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Molecular chirality under the reaction microscope

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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 up-converted 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 electron-ion 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 analysing 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.