Work plan

The angular distribution of photoelectrons ejected by absorption of N circularly polarized photons is generally given by [1]

$$I_p(\theta) = 1 + \sum_{i=1}^{2N} b_i^{\{p\}} \mathrm{P}_i(\cos\theta)$$

Where $p = \pm 1$ represents left and right circular polarization directions, θ is the angle of the emitted electron with respect to the propagation direction, and P_i are Legendre polynomials. The coefficients $b_i^{\{p\}}$ encode the amplitudes and phases of the emerging partial waves and for achiral molecules the odd coefficients are zero. For chiral molecules these are finite and switch sign for the opposite enantiomer $b_i^{\{R\}} = -b_i^{\{S\}}(i \text{ odd})$ or polarization $b_i^{\{+1\}} = -b_i^{\{-1\}}$. It is these terms which give the forward-backward asymmetry in the electron emission.

This PECD effect has been studied in single photon ionization at synchrotrons but more recently using multiphoton ionization with femtosecond lasers. While the latter brings this phenomenon closer to being used practically in a range of applications, the use of ultrashort lasers and electron imaging techniques still requires a degree of specialist knowledge.

As part of my PhD I have been working on a much simpler design, currently under construction, which directly captures the forward and backward emitted electrons in two separate detectors. This will be a portable, compact device which can be coupled to a range of light sources from the visible to VUV. In the long term it is intended for it to be coupled to a small, turnkey, high repetition rate femtosecond fibre lasers of the type which are available commercially and are reducing dramatically in price. For the present investigation the new instrument will be tested using a laser at Uppsala which has the ideal characteristics for this new instrument – high repetition rate (250 kHz), moderate pulse energy (10 μJ). In this STSM, successful tests of this instrument will be a first step towards application of this device for analysis of enantiomer excesses produced from chiral catalysis undertaken at Uppsala.

For the STSM there are two related periods of investigation at Uppsala:

1. 14th Mar – 1st Apr 16 – installation of equipment and tests to reduce instrumental asymmetries:

- Set up vacuum chamber, electronics etc.
- Install laser optics, waveplates etc., and measure quality of left- and right-circular polarisation
- Set up 2nd and 3rd harmonic generation, then align and focus laser into chamber
- Test ion/electron detection, coincidences, and acquisition system
-Use achiral molecule (Toluene or Indole) to measure and characterize systematic asymmetries

2. 9th May – 29th May 16 – validate with benchmark chiral molecule - methyloxirane (MO), and demonstrate phenylalanine identification

- Methyl oxirane is one of the simplest chiral molecules and is one of the few molecules for which multiphoton PECD has been measured, exhibiting a forward/backward asymmetry of 4%. Using the 2nd harmonic (400 nm) of the Uppsala laser for resonant 2+1 ionisation, R and S enantiomers and 50:50 racemic samples will be tested. This will allow us to compare our results from the new device and hence eliminate any instrumental asymmetries, as well as characterise the influence of variable laser parameters. Furthermore, detection limits of the device will be characterised using this molecule.

- Secondly, we aim to study a more complex chiral molecule - the amino acid Phenylalanine - as a test case by making use of its chromophore for efficient resonant 1+1 ionization using the 3rd harmonic (267 nm) of the laser. Amino acids are non-volatile and hence difficult to produce intact in the gas-phase. However, our novel device is capable of producing gas phase samples of amino acids through laser desorption. This will pave the way for detecting small enantiomer excesses in trace amounts of amino acids produced from future chiral photocatalysis experiments at Uppsala.

The mission is split over 2 shorter trips to allow time for analysis of data and any issues to be rectified before progressing to validation of the device.