier gas to expand the gas mixture through a 75  $\mu$ m diameter nozzle. In contrast to this earlier work, there was no necessity to raise the temperature of the sample reservoir in our measurement to achieve enough signal, and although it is not quantified, the molecular beam temperature can be judged to be much lower due to different fragmentation behavior around threshold ionization compared to the earlier work.

#### 4.3.2 Slow photoelectron spectrum

The DELICIOUS III spectrometer is capable of recording a mass-selected PES either as single-photon energy mode (VMI-PES) or the scanning photon energy mode. Massselected VMI-PES of limonene enantiomers, recorded at several fixed photon energies, are discussed in section 4.3.3. Here, the PES for R-limonene is presented by scanning over the 8 eV to 9.8 eV energy range in 3 meV steps.

In the scanning mode, VMI detection and tunable synchrotron radiation are employed. The VMI setup is used to focus slow electrons to the central area of the detector. An Einzel lens is employed in the setup to improve the energy resolution of slow electrons for a given extraction field. After the scanning, the position and size of the central part are selected in electron images. The PES is obtained by removing the contribution of the hot electrons from the center part [55, 56, 106]. Consequently, one can retrieve a threshold PES (TPES) where only electrons with (close to) zero kinetic energy are included.

In a direct ionization process, the kinetic energy of electrons and photon energies are linearly correlated as KE = hv - I.E. (where I.E. is the ionization energy). Figure 4.2 shows the kinetic energy of the mass-selected photoelectrons (m/z=136-138) in the range of 0-1.5 eV as a function of photon energy. As it is obvious, the diagonal lines in the figure get broader for higher electron kinetic energies as the absolute resolution of VMI is degraded. Although the threshold photoelectrons have the highest PES resolution, the drawback is that the signal statistics are very low. In order to circumvent the low statistics but still have a comparable resolution to TPES, one can retrieve the so-called slow PES (SPES). SPES comprises the photoelectrons with kinetic energies up to  $KE_{max}$  eV.  $KE_{max}$  is chosen by compromising between resolution and signal level during data treatment, after the scanning. The SPES method has been introduced by Neumark *et al.* [107] and developed in several experiments over the last decade [108–111].

Figure 4.3 (lower curve) shows SPES of R-limonene. An optimized trade-off between signal and resolution is found for  $KE_{max}$ =30 meV where the effective resolution is around 10 meV. A perviously reported high resolution He(I) PES [97] is also included in Fig. 4.3 for comparison. The two spectra are very similar by showing four distinct peaks (A-D) while a significant difference is the absence of smaller peaks (b-d) in SPES. In the following, I discuss a possible assignment for PES peaks by examining our results with respect to some earlier works.

Limonene has three low lying equatorial conformers populated at room temperature



**Figure 4.2:** Mass-selected 2D spectrum for m/z=136-138 showing the kinetic energy of the photoelectrons as a function of the photon energy. Diagonal lines are assigned to ionic states accessed by direct ionization.

[112]. The torsional potential of the neutral limonene is shown in Fig. 4.4 as a function of dihedral angle [113]. The plot is identical with one reported previously by Monero *et al.* [112]. The three minima in the plot correspond to the three most stable conformers (Eq-1, Eq-2 and Eq-3). There is a relatively low barrier between Eq-2 and Eq-3 and a much bigger barrier between Eq-1 and the others. Therefore, thanks to the low barrier, Eq-3 can possibly cool down and convert to Eq-2 in a cold molecular beam and then only Eq-1 and Eq-2 remain in the sample. This was also experimentally verified by a Fourier transform microwave spectroscopy measurement. This showed that only the rotational spectra of Eq-1 and Eq-2 conformers were detected in cold molecular samples [112].

The ionization energy of limonene derived from photoelectron spectrum has been reported previously in different studies [96, 97, 114]. The ionization of the highest occupied molecular orbital (HOMO) and second HOMO (HOMO-1) respectively correspond to ionization of the  $\pi$ -orbitals in the carbon ring and isopropenyl group in the molecule. Peak (A) and peak (B) with the maximum at 8.52 eV and 8.69 eV are assigned to the adiabatic and the vertical ionization energies of HOMO respectively. Śmiałek *et al.* have shown in their analysis that peaks (A-C) correspond to vibrational progressions in the ring carbon double bond stretching mode ( $v_{55}$ ) with mean energy of 172 meV [97]. Therefore, peak (C) with the maximum at 8.87 eV is also assigned to a further member (v=2) of the vibrational progression built on the HOMO ionization.

Moreover, the vertical ionization energy of HOMO-1 is calculated to be around 8.9 eV [96, 97] and 9.0 [113] while there is a huge peak at 9.1 eV (D). This peak is quite



**Figure 4.3:** The slow photoelectron spectrum (red line) of R-limonene recorded between 8-9.8 eV. The He(I) PES (blue line) adopted from Ref. [97]. The indicated peaks are discussed in the text.

prominent in all VMI PES recorded with different photon energies (see Fig. 4.5 and 4.7). Thus, since the HOMO and HOMO-1 bands are most likely superimposed on one another in this region, peak (D) at 9.1 eV seems to be the vertical ionization energy of second band which is distorted by the underlying HOMO band. Alternatively, the observed structure may depend upon vibronic interaction between these close-lying electronics states.

The small peak around 8.4 eV (a) is observed in both SPES and He(I) PES but much weaker in the SPES. Śmiałek *et al.* argued that this peak cannot be reproduced as a hot band on their simulations. They assigned it to the presence of a dimer. However, we can decline this supposition since we do not see any indications of any clusters in our TOF spectra although our molecular beam sample inlet is expected to be colder than Śmiałek's room temperature effusive source. On the other hand, peaks (a-d) have the mean spacing of about 175 meV, pretty much the same spacing between the big peaks (A-C). Therefore, this may suggest an alternative explanation. We have already discussed that, probably, only two conformers are present in our cold molecular beam. It is further possible to suppose that one of the conformers has about 80 meV lower adiabatic IE and also it is less strongly populated in the cold beam. This is reasonably supported by the calculated adiabatic IE for three conformers where the Eq-2 has about 0.3 eV lower IE than two others [97]. Therefore, PES of these two conformers may



**Figure 4.4:** Torsional potential curves for neutral limonene [113]. The inset shows the molecular structure of S-limonene. The three conformers differ by the a-b-c-d dihedral angle corresponded to the rotation of the isopropenyl group with respect to the ring.

be effectively offset and so interlaced, where the main peaks (A-C) may only belong to a single conformer. Moreover, it is plausible to attribute the loss of the small peaks (b-d) to sample temperature as they are stronger in the room temperature spectrum and almost eliminated in our cold SPES.

#### 4.3.3 Photoelectron circular dichroism

PECD measurements were made by recording photoelectron images of either R- or S-limonene in coincidence mode at various fixed photon energies in the range of 8.7 eV to 18 eV. Coincident detection between electron and ion allows each electron to be tagged to a given ion mass. Here, I present the mass-tagged results of limonene parent ion (m/z = 136). By that, the contributions of water and any other contaminations presented in the molecular machine can be excluded from the data, useful for photon energies above 12 eV. Secondly, since the ionization of HOMO and HOMO-1 do not produce any fragment ions, selecting electrons in coincidence with limonene parent ion helps isolate any higher energy, overlapping orbital contributions. The PECD asymmetry is derived from the difference photoelectron image following the methodology explained in section 4.2.4 and displayed as a function of ionization energy. For visual comparison the PES is also plotted in the same graph on the same energy scale.

Figure 4.5 displays mass-tagged VMI-PES and PECD spectra of the limonene



**Figure 4.5:** The mass-tagged m/z=136 PES (green line) and PECD for R- (red filled square) and S-limonene (blue open circle) measured at 8.7 eV(A), 8.8 eV(B), 9.1(C), 9.3 eV(D) and 9.5 eV(E).



Figure 4.6: PECD asymmetry plotted as a function of ionization energy for low photon energy measurements. S-enantiomer results are negated.

monomer, recorded with LCP and RCP at low photon energies ( $\leq 9.5$  eV). The anticipated mirroring between the dichroism of two enantiomers is shown clearly in panel E at hv = 9.5 eV that confirms a molecular chirality origin of the asymmetry and shows the reproducibility of data recorded under similar experimental conditions.

In Fig. 4.6 the PECD values for low photon energy measurements are plotted on the common ionization energy scale where S-enantiomer values are presented with an inverted scale. The negation of PECD can be fully anticipated for enantiomers. Plotting in this fashion gives a better visual comparison between R- and S- enantiomer data. PECD spectra are strongly structured and show a clear correlation with peaks in PES. Between the major PES peaks (A-C), the chiral asymmetry slightly drops to negative values and not zero. Therefore, it may suggest that there is something else present between the PES peaks but it is not sufficiently intense to be resolved. This observation may corroborate again what we discussed and suggested in the previous section. The PECD in the position of the vibrational peaks may correspond to only one conformer and in between the peaks may associate with the mixture of two conformers with totally different chirality effects.

Interestingly, the overall PECD sign is also changed from ionization of HOMO to HOMO-1 across the PES band. This correlation between PECD and the orbital being ionized has been noted in several experiments [21, 23–25].

At higher photon energies, the extraction field needs to be increased in order to



**Figure 4.7:** The mass-tagged m/z=136 PES (green open circle) and PECD for R- (red filled square) and S-limonene (blue filled circle) from VMI measured at hv=10.5-18 eV. Solid lines are Gaussian fits.

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detect the faster electrons; that in return degrades the absolute electron resolution. Therefore, VMI PES becomes relatively smooth and featureless. Several mass-tagged m/z=136 PES and PECD spectra recorded with higher photon energies are illustrated in Fig. 4.7. Two Gaussian functions have been fitted to the PES profile to nominally represent the two orbitals' contribution to PES. Mean PECD values can be extracted by taking the Gaussian weighted  $b_1$  values.



**Figure 4.8:** Experimental Gaussian weighted mean PECD values (open circle) for nominal HOMO orbitals as a function of electron kinetic energy (bottom axis) and photon energy (top axis). At lower photon energies the PECD values (filled circle) read-off from Fig. 4.5 in the position of peak A and B.

Fig. 4.8 plots the energy dependence of PECD in HOMO band. Data points for hv > 10 eV are the Gaussian weighted mean value of experimental  $b_1$  for the nominal HOMO orbital. The mean PECD tends toward zero at lower photon energies. It seems without adequate resolution to resolve the oscillation correlated to vibrational peaks, a PECD measurement merely see an average value that tends to zero. Due to this the Gaussian averaging is not extended down to the lowest recorded photon energies but we simply read-off the asymmetries in the position of peaks (A) and (B) for hv < 10 eV.

# 4.4 Conclusion

In this chapter, I have presented single-photon PECD of pure limonene enantiomers. PECD measurements have been performed at the SOLEIL synchrotron using the DELICIOUS III / SAPHIRS double skimmed end station, with automatic polarization switching on the DESIRS beamline. SPES shows a high resolution spectrum with very distinctive vibronic structures in HOMO and HOMO-1 bands. The assignment of limonene PES was determined by comparing between the experimental results presented here and previous studies. The torsional potential calculation of the neutral limonene shows that one out of the three most stable conformers in room temperature may be frozen out in the cold molecular beam. Therefore, the contribution of this conformer did not appear in our SPES. PECD measurements have been recorded at different photon energies among 8.7 eV to 18 eV in electron-ion coincidence imaging mode to allow filtering of electron spectra by selected ion mass. The low electron energy region is of most relevance for complementary MP-PECD measurements reported in chapter 6 and chapter 7. Detailed PECD spectra showed a strong dynamical structure. In the position of strong vibrational peaks the results may correspond only to one conformer while in between peaks the contribution of another conformer is dominated. Moreover, it is observed that the sign of PECD asymmetries also changed by passing from ionization of the HOMO to HOMO-1 orbital. Finally, the data obtained with higher photon energies can be used for implementation of reference theoretical models to describe MP-PECD laser experiments.

5

# CHIRAL ASYMMETRY IN THE MULTIPHOTON IONIZATION OF METHYLOXIRANE USING FEMTOSECOND ELECTRON-ION COINCIDENCE IMAGING

Multiphoton photoelectron circular dichroism (MP-PECD) has been observed as an asymmetry in the angular distribution of photoelectrons emitted in the ionization of pure enantiomers of the small chiral molecule methyloxirane using a femtosecond laser operated at 420 nm. Energetically, this requires the uptake of four photons. By switching the laser between left- and right-circular polarization, and observing the differences in the full three-dimensional electron momentum distribution recorded in an electron-ion coincidence technique, the chiral (odd) terms in the angular distribution expression can be isolated. Electron events can additionally be filtered by coincident ion mass, providing masstagged electron distributions and quantitative measures of the MP-PECD asymmetry that help characterize the different ionization channels. For the production of ground state parent cation, the magnitude of the mean chiral asymmetry is measured to be 4.7%, with a peak magnitude exceeding 10%.

this chapter is published as: M. M. Rafiee Fanood, I. Powis, M. H. M. Janssen, J. Phys. Chem. A, 118, 11541, 2014.

## 5.1 Introduction

As a small, rigid chiral molecule, methyloxirane (propylene oxide) has assumed a prototypical role in many formative studies of chiroptical techniques. Nevertheless, its chiroptical responses are very strongly solvent-dependent due to induced chirality in the solvation shell, even in achiral solvents such as water. This necessitates incorporation of solvent shell effects in computational models, complicating both the calculation and validation of underlying theoretical approaches to chiral light- matter interaction [115–117]. Consequently, there is a premium placed on gas phase studies able to explore methyloxirane's intrinsic chirality in an isolated, solvent-free environment [118–120]. Even then, methyloxirane proves to be a somewhat pathological case for theory [121], requiring ongoing investigation and development.

Photoelectron circular dichroism (PECD) is an addition to the rank of chiroptical methods that measures a forward- backward asymmetry in the angular distribution of photoelectrons emitted upon ionization by a beam of circularly polarized radiation [14, 122]. These asymmetries fall in the range of one to a few tens of a percent and so are at least 3 orders of magnitude greater than more typical circular dichroism in absorption spectroscopies. This inherent sensitivity, combined with the in-built experimental efficiency of charged particle detection, make PECD an ideal method to probe isolated chiral molecules in the gas phase, which can even be extended to observe minor cluster components generated in a supersonic molecular beam [25]. In the present context it is then no surprise that methyloxirane has been widely investigated, both experimentally [123–126] and theoretically [95, 123, 126, 127], by PECD. Vibrationally resolved PECD measurements have lately revealed an inversion of the chiral electron scattering asymmetry caused by weakly excited normal mode vibrations [26], highlighting the significance of complete vibronic treatments for fully understanding the chirality displayed by this molecule.

While PECD has historically been developed using synchrotron radiation sources, a very important recent development has been the demonstration of PECD in multiphoton ionization of camphor using ultrafast lasers [27, 28]. Not only does this offer greater accessibility through the use of laboratory scale light sources, it also suggests a potential for time-resolved pump-probe circular dichroism of dilute species; greater control and identification of quantum states in intermediate and final states; and species-selective ionization of multicomponent mixtures that can enhance analytical applications. These features are further discussed in a recent perspective article [29].

In this article we further explore the generality and potential of multiphoton photoelectron circular dichroism (MP-PECD) by demonstrating the chiral asymmetry in a different class of molecule, the prototypical methyloxirane. Measurements have been made on pure enantiomeric samples of methyloxirane seeded in a molecular beam. Ionization by circularly polarized laser pulses occurs in an electron-ion coincidence spectrometer (Figure 5.1). One thus obtains photoelectron spectra, electron energy-dependent angular distributions, and ion time-of-flight (ToF) mass spectra from accumulated data; moreover, the delayed coincidence between electron and ion events can be used to identify individual electron-ion pairs emanating from individual

molecule ionization events, and this allows the extracted electron distribution data to be mass-tagged and associated with selected ionization channels.

# 5.2 Experimental Section

The experimental coincidence imaging apparatus shown schematically in Figure 5.1 has been described in detail before [57, 58]. A supersonic molecular sample beam is expanded through a 150  $\mu$ m diameter conical nozzle and is then doubly skimmed by 500 and 200  $\mu$ m diameter skimmers before entering the spectrometer chamber where it is intersected at 90° by the laser beam. After ionization, electrons are extracted from the laser interaction region, passing through velocity map imaging (VMI) electron optics to be detected at a delay line imaging detector. This records time and position (t, x, y) for each individual electron, which in turn directly maps to the three electron momentum components ( $p_x, p_y, p_z$ ). Thus, full kinetic energy and angular distributions can be extracted without requiring inversion techniques for data recovery. Ions are extracted in the opposite direction to another imaging detector, but here used only to record time of arrival.

Both electron and ion ToF tube are shielded by 1 mm thick  $\mu$ -metal tube. High voltage switches (Behlke HTS-51) operated at the repetition rate of the laser system are used to sequentially apply optimized extraction potentials for electrons and then ions, exploiting the much greater residence and flight times of the ions to accommodate these differing requirements. In the present experiment we operated VMI voltages for electron detection and voltages for optimal mass resolution for ion detection. The typical voltages on the charged particle lenses (repeller (R), extractor (E), and extra lens (L); see Figure 5.1) used for detecting electrons are  $R_e = -520$  V,  $E_e = -385$  V,  $L_e = -275$  V and for detecting ions are  $R_i = 2000$  V,  $E_i = 1460$  V,  $L_i = 0$  V.

Light was provided by a commercial femtosecond laser system (Spectra Physics). It consists of a titanium:sapphire oscillator (Mai Tai), regenerative amplifier (Spitfire Ace), and pump laser (Empower 45). The output of the amplifier was optimized to deliver pulses centered at 840 nm wavelength with 4.2 W power at 3 kHz repetition rate. The fundamental beam is subsequently frequency doubled in a BBO crystal. During the measurement the second harmonic spectrum was continuously monitored by a fiber-based spectrometer (Ocean Optics USB 4000). Figure 5.5 (in the appendix) shows the frequency doubled spectrum near 420.2 nm. The frequency doubled output had a pulse duration of about 150 fs, a bandwidth of 2.6 nm, and pulse energy of about 25-30  $\mu$ J. It was focused down to a spot size of about 100  $\mu$ m× 150  $\mu$ m with a lens of 30 cm focal length. The intensity in the ionization volume is estimated to be  $10^{11} - 10^{12}$  Wcm<sup>-2</sup>.

A broadband quarter wave plate (B-Halle) was used to generate the circular polarized light. The polarization of the light was characterized in terms of the Stokes vectors by the rotating quarter wave plate method [28, 92]. The measured intensity data for both left and right circular polarized light for pulses at 420 nm are shown in Figure 5.6 in the appendix and the Stokes vectors obtained from fitted curves are



**Figure 5.1:** Schematic overview of the coincidence imaging apparatus. A molecular sample beam is produced by a nozzle (A), doubly skimmed (B) before entering the spectrometer chamber (C). Electrons produced by laser interaction in the source pass through VMI imaging optics to reach a 3-dimensional imaging detector, while the corresponding positive ions are extracted in the opposite direction, by the applied electric field, through an ion ToF spectrometer.

 $S_{RCP} = (1, -0.03, 0.01, 0.99)$  and  $S_{LCP} = (1, -0.18, 0.005, -0.97)$ . With these high, near perfect values for circular polarization  $S_3$  no corrections for ellipticity have been required.

Both R- and S-enantiomers of methyloxirane were purchased from Sigma-Aldrich with a purity of 99%. We used 1.7% of enantiomer seeded in Ne with 0.4 bar backing pressure to avoid the formation of clusters.

During the PECD measurement, the handedness of circular polarized light was switched every 500 s (1.5 million laser shots (MLS)) to reduce the effect of any experimental drift in laser intensity and molecular beam stability. The measurements on each enantiomer were performed for 45 MLS. The average number of electron events per laser shot in both experiments was about 0.08. These count rates ensure that the probability for false coincidence is less than 0.3% assuming Poisson statistics. After careful checks that, among other things, the center of electron image data are

the same, all files with the same polarization were combined together at the end of the measurement for data analysis.

## 5.3 **Results and discussions**

The full photoelectron angular distribution (PAD),  $I_p(\theta)$ , expected from an n-photon ionization of a chiral molecule with circular polarized light is given by [28]

$$I_p(\theta) = \frac{I_{tot}}{4\pi} \left( 1 + \sum_{i=1}^{2n} b_i^p P_i(\cos\theta) \right),$$
(5.1)

where *p* is the polarization of the light, and p = +1 and p = -1 correspond to left circular polarized (LCP) and right circular polarized (RCP), respectively.  $P_i(cos(\theta))$ are Legendre polynomials,  $b_i^p$  are the corresponding expansion coefficients, and  $\theta$  is the angle between the electron momentum and the propagation direction of the laser beam. Switching the helicity of the circularly polarized light (or exchanging enantiomers) can be expected to generate a sign change of the odd Legendre coefficients while leaving the even Legendre coefficients unaltered. Thus, the odd Legendre terms containing the chiral information can be isolated and extracted by examining the difference between two polarizations (LCP and RCP) for a single enantiomer [28]:

$$I_{LCP}(\theta) - I_{RCP}(\theta) = \frac{I_{tot}}{4\pi} \left( \sum_{i=1}^{n} 2b_{2i-1}^{+1} P_{2i-1}(\cos\theta) \right),$$
(5.2)

The adiabatic ionization energy of methyloxirane, 10.25 eV [26] means that at our chosen excitation wavelength, 420.2 nm, a minimum of four photons ( $\equiv 11.8 \text{ eV}$ ) must be absorbed to produce ions from methyloxirane neutral. A broad structured VUV absorption spectrum of methyloxirane covering the range 6.7 to 9 eV has been reported by Breest *et al.* [118]. The 7.01 to 8.53 eV region has been assigned to 14 calculated n = 3 Rydberg transitions [128], but there is no known absorption at the one or two photon (5.9 eV) energy. Transition to the initial member of the n = 4 Rydberg family,  $n_O \rightarrow 4s$ , is calculated at 8.65 eV with further n = 4 Rydberg expected to account for the oscillator strength observed at higher energies [128]. Thus, our three photon energy, 8.85 eV, likely coincides with n = 4 Rydberg excitations.

A typical ToF mass spectrum (estimated mass resolving power  $m/\Delta m \approx 600$ ) of methyloxirane is depicted in Figure 5.2. The spectrum is dominated by the parent monomer (C<sub>3</sub>H<sub>6</sub>O<sup>+</sup>; m/z = 58) with an abundance of 21%. In addition, several ion fragments are produced at this laser fluence. The laser intensity was adjusted to minimize fragmentation, while molecular beam conditions were optimized to avoid cluster formation. The mass peak at m/z = 18 is attributed to ionization of background water molecules (IP = 12.61 eV) in the spectrometer chamber.

Table 5.1 lists the ions and abundances observed here and presents appearance energies (AE) of methyloxirane parent and fragment ions as obtained in a recent VUV threshold photoelectron.photoion ion coincidence (TPEPICO) measurement [126]. The



**Figure 5.2:** Time-of-flight mass spectrum of S-methyloxirane measured after multiphoton ionization at 420 nm, coincident with all electrons.

420.2 nm four photon energy of 11.80 eV is in fact sufficient for the formation of most of the listed ion fragments. However, ion fragments of m/z = 15, 26, and 27 require five photons, and an ion of m/z = 40 (observed in the one photon VUV studies, though not detected in our experiment) would need the energy of six 420 nm photons.

Photoelectron kinetic energy (PEKE) spectra are shown in Figure 5.3. Panel A shows PEKE of all electrons (no ion coincidences applied) and panels B-F depict mass tagged PEKE. The PEKE spectrum of all electrons (panel A) shows two broad bands centered around 1.3 and 0.4 eV. Assuming the ionization energetics correspond to a four-photon absorption ( $\equiv$  11.8 eV) these peaks correspond to those expected from ionization of the highest and second highest occupied molecular orbitals (HOMO and SHOMO) whose vertical ionization energies are, respectively, 10.46 and 11.34 eV [126]. The HOMO is a localized O 2p lone pair, while the SHOMO has ring  $\sigma$  (C-C) and  $\sigma$  (C-O) bonding character. The parent ion (m/z = 58) mass-tagged PEKE (panel B) shows only the HOMO band centered around 1.3 eV. Conversely, the low energy SHOMO peak is very strongly enhanced in the m/z = 43 tagged spectrum. These observations fully accord with VUV TPEPICO results [126], which show the HOMO<sup>-1</sup> ground ionic state to be undissociated, whereas the SHOMO<sup>-1</sup> first excited state is essentially fully dissociated to m/z = 43.

From the evidence adduced so far we infer the dominant ionization process under

		Abundance (%)		A.E. (eV) <sup>a</sup>
m/z	Formula	<b>R-enantiomer</b>	S-enantiomer	
14	$CH_2^+$	1.2	1.1	
15	$CH_3^{\tilde{+}}$	3.3	3.2	12.74
18	$H_2O^+$	2	2.8	
26	$C_2H_2^+$	5.8	5.7	13.54
27	$C_2H_3^{\tilde{+}}$	10.9	10.7	13.04
28	$C_2H_4^+/CO^+$	16.3	16.4	11.32
29	$C_2H_5^+/HCO^+$	11.1	10.9	10.88
30	$C_2H_6^+/H_2CO^+$	1.8	1.8	10.84
31	$H_3 CO^+$	4.4	4.4	10.94
32	$H_3COH^+$	0.6	0.5	10.94
43	$C_2H_4O^+$	8.2	7.3	10.87
57	$C_3H_5O^+$	0.8	1	10.67
58	$C_3H_6O^+$	21.1	21.6	10.24
59	$C_3H_6O.H^{+\ b}$	1.6	1.5	

**Table 5.1:** Fragment and parent (m/z 58) ions in the mass spectrum and their appearance energies (AE).

<sup>a</sup> Ref. [126].

<sup>b</sup> Relative intensity of m/z = 59 exceeds that attributable to <sup>13</sup>C at natural abundance. There is most likely some contribution from protonated methyloxirane resulting from weak clustering in the molecular beam.

our experimental conditions is a four-photon ionization of the outer two valence orbitals, probably resonant with n = 4 Rydberg states at the three photon level.

The lighter m/z = 26 - 31 and m/z = 15 mass-tagged PEKE show a strong HOMO<sup>-1</sup> peak. Since the TPEPICO AEs (Table 5.1) indicate that most of these fragments require absorption of five photons we speculate that these minority channels in fact result from photodissociation of the ground state cation; that is by absorption of a further photon *after* the four-photon ionization has been accomplished. A very small shoulder around 2.1 eV in the total electron PEKE spectrum is seen to correlate with formation of m/z 18. This corresponds to the ionization of residual water (m/z = 18) molecules by a five-photon process (14.75-12.62 = 2.13 eV), see panel F.

A simple way to report the MP-PECD asymmetry as a single quantitative value has been proposed [28, 29]:

$$MP - PECD = \frac{I_{+1,f} - I_{+1,b}}{(I_{+1,f} + I_{+1,b})/2} - \frac{I_{-1,f} - I_{-1,b}}{(I_{-1,f} + I_{-1,b})/2},$$
(5.3)

where  $I_{p,f}$ ,  $I_{p,b}$  are the integrated counts in, respectively, the forward and backward hemispheres. This dichroism is readily evaluated from the detected numbers of forward/backward scattered electrons, and such MP-PECD values for both R- and



**Figure 5.3:** Photoelectron kinetic energy (PEKE) distributions of both S- and Rmethyloxirane measured after ionization by circularly polarized light. In panel A the distribution of all detected electrons is shown (coincidences not applied). In panels B-F the mass-tagged kinetic energy of electrons is shown.



**Figure 5.4:** Multiphoton PECD of both S- (blue open circle) and R-methyloxirane (red filled square) for both noncoincident (A) and coincident (B-E) data, plotted as a function of PEKE binned into bands of width  $\pm 0.1$  eV. Error bars are estimated from the Poisson count statistics in each data bin. The dashed gray curve at the background shows the photoelectron spectrum of the given data.

S- methyloxirane are plotted as a function of the photoelectron energy, in bands of width  $\pm 0.1$  eV, in Figure 5.4. All plots show the anticipated mirroring between the dichroism of the two enantiomers, confirming a molecular origin of the observed asymmetry. From preceding discussion the m/z = 58 mass filtered MP-PECD perhaps best exemplifies the dichroism associated with formation of the HOMO<sup>-1</sup> ionic state, while m/z = 43 filtering best exemplifies the SHOMO<sup>-1</sup> state. The MP-PECD for the latter is smaller, up to  $\pm 4\%$  (panel D), while the MP-PECD of the faster electrons associated with the HOMO band shows a distinct increase across the band, reaching values in excess of  $\pm 10\%$  (panel C). Such variability across the PES band profile is also apparent in the VUV single photon HOMO PECD [26]. The observed MP-PECD magnitudes are also commensurate with the single-photon PECD asymmetries, but a notable difference arises since the VUV PECD displays opposite signs for the HOMO-1 and SHOMO<sup>-1</sup> ionizations at comparably low electron kinetic energies [126]. In contrast, the MP-PECD for the two bands reported here are of the same sign. However, despite producing the same final ion states it should be recognized that the VUV results follow a direct ionization from the two outer valence orbitals, whereas in a resonantly enhanced multiphoton ionization as postulated here, the photoelectron is emitted from an excited Rydberg orbital. Given the well established orbital specificity of PECD [14], the single- and multiphoton dichroism of these two bands cannot therefore be directly compared. However, we see in this observation the first indications of the anticipated orbitally specific ionization occurring as well in MP-PECD.

It may be observed that the m/z = 26 - 32 tagged MP-PECD (Figure 5.4, panel E) essentially parallels the MP-PECD associated with production of the ground state HOMO<sup>-1</sup> parent ion (panel C). This corroborates our suggestion of a common ionization pathway leading to production of parent ion, with the light mass channels differentiated by their subsequent photodissociation by a further post-ionization absorption.

For understanding the photoionization dynamics the angular coefficients,  $b_i$ , are potentially more detailed and informative. The even coefficients are estimated by fitting the summed (LCP + RCP) PAD with an expansion as shown in Eq. 5.1. The chiral odd coefficients are better obtained by fitting the dichroism PAD, formed as the difference between normalized LCP and RCP PADs (Eq. 5.2), there being, again, the benefit that any residual instrumental asymmetry (due, for example, to detector gain inhomogeneity rather than photon helicity) can be canceled by treating this difference of alternate polarizations. In so doing by recording, or scaling, the LCP and RCP data to have the same total count we become insensitive to any CD in the photon absorptions influencing ion yields. In practice experiments designed to measure this ion yield CD have to adopt different measures to counter their residual instrumental asymmetry [120, 129–131].

By integration of the PAD expression, Eq. 5.1, over the forward and backward hemispheres, it is also possible to rewrite Eq. 5.3 in terms of these odd coefficients [28]:

$$MP - PECD = 2b_1^{+1} - \frac{1}{2}b_3^{+1} + \frac{1}{4}b_5^{+1} - \frac{5}{32}b_7^{+1},$$
(5.4)

where the inclusion here of terms up to the seventh order coefficient is appropriate for the anticipated 4 photon process. The resulting MP-PECD asymmetries obtained from Eq. 5.4 for the electron angular distributions with energies in the window  $1.3 \pm 0.2$  eV (i.e., the HOMO band) and tagged with parent m/z = 58 ions are listed in Table 5.2, while the sets of individual Legendre coefficients derived from fitting these PADs are provided in Table 5.3.

**Table 5.2:** PECD asymmetry for  $1.3\pm0.2$  eV electrons coincident with m/z = 58 parent ions.

	MP-PECD(LP) <sup>a</sup>	MP-PECD (F/B) <sup>b</sup>
S- methyloxirane	$0.047 \pm 0.012$	$0.044 \pm 0.011$
R- methyloxirane	$-0.048 \pm 0.011$	$-0.048 \pm 0.011$
Mean magnitude	$0.048 \pm 0.008$	$0.046 \pm 0.008$

<sup>a</sup> Obtained from Legendre polynomial (LP) fitting coefficients, given in Table 5.3, using Eq. 5.4. Error estimates are derived from the LP coefficient fitting uncertainty.

<sup>b</sup> Obtained from the integrated count in forward and backward hemispheres (F/B) using Eq. 5.3. Error estimates are obtained by propagation of standard deviations of the counts assuming Poisson counting statistics.

The MP-PECD asymmetry values in Table 5.2 are seem to be in excellent agreement, both between enantiomers (after the anticipated sign change) and with the corresponding values estimated in the same energy range from the forward/backward hemisphere counts. The demonstrated equivalence of these two alternate approaches to estimating the chiral asymmetry provides some corroboration for the validity of its modeling with the Legendre polynomial expansion. It is nevertheless interesting to examine the individual  $b_i$  parameters in Table 5.3. It is seen that the  $b_3$  and  $b_5$  (and probably also  $b_7$ ) coefficients do not differ significantly from zero, so that the entire chiral photoelectron asymmetry is in effect attributable to the first order Legendre polynomial term,  $b_1$ , as would necessarily be the case for a single photon ionization. The apparent noninvolvement of the higher order chiral terms is a priori unexpected for a multiphoton process and is certainly in marked contrast to the only previous investigations of MPPECD in campbor [27, 28]. In that case we found that the  $b_3$ coefficient assumed a larger magnitude and opposite sign to that of the  $b_1$  coefficient, which we were able to attribute, necessarily, to the multiphoton excitation mechanism [28].

However, examining the even coefficients in Table 5.3 one sees that the relatively large  $b_2$  coefficient (that corresponds to a traditional anisotropy parameter  $\beta = +0.69$ ) is accompanied by nonzero  $b_4$ ,  $b_6$  terms indicating involvement of at least three photons. The evident differences in the purely chiral behavior of camphor and methyloxirane merit further investigation.
	S- methyloxirane	R- methyloxirane	Mean <sup>a</sup> (R-)
b1	$0.024 \pm 0.005$	-0.021±0.005	$-0.023 \pm 0.004$
b2	-0.345±0.019	$-0.344 \pm 0.019$	$-0.345 \pm 0.014$
b3	$-0.004 \pm 0.008$	$0.006 \pm 0.007$	$0.005 \pm 0.006$
b4	$0.078 \pm 0.024$	$0.056 \pm 0.025$	$0.067 \pm 0.017$
b5	$-0.007 \pm 0.011$	$-0.019 \pm 0.010$	$-0.006 \pm 0.007$
b6	$0.069 \pm 0.031$	$0.063 \pm 0.032$	$0.066 \pm 0.022$
b7	$0.009 \pm 0.014$	$-0.012 \pm 0.012$	-0.011±0.009
b8	$0.000 \pm 0.001$	$0.000 \pm 0.001$	$0.000 \pm 0.001$

**Table 5.3:** Legendre coefficients of the mass-tagged m/z=58 PADs at 420 nm. The analysis includes electrons with energies  $1.3\pm0.2$  eV.

<sup>a</sup> Averaged values for R- and S-enantiomers. Odd coefficients for the Senantiomer are negated before averaging; values are thus directly applicable to the R-enantiomer.

# 5.4 Conclusion

The results presented here complement the only previous MPPECD studies [27, 28] and go to establish wider generality and potential of this new technique, while revealing some different behavior. Chiral asymmetries up to the order of 10% are reported, commensurate with those observed in single photon PECD. Although the informative odd  $b_i^{\pm 1}$  Legendre coefficients are, in principle, extractable from a single measurement, examining the dichroism by switching polarization usefully isolates these coefficients and cancels out instrumental asymmetry. Comparing enantiomers for the anticipated change in sign of the dichroism helps corroborate the molecular origin of this phenomenon. Finally, the use of electron-ion coincidence detection methods to record mass-tagged electron distributions has been shown to be advantageous for identifying and distinguishing different ionization channels and has assisted discrimination of the PECD associated with production of different states of the parent cation.

# **APPENDIX: SUPPORTING INFORMATION**

Figures 5.5 and 5.6 show, respectively, laser line spectrum and polarization analysis.



Figure 5.5: The typical spectrum of frequency doubled femtosecond laser pulse centered at 420.2 nm. From the Gaussian fit we obtain FWHM = 2.6 nm.



**Figure 5.6:** the measured graph for the analysis of the Stokes parameters of the circularly polarized laser pulses near 420 nm using the rotating quarter wave plate method. The blue curve (data points are open circle, best fit is line) was measured for LCP, the red curve (data points are filled square, best fit is line) for RCP.

# 6

# **ENANTIOSELECTIVE FEMTOSECOND LASER PHOTOIONIZATION SPECTROMETRY OF LIMONENE USING PHOTOELECTRON CIRCULAR DICHROISM**

Limonene is ionized by circularly polarized 420 nm femtosecond laser pulses. Ion mass and photoelectron energy spectra identify the dominant (2 + 1) multiphoton ionization mechanism, aided by TDDFT calculations of the Rydberg excitations. Photoelectron circular dichroism measurements on pure enantiomers reveal a chiral asymmetry of  $\pm 4\%$ .

this chapter is published as: M. M. Rafiee Fanood, M. H. M. Janssen, I. Powis, *Phys. Chem. Chem. Phys.*, **17**, 8614, 2015.

Terpenes are one of the most important and abundant classes of natural products. The occurrence of chiral terpenes is known to show enantiomeric variation between species, but recent studies have revealed enantiomeric variations in biogenic emissions within a single species, [132, 133] and these differences may be linked, for example, to stress conditions experienced by the plant [134]. Monitoring enantiomer variations may thus provide key indicators of the responses of crops, forests, and even the marine ecosphere [135], to environmental stresses such as climate change.

Limonene ( $C_{10}H_{16}$ - see Fig. 6.1 inset) is a frequently encountered exemplar of the chiral monoterpenes. Like many other terpenoids, its enantiomers are perceived to have different odours (R(+)-limonene: citrus fruit; S(-)-limonene: pine/turpentine), and in the biosphere such enantiomeric variations may be significant in signalling to populations of predators and/or pollinators. The R(+) enantiomer (D-limonene) finds widespread domestic uses as an odorant in food, cosmetics, and cleaning products. As a common component of biogenic volatile organic compound emissions (BVOCs), it can be expected to play a significant role in certain atmospheric processes. There is, therefore, an interest in understanding the UV photochemistry and photophysics of gaseous limonene.

In this context it is interesting to consider the potential of two more recently introduced methods for enantioselective detection and probing, both based upon laser photoionization.

Loge and Boesl [130] have reported the resonant two photon ionization yield of S-limonene at 213 nm laser wavelength (equivalent photon energy of 5.82 eV). This excitation lies in the red foot of the limonene absorption spectrum and the circular dichroism (CD) detected in the parent ion yield has a similar asymmetry factor ( $\sim 1.6 \times 10^{-3}$ ) to that seen in the absorption CD at the same wavelength [114]. In the present work we wish to evaluate the potential of an alternative new technique, photoelectron circular dichroism (PECD) using resonant ionization with an ultrafast laser [29]. PECD detects a forward-backward asymmetry in the photoelectron angular distribution relative to the photon beam propagation direction with asymmetry factors that range, for single photon ionization in the VUV and SXR regions, from 0.01 - 0.4 [14, 24, 136]. Very recently it has been shown that similar asymmetries can be seen using 400 nm fs laser pulses to ionize various bicyclic monoterpenoids [27, 28, 31] or methyloxirane [30], although very different behaviour in the higher odd Legendre moments - uniquely accessed by the multiphoton excitation - were apparent. Here we seek further insight with a different molecular system.

The experiment uses a single detector spectrometer having velocity map imaging charged particle optics for both electron and ion detection [60]. The position sensitive delay line detector [57, 58] is capable of measuring the full 3D electron momentum from the time and position of arrival of individual electrons. Alternatively, by reversal of the apparatus extraction and detector potentials the time-of-flight of ions can be measured on the same detector. Because of the much longer flight times of the ions these voltages can be rapidly switched to ion mode immediately after electron detection, allowing the delayed coincidence between an electron and ion pair from a single molecular ionization event to be detected. Electrons can then be mass-tagged according

to the identity of coincident ion.

A doubly skimmed, seeded molecular beam of limonene enantiomer samples (obtained from Sigma Aldrich and used without further purification) was produced after passing Ne gas (0.1 bar backing pressure) through an external stainless steel bubbler maintained at room temperature. The output of a 3 kHz repetition rate laser (Spectra Physics) was frequency doubled in a BBO crystal providing of ~ 20 mJ, 150 fs pulses at 420 nm, loosely focussed into the molecular beam. Circular polarization was obtained with a  $\lambda/4$  wave plate and was switched between left-(LCP) and right-(RCP) circular polarization every 500 s. Stokes parameters were determined by polarimetry measurements [28], confirming a high degree of circular polarization ( $|S_3| \ge 0.975$ ). Measurements on R- and S-enantiomers were accumulated during 49.5 and 45 million laser shots respectively and the average number of electron events per laser shots in both measurements was maintained at 0.085 to minimise false coincidences. For each enantiomer the accumulated counts were reduced to the number released into the forward (F) and backward (B) hemispheres, combining the LCP and RCP data in such a way that any residual forward-backward instrumental asymmetry (which is independent of polarization) is cancelled [28, 30]. Then, the PECD asymmetry is conveniently expressed as

$$G = 4 \times \frac{F - B}{F + B}.$$
(6.1)

Fig. 6.1 shows a ToF mass spectrum which was the same for either polarization and both enantiomers. While the parent ion mass is the dominant species there is a range of smaller daughter ions present. The adiabatic ionization potential of limonene, 8.521 eV, is well established [96, 97, 114] and so ionization requires three 420 nm photons (equivalent energy 8.86 eV). This leaves a maximum excess energy of 0.34 eV available for the photoelectrons. On the other hand, VUV ionization at 9 eV produces negligible fragmentation [96] suggesting that there may be partial uptake of at least a fourth photon by some of the fragmentation channels observed here.

Fig. 6.2 shows the photoelectron kinetic energy distributions derived from the 3D electron momenta for all detected electrons, and for electrons coincident with selected parent and fragment ion masses. Again these results do not vary with either polarization or enantiomer. These photoelectron spectra are essentially identical to one another, suggesting a common ionization path for both parent and fragment ions, although the fragment ion-tagged spectra do tail slightly more to high energy suggesting that a small subset of the fragmentation may arise from more energetic ionization processes. The range of kinetic energy observed is nevertheless broadly consistent with a net three photon ionization, although the peak in the distribution is significantly below the 0.34 eV expected at the adiabatic ionization limit. Before further assigning the dominant ionization process we consider the assignment of the resonant intermediate state accessed in our experiments.

The UV absorption, and corresponding circular dichroism (CD) of limonene vapour in the range 225-150 nm was first reported by Brint *et al.* [114] (see Fig. 6.3). Subsequently, the absorption spectrum has been re-measured at slightly higher



**Figure 6.1:** Mass spectrum of S-limonene seeded in 0.1 bar Ne after ionization by 420 nm 150p fs laser. The parent ion is m/z 136.

resolution and extended down to ~ 120 nm [97]. Above 200 nm the absorption spectrum displays a weak pedestal, albeit with a few broad structures. Brint *et al.* assigned the first feature, at 218 nm (5.69 eV), to excitation from the 2  $\pi$  HOMO, located at the C=C double bond in the cylcohexene ring. The assignment of the upper level as the 3s Rydberg state was based upon the observed 22915 cm<sup>-1</sup> term value of this excitation [114]. A second weak feature at 210 nm (5.90 eV), also clearly visible in the CD spectrum, was assigned to the same electronic transition with one quantum of vibrational excitation, probably in the ring C=C stretching mode. A third feature at 204.9 nm (6.051 eV), this more prominent in the CD spectrum, was tentatively assigned as being the same excitation but having two quanta in this C=C stretching mode.

On the other hand, making use of the high level EOM-CCSD method and a ccpVDZ basis with additional molecule-centred diffuse functions, Smialek *et al.* [97] calculated that excitations to the 3*s* and higher Rydberg series occur at somewhat higher energies, starting with the  $2\pi - 3s$  transition at 6 eV. Additionally, they calculate transitions from the second highest  $1\pi$  molecular orbital (located at the isopropenyl double bond) to n = 3 Rydberg series starting at 6.39 eV. However, accepting these suggested excitation energies leaves unaddressed a question concerning the identity of the absorptions in the pedestal region below 6 eV.

The assignment offered by Brint et al. [114] would suggest that our current choice



**Figure 6.2:** Photoelectron kinetic energy distributions of limonene measured at 420 nm for all-, and for mass-tagged-electrons, as indicated.



**Figure 6.3:** UV CD [114] and absorption [97, 114] spectra of limonene vapour, arbitrarily scaled to facilitate comparison. CAM-B3LYP/dAug-cc-pVDZ calculated Rydberg excitations for conformers Eq-1 (red), Eq-2 (green) and Eq-3 (cyan) are plotted offset with heights proportional to their oscillator strength. The two photon energy equivalent of the 420 nm fs laser excitation (5.9 eV) is marked, with grey bands indicating the two photon excitation range (derived from the measured laser bandwidth FWHM of 2.55 nm [30]).

of 420 nm wavelength is two photon resonant (equivalent energy of 5.90 eV) with the  $2\pi \rightarrow 3s \ (v = 1)$  excitation feature seen in both absorption and CD spectra (see Fig. 6.3). The inferred energy of the excited vibrational mode is ~  $1500 \text{ cm}^{-1}$  (0.186 eV). In the  $2\pi^{-1}$  cation ground state, the principal vibrational progression observed in both threshold and He I photoelectron spectra has a first spacing of 0.174 eV and the mode has been assigned as the ring C=C stretch [97]. Assuming this is the same mode excited in the Rydberg intermediate and a  $\Delta v = 0$  propensity for the Rydberg state ionization, the required ionization energy is then that for the  $2\pi^{-1}$  ( $v^+ = 1$ ) cation, determined as 8.695 eV from the He I photoelectron spectrum [97]. At the 420 nm three photon energy equivalent of 8.856 eV this then leaves an excess energy of just 0.16 eV. This accords reasonably well with the experimental electron energy distribution (Fig. 6.2) peaking at  $\sim 0.1$  eV, from which we deduce a dominant two photon resonant, three photon (2+1) ionization mechanism producing  $v^+ = 1$  cation in the current experiment. This argument also tends to support the  $2\pi \rightarrow 3s$  (v = 1) assignment of the 5.9 eV peak. Further post-ionization photon absorption by the cation states most probably accounts for the extra fragmentation noted.

To attempt further corroboration of the spectrum assignment we have performed our own TD-DFT calculations [by *Gaussian09* revision d.01 [137]] using the long-range adjusted CAM-B3LYP and M11 functionals with a double augmented cc-pVDZ basis set at B3LYP/cc-pVDZ optimised geometries, considering the three lowest energy equatorial conformers of limonene, Eq-1, Eq-2, and Eq-3 [112]. These results and previous EOM-CCSD calculations [97] are summarised in Table 6.1. While there is some spread in the absolute excitation energies calculated, these methods consistently indicate a ~ 0.4 eV energy gap between the  $2\pi \rightarrow 3s$  and first  $2\pi \rightarrow 3\pi$  excitations and oscillator strengths that are approximately an order of magnitude less for the former transitions.

	Smiale	ek <i>et al</i> .ª	This	work <sup>b</sup>	This	work <sup>c</sup>
	<i>E</i> (eV)	f	<i>E</i> (eV)	f	<i>E</i> (eV)	f
$2\pi \rightarrow 3s$						
Eq-1	6.006	0.0027	5.79	0.0046	5.426	0.0015
Eq-2	6.013	0.002	5.797	0.0039	5.437	0.0012
Eq-3	6.002	0.0026	5.785	0.0043	5.431	0.0013
$1\pi \rightarrow 3s$						
Ea-1	6 391	0.0253	6 204	0.0358	5 844	0.0028
Eq.2	6 4 4 7	0.0118	6.25	0.0327	5 893	0.0020
Eq-3	6.435	0.0133	6.238	0.0096	5.882	0.0096
$2\pi \rightarrow 3p$						
Eq-1	6.454	0.0142	6.242	0.0412	5.792	0.0304
Eq-2	6.47	0.0206	6.232	0.0419	5.815	0.0219
Eq-3	6.439	0.0247	6.214	0.068	5.803	0.025
$2\pi \rightarrow 3n$						
$E_n \neq Sp$ Fa-1	6 54	0.0107	6 34	0.0361	5 928	0.0066
Eq 1 Fa-2	6 5 5 5	0.0044	6.36	0.007	5.920	0.0000
Eq 2 Eq-3	6.538	0.0036	6.35	0.0048	5.929	0.0025
29.0	0.000	0.0020	0.00	0.0010	0.727	0.0010
$2\pi \rightarrow 3p$						
Eq-1	6.674	0.0026	6.493	0.0162	6.168	0.012
Eq-2	6.761	0.0033	6.518	0.0022	6.181	0.0035
Eq-3	6.755	0.0002	6.49	0.0066	6.17	0.0014

**Table 6.1:** Rydberg excitation energies, *E*, and oscillator strengths, *f*, calculated for limonene conformers.

<sup>a</sup> [97].

<sup>b</sup> TDDFT CAM-B3LYP/dAug-cc-pVDZ.

<sup>c</sup> TDDFT M11/dAug-cc-pVDZ.

Guided by these observations we have plotted the CAM-B3LYP transition energies and relative oscillator strengths on Fig. 6.3 with an empirically chosen -0.1 eV energy offset. Although ignoring *e.g.* Franck-Condon factors the theory-experimental spectra match with this empirical adjustment is convincing. The calculated  $2\pi \rightarrow 3s$  excitation is brought into alignment with the 5.7 eV pedestal peak previously so assigned [114] while the steep rise in the VUV absorption spectra, and in particular a weak inflection at 6.12 eV in the higher resolution spectrum [97], coincides with the cluster of  $2\pi \rightarrow 3\pi$ and  $1\pi - 3s$  transitions. Similar results are obtained by plotting the EOM-CCSD calculations with an offset of -0.32 eV. (Systematic studies have found EOM-CCSD can overestimate excitation energies by a few tenths eV, so that this adjustment is not intrinsically surprising [138].) Overall, we therefore favour assignment of the transitions in the pedestal region below 6 eV to the  $2\pi \rightarrow 3s$  electronic excitation, with higher Rydberg excitations falling above this and infer a (2 + 1) ionization mechanism at 420 nm producing vibrationally excited cations.



**Figure 6.4:** 420 nm multiphoton PECD asymmetry of limonene enantiomers using all electrons (no mass-tagging). Error bars are derived from Poisson count statistics. Also shown on the same energy scale as a dashed grey line is the normalised photoelectron energy distribution from Fig. 6.2, plotted on the same energy scale (dashed grey line, right hand axis).

Fig. 6.4 shows the multiphoton PECD asymmetry obtained for both enantiomers as a function of electron energy. The absolute magnitude is greatest in the vicinity of

the peak in the electron energy distribution, and decreases on passing towards faster electrons. The R- and S-enantiomer PECD effectively mirror each other, as would be expected, an observation which also helps establish the molecular origin of the forward-backward asymmetries that are detected. Selecting a photoelectron energy of 0.0-0.2 eV that encompasses the photoelectron energy peak region we obtain asymmetry factors of  $-0.044 \pm 0.002$  for the R-enantiomer, and  $+0.046 \pm 0.002$  for the S-enantiomer, a magnitude about 30-fold greater than the corresponding asymmetry factors previously observed in absorption [114] and ionization yield [130] measurements. There is then a decrease in the asymmetry towards higher kinetic energies which might be expected to correlate with production of vibrational ground state cation, although as noted there is no distinct structure associated with this.

# 6.1 Conclusions

These preliminary observations of fs laser multiphoton PECD in limonene demonstrate this to be a convenient and, because of the large asymmetry factors, a potentially sensitive approach to enantiomeric identification in conjunction with laser ionization mass spectrometry. They also raise some challenges and opportunities for developing better theoretical insights. First, because of the existence of various conformers of limonene it will be necessary to develop understanding of the plausible conformer populations under experimental conditions and to account for these in computational models, since PECD is known to be exceptionally sensitive to molecular conformation. Secondly, it will be necessary to consider PECD generated not by ionization from ground state neutrals, but from excited Rydberg states, and to account for additional anisotropies introduced in the two photon excitation step. A first extension of successful single photon PECD treatments in this manner, considering the MP-PECD of camphor, provided encouraging results but much remains to be done [28]. Thirdly, according to the interpretation offered here this will be the first instance in which PECD is clearly observed from a vibrationally excited state. Recent evidence suggests that vibronic interactions with odd quanta of vibrational excitation can exert a very dramatic influence on PECD asymmetries [26, 139] and such possibilities will need to be carefully checked out and validated. Further experiments using different wavelengths and excitation schemes are planned as a contribution towards tackling these challenges and opportunities.

7

# MULTIPHOTON PHOTOELECTRON CIRCULAR DICHROISM OF LIMONENE USING FEMTOSECOND LASER PULSES

# 7.1 Introduction

Photoelectron circular dichroism (PECD) is a powerful technique to study the structural and electronic characteristics of chiral molecules [15, 21, 22, 24, 123, 124] using a synchrotron radiation light source. Recently the technique has been extended to the multiphoton ionization regime utilizing femtosecond laser pulses [27, 28, 30, 31].

Two previous PECD studies on pure limonene enantiomers have been reported in the earlier chapters of this thesis. In chapter 4, the single-photon ionization of limonene with circularly polarized VUV light has been discussed and the PECD asymmetry was found to show a strong correlation with vibrational structures in the first two ionic bands. Moreover, in chapter 6, the first multiphoton PECD experiment on limonene is presented using a 420 nm laser pulse and the single detector coincidence spectrometer. At this wavelength, ionization takes place via a vibrational excited Rydberg state and PECD asymmetry of about 4.5 % is reported.

In this chapter, I present a more extended study of multiphoton PECD of limonene enantiomers using different laser wavelengths and ionization schemes. The results in this chapter are compared with those two other results to improve the understanding of multiphoton PECD.

This chapter is structured as follows. In section 7.2, I explain the experimental method and setup. In section 7.3, I present and discuss the experimental results of both limonene enantiomers ionized with femtosecond pulses at 420 nm, 412 nm and 392 nm and propose the possible multiphoton process in relation to the results reported in previous chapters. Finally, I conclude the discussion in section 7.4.

# 7.2 Experimental method and setup

#### 7.2.1 Vacuum system and coincidence spectrometer

The electron-ion coincidence spectrometer used for this work has been described in detail before [57, 58] and is shown in Fig. 7.1.

The liquid samples of both Limonene enantiomers (purchased from Sigma-Aldrich with a stated purity of 96% (S) and 97% (R)) were held in an external stainless steel bubbler maintained at room temperature. A stream of pure Ne gas sweeps the sample vapor through a stainless steel transfer line to a 150  $\mu$ m diameter nozzle in the source chamber. The Ne backing pressure was 0.2 bar for measurements at 420 nm and 412 nm and 0.6 bar for the one at 392 nm. The expanding gas mixture generates a continuous molecular beam in the source chamber. The molecular beam is double skimmed downstream from the nozzle as it passes through the buffer chamber into the imaging spectrometer chamber. In the imaging chamber, the molecular beam interacts with laser light perpendicularly. After the ionization of the molecule, electrons are extracted by velocity map imaging (VMI) [40] optics toward a time-and position sensitive delay line detector. The full three dimensional momentum of each electron is directly obtained from its position and time of arrival. Subsequently, ions are extracted downward toward the opposing delay line detector where only time of arrival is recorded. Home-built



**Figure 7.1:** Schematic overview of the experimental setup. Limonene sample is held in the stainless steel reservoir at room temperature. The vapour of limonene is swept into the coincidence machine by pure Ne gas. The continuous molecular beam is intersected by a laser beam. After the ionization of the molecule the electron and ion pair are detected in delayed coincidence on two opposing time- and position-sensitive delay line detectors mounted perpendicular to the molecular beam and photon beam.

high-voltage switches, consisting of Behlke switches (HTS-51), are used to change the magnitude and polarity of the high voltages on the ion lenses. The switches are operated at the repetition rate of the laser system (3 kHz). Both electron and ion time-of-flight (TOF) tubes are shielded by a 1mm thick  $\mu$ -metal tube. The typical voltages of the charged particle lenses (repeller (R), extractor (E) and extra lens (L)) used for detecting electrons and ions are  $R_e$ = -520 V,  $E_e$ = -385 V,  $L_e$ =-275 V and  $R_i$ =2000 V,  $E_i$ =1460 V,  $L_i$ =0 V, respectively.

#### 7.2.2 Laser systems

The commercial femtosecond laser system (Spectra Physics) consists of a Titanium:Sapphire oscillator (Mai-Tai) used for seeding the chirped regenerative amplifier (Spitfire-Ace). The fundamental output of the laser was frequency doubled in a BBO crystal and this second harmonic pulse was used for multiphoton ionization of gaseous samples. In this work, three different pulses at 420.3 ( $\Delta\lambda$ =2.5 nm), 412.5 nm ( $\Delta\lambda$ =2.4 nm) and 392.3 nm ( $\Delta\lambda$ =2.3 nm) were used. The laser pulse duration was about 150 fs and the pulse energies were about 18  $\mu$ J (420 nm), 20  $\mu$ J (412 nm) and

10  $\mu$ J (412 nm) at 3 kHz repetition rate. The light beam was loosely focused into the molecular beam sample (to a spot size approximately 100  $\mu$ m × 150  $\mu$ m) by a lens (*f*=30 cm). The corresponding intensity in the ionization volume is estimated to be 10<sup>11</sup>-10<sup>12</sup> Wcm<sup>-2</sup>.

An achromatic quarter wave plate (B-Halle) was used to generate circularly polarized light. The polarization of the light was characterized in terms of the Stokes vector [90–92] by the rotating quarter-wave plate method as described by Lehmann [36]. The Stokes parameter,  $S_3$ , was determined to be  $S_3 > 0.98$  for all circular polarization states used in this study.

#### 7.2.3 Data acquisition and treatment

During the measurement, circular polarization (LCP/RCP) was switched every 500 s (1.5 million laser shots (MLS)) in order to reduce the effect of the drift in laser intensity, signal stability and beam pointing. The measurement on each enantiomer was performed during 36 MLS at 420 nm, 45 MLS at 412 nm and 63 (58.5) MLS for R-(S-)limonene at 392 nm. The number of electron events per laser shot (e/LS) ratio was set to be about 0.07- 0.08 for all experiments.

After careful checks that the center of the electron images were the same, all files with the same polarization were combined together post measurement for data analysis. Before the subtraction of the data files of opposite polarization, each combined data file was scaled to the same total photoelectron intensity in the electron kinetic energy region of interest. Multiphoton PECD asymmetry (G) has been formulated in such a way that any residual forward-backward instrumental asymmetry can be canceled (see chapter 2):

$$G = 4 \times \left(\frac{F-B}{F+B}\right), \tag{7.1}$$

where,  $F = N_{LCP,f} + N_{RCP,b}$ ;  $B = N_{LCP,b} + N_{RCP,f}$ .  $N_{p,f}$  and  $N_{p,b}$  are the number of electrons emitted in forward and backward hemispheres respectively. The error in G is obtained by standard error propagation assuming Poisson statistics.

Equation 7.1 is used to examine the PECD spectra (Fig. 7.6) that follow in the next section. Subsequently, the angular distribution will be examined in terms of Legendre polynomials fit, to further highlight the photoionization dynamics.

## 7.3 **Results and discussion**

#### 7.3.1 Time-of-Flight

Fig. 7.2 shows ion time-of-flight (TOF) spectra of limonene after multiphoton ionization at (A) 420 nm, (B) 412 nm and (C) 392 nm. At each wavelength, TOF spectra are identical regardless of the laser polarizations and sample enantiomers.

The parent ion ( $C_{10}H_{16}^+$ ; m/z=136) clearly forms the dominant ionic channel in all measurements. The inset in Fig. 7.2(B) depicts the mass spectra in the region of 15-130



**Figure 7.2:** Ion time-of-flight spectrum of limonene resulting from multiphoton ionization at (A) 420 nm, (B) 412 nm and (C) 392 nm. Insets show a zoom-in of the parent ion (m/z=136), fragment ions ( $15 \le m/z \le 130$ ) and dimer (m/z=272) respectively. Peak at masses 137 is parent molecule isotopomer with <sup>13</sup>C.

amu where several fragment ions (labeled by their number of carbons) are observed. During the measurement, the laser intensity was adjusted to minimize fragmentation. Slightly higher Ne backing pressure in the 392 nm measurement caused the dimer cluster formation in the molecular beam (see panel C) while there is no sign of any cluster ions in the two other measurements at 420 nm and 412 nm.

The ionization energy (IE) of the highest occupied molecular orbital (HOMO) and second HOMO (HOMO-1) of limonene are 8.52 eV and 9.1 eV respectively (see chapter 4). HOMO and HOMO-1 ionizations correspond to ionization of the  $\pi$ -orbitals in the carbon ring and isopropenyl group in the molecule, respectively [96, 97]. Thus, ionization requires at least three photons of our chosen wavelengths (3hv(420 nm)=8.86 eV, 3hv(412 nm)=9.01 eV and 3hv(392 nm)=9.48 eV). Contrary to the results presented here, VUV TOF spectra obtained for single photon ionization by hv < 9.5 eV, show no fragmentation at all (see chapter 4). This may suggest that the fragmentation arising from absorption of a further photon after the ionization and/or a different ionization mechanism. I will discuss the ionization scheme further in the next section by comparing mass-selected photoelectron spectra of the parent ion and fragment ions.

#### 7.3.2 Multiphoton ionization process and PECD

Figure 7.3 displays the photoelectron spectra (PES) of limonene derived from full 3D electron momenta for all (non-coincident) electrons detected and for mass-tagged electrons (coincident with parent ion and fragment ions) at different wavelengths. Moreover, Fig. 7.4 shows the dimer-tagged PES at 392 nm. For a given photon wavelength the PES obtained for either polarization and for either enantiomer are essentially the same. The overall similarity between parent and fragment ions tagged PES suggests a similar ionization pathway for them i.e. most fragmentation comes after ionization. However, the tail of fragment ions mass-tagged spectra seems to extend more to higher photoelectron kinetic energies. This may support the supposition that a small portion of fragmentation results from a more energetic ionization process, which leads also to more fragmentation than expected from the three photon energy process. Recently, Baumert *et al.* [31] studied the laser intensity dependence of fragmentation.

Intermediate states may play a major role in multiphoton ionization experiments. Lehamnn *et al.* [28] presented a theoretical calculation considering one-photon ionization from the pre-aligned 3s-Rydberg state due to the interaction of the laser field. The calculation provided acceptable agreement with experimental results in the limit of weak-field ionization  $(10^{12} \text{ Wcm}^{-2})$  and described the importance of the resonant intermediate states on the observed multiphoton PECD effect. In support of this figure, Baumert *et al.* confirmed that the ionization from the resonant intermediate state is the origin of the PECD in their recent intensity dependence studies of PECD [31]. Therefore, it is essential to consider the assignment of the resonant intermediate states involved in a multiphoton ionization experiment.

Brint *et al.* [114] and later Smialek *et al.* [97] (with better resolution) recorded the UV absorption of limonene in the range of 5.51-8.26 eV and 3.9-10.8 eV respectively. Fig. 7.5 shows absorption spectra and corresponding circular dichroism (CD) spectrum of limonene (recorded by Brint). The total energies of two-photon excitation for







**Figure 7.4:** The photoelectron spectrum of mass-tagged m/z=272 of limonene measured at 392 nm.

the indicated laser wavelengths are also shown in the graph. The assignment of the transitions in the region below 6 eV has been already discussed in chapter 6 where the small feature at 5.68 eV is assigned to  $2\pi \rightarrow 3s$  excitation and one and two quanta of vibrational excitation in the same electronic transition respectively correspond to 5.90 eV and 6.05 eV energies [114].

I will now present and discuss the results obtained at different wavelengths individually.

#### Multiphoton PECD at 420 nm

The multiphoton ionization process of limonene at 420 nm is discussed in detail in chapter 6. Here, I present the results obtained under different experimental conditions. In the current experiment, the double-detector spectrometer setup was used and the laser wavelength was also slightly different (420.3 nm). Three-photon ionization at 420.3 nm (2.95 eV) provides an energy of 8.86 eV which is only sufficient for HOMO ionization. The maximum available excess energy of electron is 0.34 eV (=8.86 eV-8.52 eV). This value is not matched with the experimental PES peak around 0.1 eV (peak I). However, two-photon energy of 420 nm (=5.90 eV) matches the  $2\pi \rightarrow 3s$  (v = 1) state with vibrational spacing of 1500 cm<sup>-1</sup> (=0.186 eV) from the origin. On the other hand, the vibrational progression seen in the cation ground state has a first spacing of 0.172 eV, believed to correspond to a double-bond stretching mode. Assuming a  $\Delta v = 0$  propensity for Rydberg ionization to the parent ion, an energy loss of about 0.172 eV with respect to maximum electron kinetic energy is estimated. The excess energy of 0.16 eV is now in acceptable agreement with experimental data. Therefore,

we infer a two-photon resonant to 3s ( $\nu = 1$ ) Rydberg state and three-photon ionization mechanism (2+1) for the measurement at 420 nm.



**Figure 7.5:** Absorption [97, 114] and circular dichroism [114] spectra of limonene. The gray lines indicate total energies of two-photon excitation for indicated laser wavelengths.

Fig. 7.6(A) shows the PECD asymmetry values obtained at 420 nm for both enantiomers as a function of photoelectron energy in an energy window of  $\pm 0.1$  eV. All plots depict the mirroring effect expected between the dichroism of two enantiomers that in principle confirms the molecular origin of the chiral asymmetry and also shows the reproducibility of the data. Furthermore, the results presented here (double-detector mode) are very similar to the one reports in chapter 6 (single-detector mode).

#### Multiphoton PECD at 412 nm

The photoelectron spectrum of limonene from multiphoton ionization at 412.3 nm (3.0 eV) displays a prominent peak with maxima at 0.15 eV (II) with a small broad shoulder centred at 0.5 eV (III) (see Fig. 7.3). Three-photon energy at 412.3 nm is equal to 9.01 eV resulting in the maximum available excess energy of 0.49 eV. This value accords very well with the experimental PES peak III suggesting that here all the available excess energy of the photoelectron.

On the other hand, the energy shift between peak II (412 nm) and peak I (420 nm) matches very well with the energy difference of a single photon; 3.01 eV(412 nm) -

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**Figure 7.6:** Multiphoton photoelectron circular dichroism asymmetry of both limonene enantiomers for (i) all and (ii, iii) mass-tagged electrons measured at different wavelength (A-C). Error bars are calculated from Poisson count statistics. The dashed gray plot in the background is the photoelectron spectrum of given data.

2.95 eV(420 nm) = 0.06 eV, suggesting peak II in PES can be assigned again to the ionization of the vibrationally excited 3s Rydberg state while excess energy deposited in the Rydberg intermediate state at the two photon level remains as the internal energy in the ion state.

The PECD asymmetry values at 412 nm (see Fig. 7.6(B)) are very similar to the one obtained at 420 nm. In both measurements the highest asymmetry is in the middle of the PES peak and the asymmetry reduces for the faster electrons. This similarity, in fact, suggests again that peak I and II are resulted from similar ionization mechanism. Moreover, PECD values degrade to zero for photoelectron kinetic energy of about 0.4 eV. Low statistics does not allow further PECD determination around peak III.

#### Multiphoton PECD at 392 nm

The three 392 nm (=3.16 eV) photons provide an energy of 9.48 eV which is in fact sufficient to ionize both  $2\pi$  (HOMO) and  $1\pi$  (HOMO-1) orbitals. Moreover, in two-photon excitation, the Rydberg spectrum starts getting more complicated as we need to consider all possible  $(2\pi \rightarrow 3s, 2\pi \rightarrow 3p, 1\pi \rightarrow 3s)$  transitions resulting in different ionization channels. Therefore, what we may observe in the experimental data is the convolution of all of the plausible ionization paths, which makes it difficult to deduce the dominant ionization process. I will continue firstly by presenting the experimental data obtained at 392 nm followed by some possible explanations toward better understanding of our experimental data.

The mass tagged parent and fragment ions PES of limonene from multiphoton ionization at 392.3 nm show two peaks centered at 0.38 eV(IV) and 1.04 eV(V). Moreover, the dimer PES shows a single peak with maximum around 0.6 eV(VI) suggesting that a very different ionization process is taking place.

Fig. 7.7 shows slow PES (adopted from chapter 4), and He(I) PES [97], against the electron kinetic energies available by three-photon excitation of our given laser wavelength. One can use this figure to examine directly peaks (I-V) in multiphoton excitation PES with respect to VUV PES.

The expected available excess energies from the ionization of HOMO and HOMO-1 are 0.96 eV (= 9.48 eV (3hv) - 8.52 eV (HOMO IE)) and 0.38 eV (= 9.48 eV - 9.1 eV(HOMO-1 IE)) which fit well with the position of peak V (1.04 eV) and peak IV (0.38 eV) in the the PES respectively. Therefore, one possible assignment for peaks IV and V would be that they are assigned to the ionization of different orbitals. Peak V corresponds to adiabatic ionization of HOMO and peak IV could be assigned to ionization of HOMO-1.

Moreover, the  $1\pi$  to 3s Rydberg excitation is calculated to be at 6.12 eV (see chapter 6). Two-photon excitation near 392 nm (equivalent to 6.32 eV) produces a 3s Rydberg with a  $1\pi$  hole, and 0.2 eV vibrational excitation (assume that the C=C stretch is around 0.2 eV). Assuming 0.2 eV is retained in vibrational excitation of the cation, and since 9.48 eV (3hv) - 9.1 eV (HOMO-1 IE)= 0.38 eV, again, this would seem to suggest that the 9.1 eV peak in Fig. 7.7 is the HOMO-1( $v_{stretch}=1$ ) peak.

Interestingly, the sign of PECD is switched between two PES peaks for a given



**Figure 7.7:** He(I) [97] and threshold PES of limonene plotted against the electron kinetic energies available by three-photon excitation of 420 nm, 412 nm and 392 nm pulses.

enantiomer as is seen in Fig. 7.6(C). A flip in the sign of PECD between adjacent bands, corresponding to different orbital ionizations, has often been observed in single photon PECD studies [21, 23–25]. Therefore, ionization from two different orbital, proposed here, could possibly be consistent with the sign change in PECD.

A direct comparison of the VUV single photon experiment results (reported in chapter 4) and multiphoton PECD results is shown in Figure 7.8. In the top panel, single photon PECD and PES obtained with hv = 9.5 eV photons for R-limonene are plotted against a common ionization energy scale. In the bottom panel, multiphoton (non-coincidence) PECD and PES (measured at 392 nm) are displayed as a function of photoelectron kinetic energy correlated with the top axis. Although the overall ionization process between one and three photons are different, the sign (and more or less the magnitude) of PECD asymmetries in these two experiments are very similar in the position of peaks (A) and (D). This may support again the above mentioned assignment for peak IV and V.

An alternative assignment for peak IV would be the ionization of the vibrationally excited HOMO. Particularly, the two outermost bands of limonene (HOMO and HOMO-1) are very close and it seems they are somewhat overlapped in the VUV photoelectron spectra. The energy shift between peak IV (392 nm) and peak I (420 nm) fits reasonably with the energy difference of a single photon, 3.16 (392 nm)- 2.95 (420 nm)= 0.21



**Figure 7.8:** (Top panel) VUV PES (green line) and PECD (filled red squares) for R-limonene measured at hv=9.5 eV. (Bottom panel) Multi-photon PECD (filled red squares) and PES (blue line) measured by 392 nm laser light.

eV. Therefore, one may conclude that peak IV and peak I are ionized from a common electronic state. The ionization takes place through the vibrationally excited 3s Rydberg state and maintain that vibration in cation state.

The same sign of PECD asymmetry around peak I (420 nm), II (412 nm) and IV (392 nm) indicates that they correspond to a similar transition. The different signs of PECD at the position of peak IV and V could possibly imply ionization from different vibrational levels.

The sensitivity of PECD to different vibrational ion levels has been studied previously [26] for methyloxirane where the sign of the asymmetry is also switched from one vibrational level to another. It would be then feasible that the ionization from different vibrational excited states leads to different signs in PECD.

In summary, I suggested two plausible interpretations for the assignment of peak IV. Either of these is possible but in reality both might occur. At the moment I do not have any evidence which definitely rules one out in favor of the other.

Finally, the dimer PES is clearly different from the other spectra. The dominant peak is around 0.6 eV. However, due to lack of theoretical and experimental information for the cluster ions of limonene, it is difficult to interpret the ionization pathway of the



Figure 7.9: Schematic multiphoton ionization scheme of limonene for indicated femtosecond laser wavelengths.

dimer. Since there are very low dimer counts, the PECD asymmetry determination has not been done .

The multiphoton ionization mechanisms proposed in this contribution are summarized in Fig. 7.9.

#### 7.3.3 Photoelectron angular distributions and PECD

The PECD asymmetry can be determined alternatively from angular coefficients [28, 29]. The photoelectron angular distribution (PAD) arising from *n*-photon ionization of a chiral molecule with circularly polarized light is given by

$$I_p(\theta) = \frac{I_{tot}}{4\pi} \left( 1 + \sum_{i=1}^{2 \cdot n} b_i^p P_i(\cos\theta) \right),\tag{7.2}$$

where *p* is the polarization of the light, and *p*=+1 and *p*=-1 correspond to left circular polarized (LCP) and right circular polarized (RCP), respectively.  $P_i(cos\theta)$  are Legendre polynomials,  $b_i^p$  are the corresponding expansion coefficients and  $\theta$  is the angle between the electron momentum and the propagation direction of the laser beam. Switching the helicity of the circularly polarized light (or exchanging enantiomers) changes the sign of the odd Legendre coefficients while leaving the even Legendre coefficients unaltered. Therefore, the chiral information is embedded in odd Legendre terms which can be isolated by subtracting PAD of one polarization from another for a single enantiomer:

$$I_{LCP}(\theta) - I_{RCP}(\theta) = \frac{I_{tot}}{4\pi} \left( \sum_{i=1}^{n} 2b_{2i-1}^{+1} P_{2i-1}(\cos\theta) \right).$$
(7.3)

The multiphoton PECD asymmetry can be also expressed as a single value in terms of odd Legendre coefficients (assuming a three-photon process):

$$G = 2b_1^p - \frac{1}{2}b_3^p + \frac{1}{4}b_5^p.$$
(7.4)

The  $b_i$  coefficients also contain information which can be used for a better understanding of photoionization dynamics.

An alternative quantity, called quadratic PECD (QPECD) has been proposed recently [31] to quantify PECD as:

$$QPECD \approx \sqrt{12} \times \sqrt{\sum_{i_{odd}} \frac{b_i^2}{2i+1}}$$
(7.5)

This new measure is useful particularly for situations where the odd  $b_i$  coefficients have a similar sign and may cancel each other in Eq. 7.4.

Table 7.1 tabulates the multiphoton PECD asymmetries of all three experiments reported in this work plus the results from the measurement presented in chapter 6. PECD values are derived from Eq. 7.4 and Eq. 7.5 for non-coincidence electrons in selected energy windows of  $0.1\pm0.1$  eV (420 nm; peak I),  $0.15\pm0.15$  eV (412 nm; peak II),  $0.38\pm0.2$  eV (392 nm; peak IV) and  $1.04\pm0.2$  eV (392 nm; peak V). Table7.2 presents the  $b_i$  coefficients of various limonene measurements.

The asymmetry values given in Table 7.1 are not only consistent between two enantiomers at a given photon wavelength but also with values obtained from the forward-backward hemisphere analysis (Eq. 7.1 and Eq. 7.5) across the same energy ranges.

However, there are two exceptions: firstly, the absolute PECD value of S-limonene measured with the double-detector (discussed in this chapter) is rather different in magnitude from three other measurements at 420 nm that may result from the instability of laser pointing during the measurement. A slight variation in the center of the images of such slow electrons may affect PECD values. However, the data reproducibility of the three other measurements is very convincing. Secondly, the absolute asymmetry value of S-limonene is essentially half that of the corresponding R-limonene results at 412 nm. This inconsistency can be explained by examining the Legendre coefficients. Although, the odd  $b_i$  of S-limonene are much reduced, the even (non-chiral) coefficients for both enantiomers are essentially identical. The result suggests that "S" measurements may have been contaminated with "R" enantiomer and what we observed is actually the enantiomeric excess (e.e.) ratio results.

The individual evaluation of  $b_i$  coefficients show a similar trend as in the multiphoton PECD study of methyloxirane [30]. The photoelectron asymmetry strongly depends on the first Legendre coefficient,  $b_1$ , while  $b_3$  and  $b_5$  contributions are almost negligible. This would be necessarily the case for a one-photon ionization process, where the angular distribution is limited to 0, 1 and 2 order Legendre polynomials. However, the non-zero  $b_4$  and  $b_6$  coefficients corroborate the involvement of angular momenta from multiple photons. The reason why this does not appear to translate into

non-zero values for the higher odd moments remains unclear and should be a topic for future theoretical work. Finally, as we expected, G and QPECD values are very similar due to the fact that the higher odd  $b_i$  coefficients are very small and they are also altered in sign.

# 7.4 Conclusions

In this chapter, I have presented the results of a multiphoton PECD experiment performed on limonene at three wavelengths of 420 nm, 412 nm and 392 nm. The double-detector electron-ion coincidence imaging spectrometer and femtosecond laser system have been used to investigate the chiral asymmetry between both enantiomers. This work complements the experiments reported in previous chapters on limonene at 420 nm using a single detector coincidence spectrometer and the VUV single photon ionization performed at the SOLEIL synchrotron facility. PECD results showed mirroring between the dichroism of the two enantiomers corroborating the molecular origin of the observed asymmetry. The chiral asymmetry up to order of 9% is reported at 392 nm. I also discussed the possible ionization process occurring in all experiments and what intermediate excitation states would be involved. Evaluating of PES of parent and fragment ions explains that most fragmentation comes after ionization. PECD asymmetry was determined from two approaches. The integrated count in forward-backward hemispheres and also the Legendre coefficients show an excellent agreement.

		and	selected electro	n energy ranges						
	420.33 nm (Dc	ouble-detector)	419.1 nm (Sir	igle-detector)	412.5	5nm		392.3	3 nm	
range (eV)	<b>0.1</b> <sup>±</sup>	-0.1	<b>0.1</b> ±	-0.1	<b>0.15</b> ±	0.15	0.38	±0.2	1.04	±0.2
enantiomer	R	S	R	S	R	S	R	S	R	S
G(LP) <sup>a</sup> G(F/B) <sup>b</sup> QPECD <sup>c</sup> <sup>a</sup> Derived fr <sup>b</sup> Derived fr	-0.054±0.004 -0.053±0.003 0.052±0.003 om Legendre po om the integrate	0.045±0.003 0.045±0.003 0.043±0.003 olynomial (LP) sd count in forw	-0.044±0.002 -0.044±0.002 0.048±0.002 coefficients usi	0.044±0.003 0.046±0.002 0.043±0.002 ng Eq. 7.4. Errc ard hemispheres	-0.047±0.002 -0.046±0.002 0.045±0.001 ars are obtained using Eq. 7.1.	0.021±0.003 0.023±0.002 0.020±0.002 from fitting un	-0.020±0.002 -0.019±0.002 0.019±0.002 certainty.	0.016±0.003 0.016±0.002 0.015±0.003 ion of standard	0.029±0.003 0.028±0.003 0.028±0.003 derivations of c	-0.021±0.005 -0.019±0.003 0.019±0.004
μ				•	,		) 1			•

Table 7.1: Multiphoton PECD asymmetries for all electrons at different wavelengths

<sup>c</sup> Derived from Legendre polynomial (LP) coefficients using Eq. 7.5. Errors are obtained from fitting uncertainty. Poisson statistics.

 Table 7.2: Legendre coefficients of non-coincident electrons for a given energy range derived from 3D photoelectron angular distributions.

	420.33 nm (Dc	ouble-detector)	419.1 nm (Sin	gle-detector)	412	5nm		392.3	nm	
range (eV)	<b>0.1</b> <sup>±</sup>	±0.1	$0.1\pm$	0.1	<b>0.15</b> ±	-0.15	0.38	±0.2	1.04	-0.2
enantiomer	R	S	R	S	R	S	R	S	R	S
b1	$-0.026\pm0.002$	$0.019\pm0.001$	$-0.023\pm0.001$	$0.021 \pm 0.001$	$-0.022\pm0.001$	$0.009\pm0.001$	$-0.009\pm0.001$	$0.007\pm0.001$	$0.013 \pm 0.001$	$-0.009\pm0.002$
b3	$0.006\pm0.002$	$-0.014\pm0.002$	$0.000\pm0.002$	$-0.005\pm0.002$	$0.006\pm0.001$	$-0.003\pm0.002$	$0.003\pm0.002$	$-0.003\pm0.002$	$-0.008\pm0.002$	$0.004\pm0.004$
b5	$0.002\pm0.003$	$-0.001 \pm 0.003$	$0.009\pm0.002$	$-0.002\pm0.002$	$0.002\pm0.001$	$0.004\pm0.002$	$-0.001\pm0.002$	$-0.002\pm0.003$	$-0.003\pm0.003$	$-0.003\pm0.005$
b2	$-0.206\pm0.006$	$-0.215\pm0.006$	$-0.122\pm0.004$	$-0.120\pm0.005$	$-0.202\pm0.005$	$-0.198\pm0.005$	$-0.193\pm0.009$	$-0.184\pm0.009$	$-0.123\pm0.010$	$-0.145\pm0.011$
b4	$-0.074\pm0.008$	$-0.075\pm0.008$	$-0.045\pm0.006$	$-0.038\pm0.007$	$-0.059\pm0.007$	$-0.067\pm0.007$	$-0.066\pm0.012$	$-0.070\pm0.013$	$-0.122\pm0.014$	$-0.129\pm0.016$
b6	$0.070\pm0.010$	$0.071\pm0.011$	$-0.012\pm0.007$	$-0.005\pm0.010$	$0.028\pm0.009$	$0.028\pm0.010$	$0.061 \pm 0.016$	$0.059\pm0.017$	$0.054{\pm}0.017$	$0.060\pm0.020$

### MP-PECD of limonene

# 8

# ENANTIOMER SPECIFIC ANALYSIS OF MULTI-COMPONENT MIXTURES BY CORRELATED ELECTRON IMAGING-ION MASS SPECTROMETRY

Simultaneous, enantiomer specific identification of chiral molecules in multi-component mixtures is extremely challenging. Many established techniques for single-component analysis fail to provide selectivity in multi-component mixtures and lack sensitivity for dilute samples. Here we show how enantiomers may be differentiated by Mass-Selected PhotoElectron Circular Dichroism (MS-PECD) using an electron-ion coincidence imaging spectrometer. As proof of concept, vapours containing 1% of two chiral monoterpene molecules, limonene and camphor, are irradiated by a circularly polarized femtosecond laser, resulting in multiphoton near-threshold ionization with little molecular fragmentation. Large chiral asymmetries (2% - 4%) are observed in the mass-tagged photoelectron angular distributions. These asymmetries switch sign according to the handedness (R- or S-) of the enantiomer in the mixture and scale with enantiomeric excess (e.e.) of a component. The results demonstrate that mass spectrometric identification of mixtures of chiral molecules and quantitative determination of enantiomeric excess can be achieved in a table-top instrument.

this chapter is published as: M. M. Rafiee Fanood, N. B. Ram, C. S. Lehmann, I. Powis, M. H. M. Janssen, *Nature Communications*, **6**, 7511 (2015)

## 8.1 Introduction

There is an increasing awareness of the benefits stemming from enantiomer specific analysis of mixtures of volatile organics (VOCs). These advantages have long been apparent in the analysis of food odors where hundreds of chiral odorant pairs having different perceived smells are known [140]. Recent work has highlighted the role for enantiomer specific detection of for example, the monoterpene limonene in analyzing biogenic emissions of VOCs [132, 141]. In a related manner, detection of enantiomeric metabolites in clinical breath analysis may play an increasing role in the understanding and development of chiral pharmaceuticals. Much progress has been made in the analysis of mixtures of VOCs in such areas using direct injection mass spectrometry [142, 143] where "soft" ionization techniques can obviate the need for prior chromatographic separation, a particular advantage for field and in-vivo studies. Yet mass spectrometry, traditionally a "chirally blind" technique, does not directly address the identification of enantiomers in these mixtures, providing a stimulus for the development of enhanced approaches that can provide such capabilities.

Mass spectrometric techniques for determination of *single* component enantiomeric excess (e.e.) relevant to pharmaceutical development have, however, developed greatly over the past decade [144, 145] and rely on interactions with a known chiral reference reagent to discriminate enantiomers. These reference compounds have to be carefully chosen in advance according to the specific target species, and have themselves to be sourced in enantiopure form. Likely interference from contaminants in the analysed sample stream has also to be considered, although hybrid MS/MS techniques can be used to reduce such interferences.

As an alternative to chemical discriminants, a fully generic chiral reference is provided by circularly polarized light (CPL), readily prepared and characterized by well-established optical techniques. Chiroptical methods, such as electronic circular dichroism (CD) and vibrational optical activity (VOA and VCD) rely on typically rather weak chiral asymmetries (0.001-0.01%) in light-matter interaction, but are widely used techniques for the detection and structural determination of solvated chiral molecules [146, 147].

Recently, CD in ion yields generated by CPL multiphoton laser ionization of chiral molecules has been shown to be capable of discriminating enantiomers in solvent free conditions [12, 13]. An alternative, gas phase approach for the analysis of chiral isomer mixtures, based on phase sensitive microwave spectroscopy, has also been demonstrated [148, 149]. By eliminating the often indeterminate contributions from solvation [150], gas phase studies of biomolecules can be of considerable value for developing fundamental understanding [151] and permit the weak interactions responsible for chiral molecular recognition to be directly examined [152, 153].

In this report we describe a proof of concept demonstration of a direct, generic method for the simultaneous determination of enantiomeric components of a gaseous mixture by laser-based mass spectrometric detection, coupled with coincident electron imaging detection in a single table-top instrument. The detection of mass selected parent ions in coincidence with energy dispersed electrons allows the electron spectra

to be tagged by the precursor neutral. Recent work with synchrotron radiation has demonstrated the analytical potential of recording correlated ion and photoelectron ion spectra in this fashion [154]. Here, we add the convenience and additional capabilities of a laboratory based ultrafast laser ionization source for optimized parent ion production with, crucially, the use of circular polarizations and energy- and angleresolved imaging detection of the coincident electron. The latter provides the capability of enantiomeric differentiation by photoelectron circular dichroism (PECD) [14, 17, 29, 33]. PECD derives from chiral asymmetries in the photoelectron angular distribution that, for single VUV photon ionization, routinely fall in the range 1-10%. These expectations are maintained in the recent emergence of multiphoton PECD where, again, asymmetries of up to 10% have been reported from single pure enantiomers [27, 28, 30, 31, 155]. Such large asymmetries provide more than sufficient sensitivity to identify enantiomers of even minor (i.e. few %) components in a mass spectrum [25]. Hence, electron-ion coincidence imaging [58] is here shown to create the capability to record fully multiplexed mass-tagged photoelectron circular dichroism spectra of chiral molecules in multi-component mixtures.

# 8.2 Results

## 8.2.1 Coincidence detection of electrons and ions

Key features of the mass-selective photoelectron circular dichroism (MS-PECD) experiment are provided in Fig. 8.1. Briefly the electron and ion from an individual molecular ionization by a laser pulse are projected to respective detectors by electric fields. The 3-D momentum distribution of the electron is recovered from its position and time of flight (ToF) at the detector, while the mass of the ion can be determined from its ToF. Coincident detection of the pair establishes their common origin, and allows the electron data to be "tagged" according to the parent molecular mass. The accumulated electron data from many such tagged coincidence detections can be used to create the species-specific photoelectron energy and angular distributions required for PECD analysis.

## 8.2.2 Mixture analysis

As a demonstration we sample prepared mixtures containing < 1% of two enantiomeric monoterpenes, camphor ( $C_{10}H_{16}O$ ) and limonene ( $C_{10}H_{16}$ ), in an inert carrier gas (Ne). Both terpenes occur as biogenic VOCs with stereoiosomerism of limonene, in particular, being of significant interest in odor analysis and monitoring terrestrial plant emissions [132]. Very recently, PECD asymmetries of ~8% have been demonstrated for pure camphor enantiomers in multiphoton ionization using femtosecond (fs) laser pulses around 400 nm [27–29, 33] while multiphoton PECD asymmetries of ~4% have been reported for limonene using fs laser pulses centered at 420 nm [155]. Figure 8.2 shows schematically the simultaneously excited two-photon resonant, three-photon ionization scheme for this mixture.



**Figure 8.1:** Concept and implementation of Mass-Selected PhotoElectron Circular Dichroism (MS-PECD). (A) Following an ionizing laser pulse that crosses a molecular sample beam, ions and electrons are extracted in opposing directions by electric fields to reach their respective detectors. Electrons are focussed using a velocity mapped imaging (VMI) arrangement of electrodes to yield the complete  $(p_x, p_y, p_z)$  momentum from the time- and position-sensitive imaging detector [57]. For the present experiment mass analysis is achieved from measuring just the ion time-of-flight (ToF). Detection of a mass-selected ion in delayed coincidence with an electron identifies particles from a single molecular ionization event and these electron-ion correlations can be used to "tag" the accumulated electron data by their respective parent molecular masses. Panel (B) shows how the mass-tagged electron angular distributions recorded with circular polarized light display a forward-backward asymmetry that can distinguish between enantiomers, while the radius maps the electron kinetic energy.

In Figure 8.3, the ion ToF mass spectra for two different mixtures of enantiomeric vapours, Mix-RR (R-limonene/R-camphor) and Mix-RS (R-limonene/S-camphor), are shown after ionization with circular polarized 150 fs duration laser pulses with wavelength centered at 392.3 nm. The bandwidth of these fs laser pulses simultaneously encompasses two-photon resonant excitations to excited 3s Rydberg states of either molecular species [28, 97], followed by absorption of a third photon taking each system above its ionization limit (Fig. 2A). Ion ToF analysis produces similar mass spectra from both RS-(Fig. 8.3A) and RR-(Fig. 8.3B) mixtures. Only a small change in relative peak heights of the camphor versus limonene is observed between the Mix-RS and Mix-RR samples, due to slightly different experimental conditions, of no relevance here.



**Figure 8.2:** Multiphoton ionization by femtosecond laser excitation for a two component mixture. Panel (A) shows schematically the "soft", two photon-resonant, three photon-ionization producing parent molecular ions and coincident electrons  $(e_1, M_1^+)$  and  $(e_2, M_2^+)$ . Panel (B) indicates how the laser may be tuned to excite via specific resonant neutral states. The different photoelectron energy distributions (spectra) obtained from the mass-tagged coincident electrons  $e_1$  and  $e_2$  are shown schematically and may be used to help chemical identification.

The insets in Figure 8.3 show the mass spectra in the region of 136-152 amu where the peaks corresponding to the parent ions of limonene (136 amu) and camphor (152 amu) can be clearly observed. From the width of the peaks in the mass spectra we can extract a mass resolution of  $m/\Delta m \sim 1100$  in this mass region. In this study we aimed for soft ionization with as low as possible fragmentation. The intensity and focus position of the femtosecond laser were adjusted such that the peaks due to fragmentation of the parent ion were only minor components in the mass spectra. As was reported before for ionization of pure camphor samples near 400 nm [28], parent ion fragmentation can be easily induced by increasing the laser fluence although, noting the invariance of mass-selected photoelectron spectra of various ionic fragments, it was concluded that fragmentation was induced after photoionization of the neutral molecule. So, in principle, the laser fluence could be adjusted to obtain further structural identification from the fragmentation fingerprint [156, 157], and furthermore, the wavelength could be varied to achieve more selective ionization of preferred mixture components.


**Figure 8.3:** Measured time-of-flight (ToF) spectra of two mixtures of limonene (136 amu) and camphor (152 amu). In panel (A) the ToF spectrum of a mixture containing R-limonene and S-camphor is shown, while in panel (B) the ToF spectrum of a mixture containing R-limonene and R-camphor is shown. The mixtures were seeded in neon and expanded through a nozzle as a molecular beam. The parent mass region is expanded in the insets. The small peaks at masses 137 and 153 are parent molecule isotopomers with <sup>13</sup>C at natural abundance.



**Figure 8.4:** Photoelectron kinetic energy (K.E.) spectra. The mixtures Mix-RR and Mix-RS were irradiated with a femtosecond laser beam at 392 nm with either left circular polarization (LCP) or right circular polarization (RCP). In panel (A) the kinetic energy of all detected electrons is shown; below that are shown the kinetic energy of coincident mass tagged electrons at m/z = 136 (limonene - panel (B)) and m/z = 152 (camphor - panel (C)). The mass-tagged electrons in the shaded areas around the main peaks,  $(0.25\pm0.25)$  eV for limonene and  $(0.6\pm0.2)$  eV for camphor, were used to extract the three-dimensional angular distribution from which the PECD asymmetry was calculated, see Fig. 8.5.

In Figure 8.4, we show the photoelectron spectra (PES) obtained after ionization at 392 nm with circularly polarized light. The electron kinetic energy distributions are extracted from their full three-dimensional (3D) momentum distributions recorded by position and time of arrival encoding of individual electrons at our imaging delay line detector [57]. Furthermore, the coincidence between ion and electron events allows each electron to be associated with formation of an ion of given mass. For each mixture PES are shown for ionization with both Right and Left Circular Polarized (RCP and LCP) light. In panel 8.4A the PES obtained from the arrival of all electrons without any correlation of the electron with the mass of the coincident ion are shown; in panel 8.4B the PES of electrons coincident with an ion mass 136 (limonene) are shown, and in panel 8.4C the spectra of electrons coincident with an ion mass 152 (camphor) are presented. As expected the PES for the mixtures Mix-RR and Mix-RS and the two light helicities are all the same for a given choice of electron mass-tagging. However, we do see clear differences between the mass-tagged electron spectra coincident with camphor or limonene parent ions within a single mixture. A prominent peak around 0.6 eV is observed in the camphor tagged PES. Using the ionization energy of camphor of 8.7 eV and a laser photon energy of 3.16 eV the electron peak at 0.6 eV is assigned to three-photon ionization of the HOMO orbital [28], leaving only 0.18 eV of internal vibrational excitation in the camphor parent ion. The limonene tagged PES shows somewhat broader structures with a dominant peak around 0.3 eV. This peak is assigned to three-photon ionization of the HOMO-1 orbital [97].

Multiphoton PECD measurements can be used to characterise the selected enantiomer by means of a simple asymmetry factor, defined for a given CPL as [28]:

$$G = 4\left(\frac{N_f - N_b}{N_f + N_b}\right),\tag{8.1}$$

where  $N_f$  and  $N_b$  are, respectively, the number of electrons emitted into forward and backward hemispheres (i.e.  $0 \le \theta < \pi/2$  and  $\pi/2 \le \theta < \pi$  relative to the light propagation direction) and are derived from the accumulated electron distribution data after filtering by coincident ion mass and the preferred energy range. In practice, measurements are made by alternating LCP and RCP light and the two counts,  $N_f$ and  $N_b$ , obtained by combining the two polarization measurements in a manner that cancels any residual instrumental forward-backward asymmetry, as detailed below in Methods and section II of ref. [28]).

In Figure 8.5 the mass-tagged PECD asymmetries for 392 nm excitation, determined across the respective PES peak ranges identified in Fig. 8.4, are plotted for Mix-RR and Mix-RS. It is observed that PECD is different from zero (absolute PECD values around 2% and 4%), indicating that the compounds in this gaseous mixture at both the mass 136 and mass 152 are chiral. Furthermore, when changing from Mix-RR to Mix-RS the mass 136 (limonene) tagged PECD does not change (within experimental error, see Table 8.1), while for mass 152 (camphor) PECD reverses sign when changing the mixture. This latter sign reversal is anticipated and clearly correlates with the change of the camphor enantiomer in the mixture. Conversely, the absence of change in the mass 136 tagged PECD indicates that the enantiomer composition of limonene has not



**Figure 8.5:** Mass selected PECD asymmetries, G, measured by multiphoton MS-PECD for two mixtures of enantiomerically pure limonene and camphor. Between Mix-RR (Rlimonene/R-camphor) and Mix-RS (R-limonene/S-camphor) the camphor MS-PECD asymmetry flips sign, as anticipated for a change from R- to S-camphor, while for limonene the MS-PECD asymmetry remains the same. See also Table 8.1 for explicit values with uncertainties.

changed between the two mixtures. This is exactly in agreement with the composition of the two mixtures that we prepared in this experiment.

#### 8.2.3 Analysis for enantiomeric excess

As a final demonstration recordings were made with Mix-S[Rs], a combination of Slimonene and a 3:1 mix of R:S camphor vapours (50% e.e.). The results are compared with those for the previous two mixtures in Table 1. The S-limonene PECD retains the same magnitude but, as would be predicted, opposite sign to the previous R-limonene mixtures while the camphor PECD is reduced in magnitude, reflecting the reduction in enantiomeric purity.

For any component the observed PECD can be written as  $G=f_RG_R+f_SG_S=(2f_R-1)G_R$ , where  $f_X$  is the fractional abundance of enantiomer X and  $G_X$  its PECD asymmetry. But since  $e.e.=(f_R-f_S)\times 100\%$  it is straightforward to show that  $e.e.=G/G_R\times 100\%$ . We can obtain a value for camphor  $G_R$  under the conditions of these measurements, assuming 100% *e.e.* of our commercial R- and S- camphor products, from the mean

	Mass-tagged data		Non-Mass-tagged data	
Component	limonene	camphor	All ions	All ions
Ion Mass (m/z)	136	152		
Electron Energy Range (eV)	0.0-0.5	0.4-0.8	0.0-0.5	0.4-0.8
Mix-RR Mix-RS Mix-S[Rs]	-0.022(9) -0.023(9) 0.024(7)	0.042(11) -0.039(12) 0.022(9)	-0.003(4) -0.019(4) 0.017(4)	0.023(5) -0.015(4) 0.020(4)
Pure R-limonene Pure S-limonene	-0.019(11) 0.020(11)			

 Table 8.1: MS-PECD asymmetry factor G measured for the various mixtures and pure samples.

**Mean**  $|G| = 0.022(2)^{b} = 0.041(2)^{c}$ 

<sup>a</sup> G value derived by Forward/Backward differences in coincident electron counts, see Eq. 8.4. Quoted uncertainties (in brackets of last digits) are estimated assuming Poisson counting statistics and using standard error propagation. The filtered electron energy ranges are those shown shaded in panels B and C of Fig. 8.4.

<sup>b</sup> Mean absolute value of MS-PECD, G, for limonene obtained from the 5 values above. The sign corresponds to the value for S-limonene and ionization with LCP light. The standard deviation of the sample (in brackets of last digits) is shown.

<sup>c</sup> Mean absolute value of MS-PECD, *G*, for camphor obtained from the 2 values above and excluding the value of the enantiomerically mixed camphor in Mix-S[Rs]. The sign corresponds to the value for R-camphor and ionization with LCP light. The standard deviation of the sample (in brackets of last digits) is shown.

magnitude measured for Mix-RR and Mix-RS, which from Table 8.1 gives  $G_R$ = 0.041(2) where the uncertainty in the last digit is the sample standard deviation. Hence the measured camphor PECD for Mix-R[Rs] (Table 1) suggests the result *e.e.*=0.5±0.2, in excellent agreement with the prepared composition of this sample.

#### 8.3 Discussion

It is evident from the preceding results that the PECD asymmetry factor, G (Eqs. 8.1 and 8.4), evaluated simply from the electron emission yields in forward and backward directions (relative to the laser beam direction) provides a convenient, quantitative characterization of enantiomeric composition. These are identical to asymmetry factors obtained from the full analysis of the photoelectron angular distribution (see Methods section and Supplementary Table 8.2) allowing us to conclude that a full angular resolving electron detector is not a prerequisite for MS-PECD enantiomeric analysis;

in principle a bi-detector, capable of discriminating just forward and backward electron scattering directions would be sufficient. Table 8.1 includes another comparison, this of results obtained with energy selection but without mass-tagging of the electrons. Even the partial overlapping of the photoelectron spectra regions assigned to camphor and limonene in Fig. 8.4 leads to a complete scrambling of the non-tagged PECD G values which no longer display an intuitively discernable pattern. Interpretation of such data therefore poses at best a considerably greater challenge and would require far greater a priori knowledge concerning the mixture under examination. The correlation of electron and ion data by coincidence detection methods therefore is capable of yielding a level of insight additional to either the electron- or ion mass-spectroscopy alone.

Many (chiral) molecules have two-photon absorptions accessible at single photon wavelengths around 400 nm and ionization energies in a corresponding three-photon region around 9 eV. Combined with the large spectral bandwidth of an ultrafast laser pulse, the simultaneous ionization of multiple molecular components in a mixture can be expected to be relatively facile. Conversely, at longer wavelengths more selective ionization via selected chromophores becomes feasible. PECD itself provides a very rich signature of the ionized species, with asymmetries that vary depending on initial orbital, photon energy, and molecular conformation [14, 29]. Variation of the resonant laser ionization scheme would allow for effective exploitation of these properties, perhaps by employing more selective excitation through different resonant states (see Fig. 8.2) or by establishing conditions that optimize the magnitude of detectable PECD asymmetry - and hence further enhance sensitivity. (In this context it may be noted that despite the large excess of neon carrier gas (>99%) ionization of Ne is completely suppressed precisely because there is no accessible resonantly enhanced pathway with 392 nm photons, and a non-resonant mechanism would demand much higher laser intensity.) Furthermore, with picosecond lasers one can selectively excite individual vibrational bands within the electronically excited intermediate. This may provide opportunities for conformer specific resonant ionization [158] and also open the door to possible rich vibronic phenomena in PECD capable of providing further structural insights [26, 139].

The precision of our e.e. determination is comparable to that achieved, with comparable data acquisition times, using a polarized microwave double resonance technique [148, 149, 159] with detected phase providing enantiomer discrimination; for example an e.e. for (-)-menthone was measured as  $0.625\pm0.242$  [160]. Shorter acquisition times have been reported using a variation of this technique, permitting an e.e. of  $0.025\pm0.005$  to be measured with a 1,2- propanediol mixture with a known prepared 0.02 enantiomeric excess [161]. The asymmetry factors reported here are determined as a relatively simple function of two effective counters recording the number of electrons emitted into forward and backward hemispheres. These counts are assumed to be subject to Poisson statistics, which will determine the precision of the reported asymmetries, and especially the e.e. ratio. The reproducibility of repeated MS-PECD determinations, in both single and multi-component samples is, as shown in Table 8.1, very encouraging. Nevertheless, it is clear that an increase in data acquisition rate would provide benefits of reduced uncertainty associated with measurements

and/or reduced measurement times with correspondingly improved convenience and sample consumption.

One obvious, and (in a limited sense) trivial to implement improvement would be an increase in laser repetition rate. A hundred-fold increase from the current 3 kHz, would yield a tenfold improvement in statistical uncertainty, reducing that in the e.e. determination reported here to the level of a few %. Coincidence measurements with high (MHz) repetition rate sources are well established using synchrotron sources operating in their "few bunch" temporal modes; indeed the first electron-ion coincidence imaging PECD measurements were obtained in such conditions [20]. More recently, electron-ion coincidence experiments with a 400 kHz short pulse laser source have been reported [52] and indeed suitable high rep-rate fibre lasers providing ps-fs pulse durations are now commercially available. An alternative, and not mutually exclusive, possibility would be a relaxation of the severe ionization rate limitation, here set at less than 0.08 electrons per laser shot, imposed to minimise false coincidences. The adoption of covariance mapping techniques to replace electron-ion coincidence detection [162], may offer one route to accommodate significantly enhanced count rates without loss of the fundamental capabilities we have demonstrated. But this limitation can be eliminated completely if mass tagged electron detection were not required for discriminating mixture components; for example if wavelength selective excitation/ionization techniques could instead be employed, or for e.e. determinations on single components. It is clear in such cases that, subject to detector dynamic range, ionization rates increased by three or more orders of magnitude could then be utilized. A combination of higher laser repetition rate and relaxation of the limiting ionization rate per laser shot can feasibly be expected to yield an order of magnitude improvement in both precision and acquisition times.

There is an alternative approach to enantioselective laser ionization mass spectrometry, LIMS-CD, that measures CD in the overall ion yield. To date, most reported experiments have utilised low-order (n+n') resonance enhanced excitations by ns UV lasers [13, 129, 130], although recently Weitzel and co-workers have demonstrated fs laser LIMS-CD, including non-resonant 800 nm excitation [12] LIMS-CD and MS-PECD experiments with an ultrafast laser can thus share the potential capabilities of this ionization technique, as detailed above. Beyond that, while the (multiphoton) PECD effect develops in the pure electric-dipole approximation, LIMS-CD appears to depend on higher order multipole interactions, and in some way conflates CD contributions from various linear and non-linear photon absorption steps. This can be evidenced by the observation of different CD from nascent parent ion and more photon hungry fragmentation channels [12, 163]. In MS-PECD any post-ionization absorption should not contribute differently to the measured asymmetry.

Both LIMS-CD and MS-PECD require steps to reduce instrumental asymmetry. In LIMS-CD intensity differences in the LCP and RCP beams, and pulse-to-pulse fluctuations of the temporal and spatial distribution of the laser pulse energy are most effectively overcome for a single chiral component by concurrent measurement of an achiral reference which is thus required to have a similar absorption spectra and laser intensity dependence [12, 130, 131] ideally for both parent and daughter ion channels.

In some circumstances this might be quite demanding to arrange in a multi-component simultaneous measurement. In contrast, our MS-PECD data acquisition methodology (outlined in Methods, below) deliberately accumulates equal counts from the two polarizations such that when forming the dichroism as a difference between the two polarizations any residual, polarization independent instrumental asymmetry in the angular distributions, e.g. resulting from detector spatial inhomogeneities, gets fully cancelled. This precaution is trivially implemented for all species, but so doing actively precludes observation of any CD that may be present in the ionization yields.

A laboratory scale ultrafast laser imaging mass spectrometer capable of simultaneously detecting multiple enantiomeric species in gaseous mixtures without requiring prior separation techniques or reactions with complexing reagents, such as we have considered here, will open new analytical applications for the sensitive and selective detection of chiral molecules. As the measurements are performed on mass-selected species we can envisage extending the the technique to molecular complexes like chiral dimers, or microsolvated chiral molecules [25]. Furthermore, the combination of MS-PECD with laser desorption of chiral molecules from site-selected regions of surface samples [151], will extend the MS-PECD technique to sample chiral molecules directly from spatially selected regions on a two dimensional surface [164]. A complementary approach using a table-top laser source of elliptically polarized VUV for single photon PECD measurements has also been recently described [165].

Finally we note that theoretical modeling of single photon PECD is generally of sufficient quality to identify unambiguously absolute molecular configuration from the experimental observations [14, 122]. The current theoretical modeling for multiphoton PECD is less developed [28, 166] although work such as that presented here should help stimulate further theoretical efforts to model and quantify multiphoton PECD.

## 8.4 Methods

#### 8.4.1 Experimental setup

The experimental setup used in the present work has been described in detail before [57] and is schematically shown in Figure 8.1. The expanding gas mixture generates a continuous molecular beam in the source chamber which is doubly skimmed downstream of the nozzle as it passes through the buffer chamber into the imaging spectrometer chamber. In the imaging chamber the molecular beam intersects the laser beam at  $90^{\circ}$ . After ionization of a molecule, the electron and ion are detected in coincidence on two opposing time- and position-sensitive delay line detectors. In our experiment we operated velocity map imaging (VMI) voltages for electron detection and optimized voltages for optimal mass resolution (and not necessarily optimal voltages for VMI of ions) for ion detection.

Camphor and limonene enantiomers - R and S forms - of high purity (> 96%) were purchased from Sigma-Aldrich. The liquid limonene samples were held in an external stainless steel reservoir maintained at room temperature. A stream of pure neon gas at 0.6 bar backing pressure sweeps the vapor of limonene through a stainless steel transfer line and through a further sample reservoir, containing camphor solids, also at room temperature . A continuous seeded molecular beam is created by expanding the gas mixture through a nozzle into the first vacuum chamber from where it is doubly skimmed before entering the ionization region. To prepare Mix-S[Rs] a 3:1 mixture of R:S camphor (*e.e.*=50%) was accurately weighed out. It was then ground together to ensure a homogeneous sample of the enantiomers before being placed in the reservoir.

A commercial femtosecond laser system manufactured by Spectra Physics was used. The laser had a pulse duration of about 150 fs with 3 kHz repetition rate, and the frequency doubled output at 392 nm was attenuated to provide pulse energies of about 10-12  $\mu$ J (Mix-RR and Mix-S[Rs]) and 13-16  $\mu$ J (Mix-RS). It was loosely focused into the molecular beam with a lens of about 30 cm focal length. The corresponding intensity in the ionization volume is estimated to be 10<sup>11</sup>-10<sup>12</sup> W cm<sup>-2</sup>. Further details are provided in Supplementary Figures 8.6-8.9 and Supplementary Methods.

#### 8.4.2 Data acquisition and analysis

For each mixture data were accumulated for  $\sim 2 \times 10^8$  laser shots, during which the circular polarization (LCP/RCP) was switched every 500 seconds in order to reduce the effect of any experimental drift. The average number of electron events per laser shot, independent of coincident ion was limited to about 0.08. This count rate ensures that the probability for false coincidences is less than 0.3% assuming Poisson statistics.

The photoelectron angular distribution,  $I_p(\theta)$ , arising from an n-photon ionization of a chiral molecule with circular polarized light is given by [28]

$$I_p(\theta) = \frac{I_{tot}}{4\pi} \left( 1 + \sum_{i=1}^{2 \cdot n} b_i^p P_i(\cos\theta) \right),\tag{8.2}$$

where p is the polarization ( p=+1 and p=-1 correspond to left circular polarized (LCP) and right circular polarized (RCP) radiation, respectively). Here,  $\theta$  is the angle between the electron momentum and the propagation direction of the laser beam,  $P_i(\cos\theta)$  are Legendre polynomials, and  $b_i^p$  are the corresponding coefficients. Because the odd  $b_i^p$  coefficients are antisymmetric with respect to circular polarization switching  $(b_i^{+1} = -b_i^{-1}, i = 1,3,5,...)$ , whereas the even coefficients are unaltered [28, 29, 33] the chiral (odd) coefficients can be isolated by forming the dichroism or difference angular distribution:

$$I_{LCP}(\theta) - I_{RCP}(\theta) = I_{+1}(\theta) - I_{-1}(\theta)$$

$$= \frac{I_{tot}}{4\pi} \left( \sum_{i=1}^{n} 2b_{2i-1}^{+1} P_{2i-1}(\cos\theta) \right).$$
(8.3)

Forward-backward asymmetry arises from these odd polynomials in  $\cos\theta$ . A useful measure to quantify the enantiomeric sensitivity of multiphoton PECD in a single

asymmetry parameter has been suggested as

$$G = 2b_1^{+1} - \frac{1}{2}b_3^{+1} + \frac{1}{4}b_5^{+1} + \dots,$$
(8.3)

(truncated as shown for a three photon process) and this can be trivially evaluated from considering, for each polarization p, the numbers of electrons emitted in the forward and backward hemispheres (respectively  $N_{p,f}$  and  $N_{p,b}$ ) [28, 29, 33]:

$$G = 4 \times \left(\frac{F-B}{F+B}\right);$$

$$F = N_{+1,f} + N_{-1,b} \quad ; \quad B = N_{+1,b} + N_{-1,f}.$$
(8.4)

This form of combining polarization measurements has the experimental advantage of cancelling any polarization-independent residual instrumental asymmetry that might result e.g. from detector gain inhomogeneity. To ensure optimum cancellation it is arranged that we achieve the same total count for each polarization such that  $(N_{+1,f} + N_{+1,b})=(N_{-1,f} + N_{-1,b})$ . Assuming Poisson counting statistics there is an uncertainty  $\sqrt{N}$  in each count and so the error in *G* is obtained by standard error propagation.

Mass-tagged and photoelectron-energy selected coincidence events were filtered from the data for the various polarization settings, and PECD asymmetry factors calculated using Eq. 8.4 are presented in Table 8.1, with errors estimated by error propagation assuming Poisson counting statistics.

Further experimental details are provided in Supplementary Methods and we also compare G factors derived from the full electron angular distribution analysis (Eq. 8.3) with those from application of Eq. 8.4 in Supplementary Table 8.2.

# **APPENDIX: SUPPLEMENTARY METHODS**

## 8.5 Electron-ion coincidence imaging apparatus

The experimental setup used in the present work, shown schematically in Figure 8.1, has been described in detail before [57]. In brief, the coincidence imaging apparatus consists of three UHV chambers, the source chamber, a buffer chamber and the imaging chamber. A continuous molecular beam is generated by expansion through a 150 m diameter conical nozzle into the source chamber and is doubly skimmed downstream of the nozzle by a 500 m diameter skimmer followed by a 200 m diameter skimmer as it passes through the buffer chamber into the imaging spectrometer chamber. The overall distance between nozzle and interaction region is about 45 cm. In the imaging chamber the molecular beam intersects the laser beam at  $90^{\circ}$ . The electron and ion resulting from a molecule's ionization are detected in coincidence on two opposing time- and position-sensitive delay line detectors. High voltage switches are used to change the magnitude and polarity of the high voltages on the ion lenses. The switches are operated at the repetition rate of the laser system (3 kHz). Both electron and ion time-of-flight (ToF) tubes are shielded by a 1mm thick -metal tube. In our experiment we operated velocity map imaging (VMI) voltages for electron detection and tuned voltages for optimal mass resolution (and not necessarily optimal voltages for VMI of ions) for ion detection. The typical voltages on the particle lenses (repeller (R), extractor (E) and extra lens (L), see Figure 2 in ref. [57]) that were operated for detecting electrons are  $R_e$  = -520 V,  $E_e$  = -385 V,  $L_e$  = -275 V and for detecting ions are  $R_i$  = 2000 V,  $E_i$  = 1460 V,  $L_i = 0$  V.

## 8.6 Energy calibration of the electron detector

The three-dimensional (3D) electron velocity distribution is obtained directly from the position encoding delay-line detector and Micro-Channel-Plate arrival time pickup [57]. Unlike the more conventional arrangement using CCD camera imaging of the 2D projection image of (non-coincident) photoelectrons, no inversion routine (like Abel transformation or *pBasex* deconvolution [105]) is needed to recover data. The energy

scale and the origin of the 3D electron velocity distribution were carefully calibrated on multiphoton ionization of a seeded beam of 5% Xe in Ne. In Supplementary Figure 8.6 we show a typical mass spectrum of Xe, showing all the isotopes with clear mass resolution. In Supplementary Figure 8.7 a typical photoelectron spectrum as measured for Xe is shown. These calibration images on Xe photoionization were taken under the same conditions, using the same position and polarization settings of the laser beam, within the same experimental runs. This allows for a careful analysis of the calibration of the photoelectron images.



**Figure 8.6:** Typical mass spectrum as obtained on a seeded beam of 5% xenon in neon. The mass spectrum is measured under similar experimental conditions regarding laser and imaging spectrometer settings as the mixtures of limonene and camphor. All the isotopes of xenon can be clearly observed with good mass separation.

# 8.7 Laser system, characterization of spectrum and polarization of pulses

In the present experiments a commercial femtosecond laser system manufactured by Spectra Physics was used. It consists of a Titanium:Sapphire oscillator (Mai-Tai) that seeds the chirped regenerative amplifier (Spitfire-Ace). The output of the amplifier was optimized to deliver pulses centered at 784.6 nm wavelength with >5 W power at 3 kHz repetition rate and 120-150 fs pulse duration. The fundamental beam is subsequently



**Figure 8.7:** Typical photoelectron spectrum as measured in coincidence with Xe<sup>+</sup> ions. With the ionization energy of xenon (IP = 12.12984 eV) and the measured wavelength of the femtosecond laser it can be concluded that the electrons result from 4 photon ionization. The electron kinetic energy can then be calibrated using energy conservation: 4\*photon energy - IP = photoelectron energy.

frequency doubled in a BBO crystal. The spectral width and centre wavelength are continuously monitored with a fiber-based spectrometer (Ocean Optics USB 4000). In Supplementary Figure 8.8 a typical spectrum of the frequency doubled femtosecond laser pulse near 392.3 nm is shown.

A broadband quarter wave plate (B-Halle) was used to generate circular polarized light. The polarization of the light was characterized in terms of the Stokes vector by the rotating quarter wave plate method [92]. The measured intensity curves for both left- and right circular polarized light for the pulses at 392 nm are shown in Supplementary Figure 8.9 and the Stokes vectors obtained from the curves are: RCP: S = (1,-0.01,0.03,0.99) and LCP: S = (1, -0.11, 0.08, -0.99). Hence, we achieve nearly perfect circular polarization of the laser light source ( $S_3 \approx \pm 1$ ).

## 8.8 Sample composition and consumption

The samples of limonene/camphor, held in room temperature reservoirs, are coexpanded with 0.6 bar Ne behind the nozzle into the spectrometer. Taking the room temperature sample vapour pressures to be 2 mbar (limonene) and 0.5 mbar (camphor)



**Figure 8.8:** Typical spectrum of the frequency doubled femtosecond laser pulse with a central wavelength of 392.3 nm and a Full-Width-Half-Maximum of 2.3 nm.

[167] we can estimate the respective composition in the molecular beam, assuming seeding fractions correspond to the relative partial pressures, to be 0.33% and 0.08%, respectively. An estimate of the sample consumption can be made using the pressure and pump speed in the source chamber. Given the observed pressure increase in the source chamber to be about  $2 \times 10^{-4}$  mbar when the beam is on, we can derive an estimate for the partial pressure of limonene as  $(2 \times 10^{-3}/0.6) \times 2 \times 10^{-4}$  mbar =  $6.7 \times 10^{-7}$  mbar. With an effective pump speed of about 1000 liter per sec in the source chamber the pumped limonene sample volume is  $1000 \times 6.7 \times 10^{-7}$  mbar liter per sec =  $6.7 \times 10^{-7}$  bar liter per sec ~  $2.7 \times 10^{-8}$  mol per sec of limonene sample. In the present experiment we measured about  $10^{8}$  laser shots per polarization which corresponds to  $7 \times 10^{4}$  sec for a complete measurement made with the current laser rep rate of 3 kHz. From this we estimate that we used about 1.9 mmol of limonene, will therefore be about 0.5 mmol.

## **8.9** Measurement procedure and data analysis

The measurements on each mixture were performed switching between LCP and RCP polarization at 500 sec intervals. After careful checks that, among other things, the



**Figure 8.9:** Measured graph for the analysis of the Stokes parameters of the circularly polarized laser pulses near 392 nm using the rotating quarter wave plate method [92]. The green data (data points are green squares, best fit is green line) was measured for LCP, the dark red data (data points are solid dots, best fit is red line) for RCP. The Stokes parameters obtained from the best fit lines are given in the text.

centre of the electron data are the same (by checking the xenon data files taken during the measurements), all files with the same polarization were combined together at the end of the measurement for data analysis. The coincident data on electrons and ions provide direct time and position information for each event that can be converted directly (after calibration of the electron and ion spectrometers with Xe) to ion mass and full three-dimensional momenta ( $p_x$ ,  $p_y$ ,  $p_z$ ) of the electron. The latter is in turn reduced further to an emission direction into either the forward or backward direction (relative to the laser beam). Under our present experimental conditions of laser fluence, sample density and detector efficiencies, we detect about 0.08 electrons per laser shot, and obtain about 0.012 detected (e,ion) coincidence events per laser shot. Selection of ion mass and electron energy range filters a total of about 50000-80000 mass-tagged, energy selected (e,ion) events out of the total set of coincidence events per LCP or RCP polarization measurement per mixture.

Although equal recording time is devoted to the two polarizations, small intensity differences mean that there is a need to adjust the two data sets to have the same total count after which the PECD asymmetry, G, is calculated using Eq. 8.4. Because of this adjustment we are effectively insensitive to any differences of overall detection

efficiency between LCP and RCP in this multiphoton excitation scheme.

The analysis (see main text) using the forward/backward differences in events is compared with the alternative analysis of fitting the full angular distribution of electron scattering by a Legendre polynomial series up to rank six in the Supplementary Table 8.2. As expected these two alternative analysis methods to extract MS-PECD *G*-values agree very well. Hence the forward/backward analysis presented in the main paper and Figure 8.5 can be judged as a representative method to report MS-PECD *G*-values.

	Fwd/Bkwd Analysis <sup>a</sup>		LP Analysis <sup>b</sup>	
Component	limonene	camphor	limonene	camphor
Ion Mass (m/z)	136	152	136	152
Electron Energy Range (eV)	0.0-0.5	0.4-0.8	0.0-0.5	0.4-0.8
Mix-RR	-0.022(9)	0.042(11)	-0.025(11)	0.042(8)
Mix-RS	-0.023(9)	-0.039(12)	-0.022(11)	-0.043(16)
Mix-S[Rs]	0.024(7)	0.022(9)	0.025(7)	0.025(6)

**Table 8.2:** A comparison of MS-PECD G values, obtained by two alternative analyses (see main text) for the various multi-component mixtures.

<sup>a</sup> *G* value derived by Forward/Backward differences in coincident electron counts, see Eq. 8.4. Quoted uncertainties (in brackets of last digits) are estimated assuming Poisson counting statistics and using standard error propagation.

<sup>b</sup> G value derived from fitted electron angular distribution Legendre polynomial coefficients, see Eq. 8.3. Quoted uncertainties (in brackets of last digits) are derived from the errors in the fitted Legendre polynomial coefficients and using standard error propagation.

# BIBLIOGRAPHY

- F. Cava, H. Lam, M. A. de Pedro, and M. K. Waldor, Cell. Mol. Life Sci. 68, 817 (2011).
- [2] W. T. B. Kelvin, *Baltimore lectures on molecular dynamics and the wave theory of light* (CJ Clay and Sons, 1904).
- [3] V. Prelog, Croatica Chemica Acta 79, XLIX (2006).
- [4] R. S. Cahn, C. Ingold, and V. Prelog, Angew. Chem. Int. Ed. 5, 385 (1966).
- [5] G. Moss, Pure Appl. Chem. 68, 2193 (1996).
- [6] A. Fresnel, Bull. Soc. Philomath. p. 147 (1824).
- [7] P. Valery-Radot, Pages illustres de Pasteur. (Hachette, Paris, 1968).
- [8] J.H. van 't Hoff (Utrecht, J. Greven, 1874): (translated from Dutch) A Proposal for Extending the Currently Employed Structural Formulae in Chemistry into Space, Together With a Related Remark on the Relationship Between Optical Activating Power and Chemical Constitution of Organic Compounds.; a paper on the history of the first publication of the pamphlet in Dutch is by P. J. Ramberg and G. J. Somsen, Annals of Science 58, 51 (2001).
- [9] S. R. Domingos, M. R. Panman, B. H. Bakker, F. Hartl, W. J. Buma, and S. Woutersen, Chem. Commun. **48**, 353 (2012).
- [10] U. Boesl and A. Bornschlegl, ChemPhysChem 7, 2085 (2006).
- [11] H. G. Breunig, G. Urbasch, P. Horsch, J. Cordes, U. Koert, and K.-M. Weitzel, ChemPhysChem 10, 1199 (2009).
- [12] P. Horsch, G. Urbasch, and K.-M. Weitzel, Chirality 24, 684 (2012).
- [13] U. Boesl, A. Bornschlegl, C. Logé, and K. Titze, Anal. Bioanal. Chem. 405, 6913 (2013).
- [14] I. Powis, Adv. Chem. Phys. 138, 267 (2008).
- [15] L. Nahon and I. Powis, Chiral Recognition in the Gas Phase p. 1 (2010).
- [16] L. Nahon, G. A. Garcia, and I. Powis, J. Electron Spectrosc. Relat. Phenom. (2015).
- [17] B. Ritchie, Phys. Rev. A 13, 1411 (1976).
- [18] I. Powis, J. Phys. Chem. A 104, 878 (2000).
- [19] N. Böwering, T. Lischke, B. Schmidtke, N. Müller, T. Khalil, and U. Heinzmann, Phys. Rev. Lett. 86, 1187 (2001).

- [20] G. A. Garcia, L. Nahon, M. Lebech, J.-C. Houver, D. Dowek, and I. Powis, J. Chem. Phys. 119, 8781 (2003).
- [21] L. Nahon, G. A. Garcia, C. J. Harding, E. Mikajlo, and I. Powis, J. Chem. Phys. 125, 114309 (2006).
- [22] I. Powis, C. J. Harding, G. A. Garcia, and L. Nahon, ChemPhysChem 9, 475 (2008).
- [23] G. A. Garcia, L. Nahon, C. J. Harding, and I. Powis, Phys. Chem. Chem. Phys. 10, 1628 (2008).
- [24] S. Daly, I. Powis, G. A. Garcia, H. Soldi-Lose, and L. Nahon, J. Chem. Phys. 134, 064306 (2011).
- [25] I. Powis, S. Daly, M. Tia, B. C. de Miranda, G. A. Garcia, and L. Nahon, Phys. Chem. Chem. Phys. 16, 467 (2014).
- [26] G. A. Garcia, L. Nahon, S. Daly, and I. Powis, Nature Communications 4, 2132 (2013).
- [27] C. Lux, M. Wollenhaupt, T. Bolze, Q. Liang, J. Köhler, C. Sarpe, and T. Baumert, Angew. Chem. Int. Ed. 51, 5001 (2012).
- [28] C. S. Lehmann, N. B. Ram, I. Powis, and M. H. M. Janssen, J. Chem. Phys. 139, 234307 (2013).
- [29] M. H. M. Janssen and I. Powis, Phys. Chem. Chem. Phys. 16, 856 (2014).
- [30] M. M. Rafiee Fanood, I. Powis, and M. H. M. Janssen, J. Phys. Chem. A 118, 11541 (2014).
- [31] C. Lux, M. Wollenhaupt, C. Sarpe, and T. Baumert, ChemPhysChem 16, 115 (2015).
- [32] M. M. Rafiee Fanood, N. B. Ram, C. S. Lehmann, I. Powis, and M. H. M. Janssen, Nature Communications **6** (2015).
- [33] N. B. Ram, C. Lehmann, and M. H. M. Janssen, 41, 02029 (2013).
- [34] G. Scoles, Atomic and Molecular Beam Methods, vol. 1 and 2 (Oxford University Press, New York Oxford, 1989-1992).
- [35] R. Campargue, Atomic and Molecular beams: The state of the art 2000 (Springer Science & Business Media, 2001).
- [36] C. S. Lehmann, Novel applications of femtosecond electron-ion coincidence imaging, PhD thesis, Vrije Universiteit Amsterdam, 2014.
- [37] D. W. Chandler and P. L. Houston, J. Chem. Phys. 87, 1445 (1987).
- [38] J. L. Wiza, Nuclear Instruments and Methods 162, 587 (1979).
- [39] B. J. Whitaker, *Imaging in Molecular Dynamics, Technology and Applications* (Cambridge University Press, 2003).
- [40] A. T. Eppink and D. H. Parker, Rev. Sci. Instrum. 68, 3477 (1997).
- [41] C. R. Gebhardt, T. P. Rakitzis, P. C. Samartzis, V. Ladopoulos, and T. N. Kitsopoulos, Rev. Sci. Instrum. 72, 3848 (2001).
- [42] D. Townsend, M. P. Minitti, and A. G. Suits, Rev. Sci. Instrum. 74, 2530 (2003).
- [43] M. L. Lipciuc, J. B. Buijs, and M. H. M. Janssen, Phys. Chem. Chem. Phys. 8, 219 (2006).
- [44] A. Chichinin, K.-H. Gericke, S. Kauczok, and C. Maul, Int. Rev. Phys. Chem. 28, 607 (2009).

- [45] R. Stockbauer, J. Chem. Phys. 58, 3800 (1973).
- [46] W. Radloff, V. Stert, T. Freudenberg, I. Hertel, C. Jouvet, C. Dedonder-Lardeux, and D. Solgadi, Chem. Phys. Lett. 281, 20 (1997).
- [47] V. Stert, W. Radloff, T. Freudenberg, F. Noack, I. Hertel, C. Jouvet, C. Dedonder-Lardeux, and D. Solgadi, Europhys. Lett. 40, 515 (1997).
- [48] P. Downie and I. Powis, Phys. Rev. Lett. 82, 2864 (1999).
- [49] J. A. Davies, J. E. LeClaire, R. E. Continetti, and C. C. Hayden, J. Chem. Phys. 111, 1 (1999).
- [50] R. Dörner, V. Mergel, O. Jagutzki, L. Spielberger, j. Ullrich, R. Moshammer, and H. Schmidt-Böcking, Phys. Rep. 330, 95 (2000).
- [51] J. Ullrich, R. Moshammer, A. Dorn, R. Dörner, L. P. H. Schmidt, and H. Schmidt-Böcking, Rep. Prog. Phys. 66, 1463 (2003).
- [52] F. J. Furch, S. Birkner, F. Kelkensberg, A. Giree, A. Anderson, C. P. Schulz, and M. J. Vrakking, Opt. Express 21, 22671 (2013).
- [53] X. Tang, X. Zhou, M. Niu, S. Liu, J. Sun, X. Shan, F. Liu, and L. Sheng, Rev. Sci. Instrum. 80, 113101 (2009).
- [54] A. Bodi, P. Hemberger, T. Gerber, and B. Sztáray, Rev. Sci. Instrum. 83, 083105 (2012).
- [55] G. A. Garcia, H. Soldi-Lose, and L. Nahon, Rev. Sci. Instrum. 80, 023102 (2009).
- [56] G. A. Garcia, B. K. C. de Miranda, M. Tia, S. Daly, and L. Nahon, Rev. Sci. Instrum. 84, 053112 (2013).
- [57] A. Vredenborg, W. G. Roeterdink, and M. H. M. Janssen, Rev. Sci. Instrum. 79, 063108 (2008).
- [58] A. Vredenborg, C. S. Lehmann, D. Irimia, W. G. Roeterdink, and M. H. M. Janssen, ChemPhysChem 12, 1459 (2011).
- [59] A. Vredenborg, *Coincidence electron and ion imaging of femtosecond laser induced dynamics in atoms and molecules*, PhD thesis, Vrije Universiteit Amsterdam, 2009.
- [60] C. S. Lehmann, N. B. Ram, and M. H. M. Janssen, Rev. Sci. Instrum. 83, 093103 (2012).
- [61] C. S. Lehmann, N. B. Ram, D. Irimia, and M. H. M. Janssen, Faraday Discuss. 153, 173 (2011).
- [62] See: http://www.roentdek.com.
- [63] See: http://www.becker-hickl.de/.
- [64] J. Eland, Int. J. Mass. Spectrom. Ion Phys. 8, 143 (1972).
- [65] M. Gellender and A. Baker, International Journal of Mass Spectrometry and Ion Physics **17**, 1 (1975).
- [66] I. Powis and P. Downie, Rev. Sci. Instrum. 69, 3142 (1998).
- [67] A. Bodi, B. Sztáray, T. Baer, M. Johnson, and T. Gerber, Rev. Sci. Instrum. 78, 084102 (2007).
- [68] V. Stert, W. Radloff, C. Schulz, and I. Hertel, Eur. Phys. J. D 5, 97 (1999).
- [69] T. S. Rose, M. J. Rosker, and A. H. Zewail, J. Chem. Phys. 88, 6672 (1988).
- [70] A. H. Zewail, J. Chem. Phys. 100, 12701 (1996).

- [71] A. H. Zewail, J. Phys. Chem. A 104, 5660 (2000).
- [72] R. E. Carley, E. Heesel, and H. H. Fielding, Chem. Soc. Rev. 34, 949 (2005).
- [73] X. Délen, Y. Zaouter, I. Martial, N. Aubry, J. Didierjean, C. Hönninger, E. Mottay, F. Balembois, and P. Georges, Opt. Lett. 38, 109 (2013).
- [74] T. Wilhelm, J. Piel, and E. Riedle, Opt. Lett. 22, 1494 (1997).
- [75] E. Riedle, M. Beutter, S. Lochbrunner, J. Piel, S. Schenkl, S. Spörlein, and W. Zinth, Appl. Phys. B 71, 457 (2000).
- [76] T. Kobayashi and A. Baltuska, Meas. Sci. Technol. 13, 1671 (2002).
- [77] M. K. Reed, M. K. Steiner-Shepard, M. S. Armas, and D. K. Negus, JOSA B 12, 2229 (1995).
- [78] G. Cerullo and S. De Silvestri, Rev. Sci. Instrum. 74, 1 (2003).
- [79] R. Fork, O. Martinez, and J. Gordon, Opt. Lett. 9, 150 (1984).
- [80] L. Ziegler, J. Morais, Y. Zhou, S. Constantine, M. Reed, M. Steiner-Shepard, and D. Lommel, IEEE J. Quant. Electron. 34, 1758 (1998).
- [81] P. Baum, S. Lochbrunner, and E. Riedle, Opt. Lett. 29, 1686 (2004).
- [82] I. Z. Kozma, P. Baum, S. Lochbrunner, and E. Riedle, Opt. Express 11, 3110 (2003).
- [83] A. Kummrow, M. Wittmann, F. Tschirschwitz, G. Korn, and E. Nibbering, Appl. Phys. B 71, 885 (2000).
- [84] I. A. Walmsley and C. Dorrer, Adv. Opt. Photon. 1, 308 (2009).
- [85] M. Wollenhaupt, A. Assion, and T. Baumert, Springer handbook of lasers and optics, chapter 12 (Springer Science & Business Media, 2007).
- [86] A. Brun, P. Georges, G. Le Saux, and F. Salin, J. Phys. D: Appl. Phys. 24, 1225 (1991).
- [87] J.-C. M. Diels, J. J. Fontaine, I. C. McMichael, and F. Simoni, Appl. Opt. 24, 1270 (1985).
- [88] K. Ihara, S. Zaitsu, and T. Imasaka, Rev. Sci. Instrum. 76, 026109 (2005).
- [89] J. Möhring, T. Buckup, C. S. Lehmann, and M. Motzkus, J. Opt. Soc. Am. B 26, 1538 (2009).
- [90] G. G. Stokes, Transactions of the Cambridge Philosophical Society **9**, 399 (1851).
- [91] E. Wolf, Il Nuovo Cimento **12**, 884 (1954).
- [92] B. Schaefer, E. Collett, R. Smyth, D. Barrett, and B. Fraher, Am. J. Phys. 75, 163 (2007).
- [93] See: RAC 2.4.10L in http://www.b-halle.de/.
- [94] S. Turchini, D. Catone, N. Zema, G. Contini, T. Prosperi, P. Decleva, M. Stener, F. Rondino, S. Piccirillo, K. C. Prince, et al., ChemPhysChem 14, 1723 (2013).
- [95] D. Di Tommaso, M. Stener, G. Fronzoni, and P. Decleva, ChemPhysChem 7, 924 (2006).
- [96] G. A. Garcia, L. Nahon, and I. Powis, Int. J. Mass. Spectrom. 225, 261 (2003).
- [97] M. Smiałek, M.-J. Hubin-Franskin, J. Delwiche, D. Duflot, N. Mason, S. Vrønning-Hoffmann, G. De Souza, A. F. Rodrigues, F. Rodrigues, and P. Limão-Vieira, Phys. Chem. Chem. Phys. 14, 2056 (2012).
- [98] http://www.synchrotron-soleil.fr/portal/page/portal/

Recherche/LignesLumiere/DESIRS.

- [99] L. Nahon, N. de Oliveira, G. A. Garcia, J.-F. Gil, B. Pilette, O. Marcouille, B. Lagarde, and F. Polack, J. Synchrot. Radiat. 19, 508 (2012).
- [100] L. Nahon and C. Alcaraz, Appl. Opt. 43, 1024 (2004).
- [101] B. Mercier, M. Compin, C. Prevost, G. Bellec, R. Thissen, O. Dutuit, and L. Nahon, J. Vac. Sci. Technol. A 18, 2533 (2000).
- [102] W. Wiley and I. H. McLaren, Rev. Sci. Instrum. 26, 1150 (1955).
- [103] D. Céolin, G. Chaplier, M. Lemonnier, G. Garcia, C. Miron, L. Nahon, M. Simon, N. Leclercq, and P. Morin, Rev. Sci. Instrum. 76, 043302 (2005).
- [104] I. Powis, J. Chem. Phys. 112, 301 (2000).
- [105] G. A. Garcia, L. Nahon, and I. Powis, Rev. Sci. Instrum. 75, 4989 (2004).
- [106] B. Sztáray and T. Baer, Rev. Sci. Instrum. 74, 3763 (2003).
- [107] A. Osterwalder, M. J. Nee, J. Zhou, and D. M. Neumark, J. Chem. Phys. 121, 6317 (2004).
- [108] Y. Pan, K.-C. Lau, L. Poisson, G. A. Garcia, L. Nahon, and M. Hochlaf, J. Phys. Chem. A 117, 8095 (2013).
- [109] S. Leach, M. Schwell, G. A. Garcia, Y. Bénilan, N. Fray, M.-C. Gazeau, F. Gaie-Levrel, N. Champion, and J.-C. Guillemin, J. Chem. Phys. 139, 184304 (2013).
- [110] J. Poully, J. Schermann, N. Nieuwjaer, F. Lecomte, G. Grégoire, C. Desfrançois, G. Garcia, L. Nahon, D. Nandi, L. Poisson, et al., Phys. Chem. Chem. Phys. 12, 3566 (2010).
- [111] G. A. Garcia, B. Gans, X. Tang, M. Ward, S. Batut, L. Nahon, C. Fittschen, and J.-C. Loison, J. Electron Spectrosc. Relat. Phenom. 203, 25 (2015).
- [112] J. R. A. Moreno, T. R. Huet, and J. J. L. González, Struct. Chem. 24, 1163 (2013).
- [113] I. Powis, University of Nottingham, UK, private communication.
- [114] P. Brint, E. Meshulam, and A. Gedanken, Chem. Phys. Lett. 109, 383 (1984).
- [115] M. Losada, P. Nguyen, and Y. Xu, J. Phys. Chem. A 112, 5621 (2008).
- [116] P. Mukhopadhyay, G. Zuber, M.-R. Goldsmith, P. Wipf, and D. N. Beratan, ChemPhysChem 7, 2483 (2006).
- [117] M. Pecul, D. Marchesan, K. Ruud, and S. Coriani, J. Chem. Phys. 122, 024106 (2005).
- [118] A. Breest, P. Ochmann, F. Pulm, K. Gödderz, M. Carnell, and J. Hormes, Mol. Phys. 82, 539 (1994).
- [119] S. M. Wilson, K. B. Wiberg, J. R. Cheeseman, M. J. Frisch, and P. H. Vaccaro, J. Phys. Chem. A 109, 11752 (2005).
- [120] P. Horsch, G. Urbasch, and K.-M. Weitzel, Zeitschrift f
  ür Physikalische Chemie 225, 587 (2011).
- [121] T. D. Crawford, M. C. Tam, and M. L. Abrams, J. Phys. Chem. A 111, 12057 (2007).
- [122] I. Powis, *Photoelectron Circular Dichroism* (John Wiley & Sons, Inc., 2012), pp. 407–431.
- [123] S. Turchini, N. Zema, G. Contini, G. Alberti, M. Alagia, S. Stranges, G. Fronzini, M. Stener, P. Declava, and T. Prosperi, Phys. Rev. A 70, 014502 (2004).

- [124] S. Stranges, S. Turchini, M. Alagia, G. Alberti, G. Contini, P. Decleva, G. Fonzoni, M. Stener, N. Zema, and T. Prosperi, J. Chem. Phys. 122, 244303 (2005).
- [125] G. Contini, N. Zema, S. Turchini, D. Catone, T. Prosperi, V. Carravetta, P. Bolognesi, L. Avaldi, and V. Feyer, J. Chem. Phys. **127**, 124310 (2007).
- [126] G. A. Garcia, H. Dossmann, L. Nahon, S. Daly, and I. Powis, Phys. Chem. Chem. Phys. 16, 16214 (2014).
- [127] M. Stener, G. Fronzoni, D. Di Tommaso, and P. Decleva, J. Chem. Phys. 120, 3284 (2004).
- [128] T. Miyahara, J.-y. Hasegawa, and H. Nakatsuji, Bull. Chem. Soc. Jpn. 82, 1215 (2009).
- [129] R. Li, R. Sullivan, W. Al-Basheer, R. Pagni, and R. Compton, J. Chem. Phys. 125, 144304 (2006).
- [130] C. Logé and U. Boesl, ChemPhysChem 12, 1940 (2011).
- [131] K. Titze, T. Zollitsch, U. Heiz, and U. Boesl, ChemPhysChem 15, 2762 (2014).
- [132] W. Song, M. Staudt, I. Bourgeois, and J. Williams, Biogeosciences 11, 1435 (2014).
- [133] J. Williams, N. Yassaa, S. Bartenbach, and J. Lelieveld, Atmos. Chem. Phys. 7, 973 (2007).
- [134] N. Yassaa and J. Williams, J. Chromatogr. A **1141**, 138 (2007).
- [135] N. Yassaa, I. Peeken, E. Zöllner, K. Bluhm, S. Arnold, D. Spracklen, and J. Williams, Environ. Chem. 5, 391 (2008).
- [136] V. Ulrich, S. Barth, S. Joshi, U. Hergenhahn, E. Mikajlo, C. J. Harding, and I. Powis, J. Phys. Chem. A 112, 3544 (2008).
- [137] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, et al., *Gaussian 09 revision d.01* (2013).
- [138] J. D. Watts, S. R. Gwaltney, and R. J. Bartlett, J. Chem. Phys. 105, 6979 (1996).
- [139] I. Powis, J. Chem. Phys. 140, 111103 (2014).
- [140] E. Brenna, C. Fuganti, and S. Serra, Tetrahedron: Asymmetry 14, 1 (2003).
- [141] G. Eerdekens, N. Yassaa, V. Sinha, P. Aalto, H. Aufmhoff, F. Arnold, V. Fiedler, M. Kulmala, and J. Williams, Atmos. Chem. Phys 9, 8331 (2009).
- [142] F. Biasioli, C. Yeretzian, T. D. Märk, J. Dewulf, and H. Van Langenhove, Trends Anal. Chem. 30, 1003 (2011).
- [143] I. Déléris, A. Saint-Eve, E. Sémon, H. Guillemin, E. Guichard, I. Souchon, and J.-L. Le Quéré, J. Mass Spectrom. 48, 594 (2013).
- [144] W. A. Tao, F. C. Gozzo, and R. G. Cooks, Anal. Chem. 73, 1692 (2001).
- [145] L. Wu and F. G. Vogt, J. Pharm. Biomed. Anal. 69, 133 (2012).
- [146] N. Berova, K. Nakanishi, and R. Woody, *Circular dichroism: principles and applications* (John Wiley & Sons, 2000).
- [147] N. Berova, P. L. Polavarapu, K. Nakanishi, and R. W. Woody, Comprehensive chiroptical spectroscopy, applications in stereochemical analysis of synthetic compounds, natural products, and biomolecules, vol. 2 (John Wiley & Sons, 2012).

- [148] D. Patterson, M. Schnell, and J. M. Doyle, Nature **497**, 475 (2013).
- [149] V. A. Shubert, D. Schmitz, D. Patterson, J. M. Doyle, and M. Schnell, Angew. Chem. Int. Ed. 53, 1152 (2014).
- [150] P. Mukhopadhyay, G. Zuber, P. Wipf, and D. N. Beratan, Angew. Chem. Int. Ed. 46, 6450 (2007).
- [151] M. S. de Vries and P. Hobza, Annu. Rev. Phys. Chem. 58, 585 (2007).
- [152] A. Zehnacker and M. A. Suhm, Angew. Chem. Int. Ed. 47, 6970 (2008).
- [153] A. Zehnacker, Editor, *Chiral Recognition in the Gas Phase* (CRC Press, Boca Raton, 2010).
- [154] A. Bodi, P. Hemberger, D. L. Osborn, and B. Sztaray, J. Phys. Chem. Lett. 4, 2948 (2013).
- [155] M. M. Rafiee Fanood, M. H. M. Janssen, and I. Powis, Phys. Chem. Chem. Phys. 17, 8614 (2015).
- [156] V. V. Lozovoy, X. Zhu, T. C. Gunaratne, D. A. Harris, J. C. Shane, and M. Dantus, J. Phys. Chem. A **112**, 3789 (2008).
- [157] M. J. Duffy, O. Kelly, C. R. Calvert, R. B. King, L. Belshaw, T. J. Kelly, J. T. Costello, D. J. Timson, W. A. Bryan, T. Kierspel, et al., J. Am. Soc. Mass Spectrom. 24, 1366 (2013).
- [158] R. Karaminkov, S. Chervenkov, V. Delchev, and H. Neusser, J. Phys. Chem. A 115, 9704 (2011).
- [159] D. Patterson and M. Schnell, Phys. Chem. Chem. Phys. 16, 11114 (2014).
- [160] V. A. Shubert, D. Schmitz, and M. Schnell, J. Mol. Spectrosc. 300, 31 (2014).
- [161] D. Patterson and J. M. Doyle, Phys. Rev. Lett. 111, 023008 (2013).
- [162] J. Mikosch and S. Patchkovskii, J. Mod. Opt. 60, 1426 (2013).
- [163] C. Logé and U. Boesl, ChemPhysChem 13, 4218 (2012).
- [164] J. H. Jungmann and R. M. Heeren, Journal of proteomics 75, 5077 (2012).
- [165] A. Ferré, C. Handschin, M. Dumergue, F. Burgy, A. Comby, D. Descamps, B. Fabre, G. Garcia, R. Géneaux, L. Merceron, et al., Nature Photonics (2014).
- [166] I. Dreissigacker and M. Lein, Phys. Rev. A 89, 053406 (2014).
- [167] C. L. Yaws, Yaws' Critical Property Data for Chemical Engineers and Chemists (Knovel, 2012).

# LIST OF PUBLICATIONS

#### This thesis is based on the following publications:

- Enantiomer specific mixture analysis by correlated electron imaging-ion mass spectrometry.
  M. M. Rafiee Fanood, N. B. Ram, C. S. Lehmann, M. H. M. Janssen and I. Powis.
  Nature Communications, 6, 7511 (2015). (Chapter 8)
- Enantioselective femtosecond laser photoionization spectrometry of limonene using photoelectron circular dichroism.
  M. M. Rafiee Fanood, M. H. M. Janssen and I. Powis.
  Phys. Chem. Chem. Phys., 17, 8614 (2015). (Chapter 6)
- Chiral Asymmetry in the Multiphoton Ionization of Methyloxirane using Femtosecond Electron-Ion Coincidence Imaging.
   M. M. Rafiee Fanood, I. Powis and M. H. M. Janssen.
   J. Phys. Chem. A, 118, 11541 (2014). (Chapters 5)
- Multiphoton photoelectron circular dichroism of limonene using femtosecond electron-ion coincidence imaging.
  M. M. Rafiee Fanood, I. Powis and M. H. M. Janssen (in preparation).

#### (Chapters 7)

Photoionization study of pure limonene enantiomers using circularly polarized VUV light and electron-ion coincidence imaging.
M. M. Rafiee Fanood, G. A. Garcia, L. Nahon and I. Powis (in preparation). (Chapters 4)

## ACKNOWLEDGMENTS

My sincerest gratitude goes to Professor Ivan Powis who agreed to supervise my research after the upheavals at VU. A heartfelt thank you for all your support and guidance over the last few years, particularly, for all of our looooong Skype meetings started at 9 pm. It was also a unique opportunity and pleasure to be involved in your project at the SOLEIL synchrotron facility to complement my research.

I also wish to express my deep gratitude to my first supervisor, Professor Maurice Janssen, who offered me the opportunity to work at VU. It has been a great honour to have worked in the state-of-the-art coincidence lab under your guidance. I wish you success in your new endeavours.

I am very much indebted to Professor Wim Ubachs. I was fortunate to join your group after all the upheavals during the reorganization program. Particularly, I would like to thank you for giving me the freedom to find my way to the end of this long journey.

Many thanks also to Professor Steven Stolte who was always willing to discuss ideas and make valuable suggestions. I can clearly remember the evening you came to our office directly after returning from China. We were shocked by the decision to close down the Physical Chemistry group. You energized us to take a firm stand. I will never forget what you did for me.

I am grateful to Professor F.M. Bickelhaupt, Professor W.J. Buma, Dr J.T.M. Kennis, Professor D.H. Parker and Professor K.-M. Weitzel for accepting to be part of the reading committee and for the kind comments that helped me revise and improve the thesis.

Professor Harold Linnartz and Professor David Parker provided very valuable advice and support during the reorganization period. Thank you for your help in finding a solution to the problems.

I am greatly indebted to Rob Kortekaas for the technical assistance and for sharing your experiences on diving and Dutch culture. I also would like to thank people from the electronic and mechanical workshops for their help and supports. Without all this excellent technical support, it would have been impossible to perform such advanced experiments.

#### Acknowledgments

I am very grateful to our secretary Marja Herronen and department manager Dr Niels Laurens for your kind help in solving all our bureaucracy issues.

Many thanks also to former members of Physical Chemistry group: Arjan Wiskerke, Vincent Tuinder, Daniel Irimia, Dimitar Dobrikov, Dimitris Sofikitis, Niels Ligterink and Pradeep Kashyap. It was a great pleasure to spend time and work with you. I would especially like to thank Stefan Lehmann for all the help and support from the first moment we met. I learned all I know about the coincidence machine from you. You always gave your time to help solve problems. Thank you Bhargava Ram Niraghatam for always being open and willing to share your knowledge - even after you left VU. I enjoyed the Indian inspiration that you brought to the group. Laura Lipciuc, you spent a very short time in our group in one of the toughest periods. I appreciate your support and advice, and I wish the best for you. Hector Alvaro Galue and Congsen Meng, I greatly enjoyed working with you, and your company in the lab also. You all will be missed.

I would like to express gratitude to all members of the Atomic, Molecular and Laser Physics group for their warm welcome after the dismantling of the Physical Chemistry group. Ali Haddad, Hari Prasad Mishra and Jurriaan Biesheuvel I have greatly benefited from our scientific and non-scientific discussions. I would also like to thank my colleagues and friends at VU: Abhinav Sharma, Albert Licup, Robbie Rens, lucka Liebrand, Alina Chanaewa, Sabrina Jüchter, Jan-Hein Hooijschuur, Amin Tabatabie, Mehran Aflakparast and Mojtaba Mirakhorlo for all our short talks, lunch time discussions and coffee breaks. I have very much enjoyed your company in the last few years. I also would like to express my gratitude to Gustavo Garcia, Laurent Nahon and the staff of the DESIRS beamline at the SOLEIL synchrotron facility in France for their kind support during and after my visits.

I would like to thank all my Iranian friends in the Netherlands that their company has been very pleasant to me. Special gratitude goes to my dear friends Rojman Zargar, Elaheh Hamraz, Ali Rahmati, Maryam Shirazi, Saeed Raoufmoghaddam, Azadeh Bahreman, Mahdi Motazacker and Maryam Hashemi for many many beautiful memories. Your support provided me motivations in very stressful moments. Thank you Iman Dadgar and Ida Iranmanesh for staying in contact throughout the years, you were always available when I needed you. My thanks also go to Ali Raiss-Tousi for his time and help with proofreading.

I would like to thank my parents and sister for their support and love. My biggest regret is being far from you during your hard times in the last few years. My gratitude towards you is beyond words. Many thanks also goes to Aydin for his very useful helps from the other side of the Atlantic ocean. And last, but certainly not least, I would like to thank Mahsa who has contributed to this thesis in many ways and levels. Your inspiration and encouragement over the last few years were priceless to me. I am thankful for all those positive changes that you made in my life.