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A new technique for probing chirality via photoelectron circular dichroism

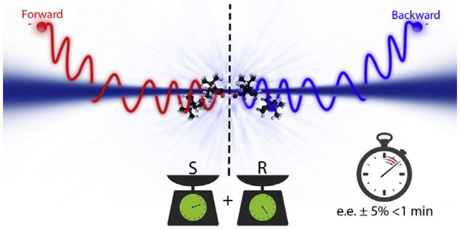
J. Miles [a], D. Fernandes [b], A. Young [a], C.M.M. Bond [a], S.W. Crane [d], O. Ghafur [d], D. Townsend [d, e], J. Sá [b, c], J.B. Greenwood [a, *]

[a] *Centre for Plasma Physics, School of Mathematics and Physics, Queen's University Belfast, Belfast BT7 1NN, UK*
[b] *Ångström Laboratory, Department of Chemistry, Uppsala University, Uppsala, Sweden*
[c] *Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland*
[d] *Institute of Photonics and Quantum Sciences, Heriot-Watt University, Edinburgh EH14 4AS, UK*
[e] *Institute of Chemical Sciences, Heriot-Watt University, Edinburgh EH14 4AS, UK*

HIGHLIGHTS

- Chiral analysis remains a challenging proposition in modern analytical chemistry.
- The phenomenon of Photoelectron Circular Dichroism offers a route to faster more sensitive analysis.
- Electrons are ionized with circular polarized femtosecond laser pulses.
- The asymmetry in electron angular emission is measured with a novel stereo-detection system.
- In identifying chiral molecules, speed and sensitivity equivalent to mass spectrometry can be achieved.

GRAPHICAL ABSTRACT



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ABSTRACT

We present a proof-of-principle approach for discriminating chiral enantiomers based on the phenomenon of multiphoton photoelectron circular dichroism. A novel stereo detection setup was used to measure the number of photoelectrons emitted from chiral molecules in directions parallel or anti-parallel to the propagation of the ionising femtosecond laser pulses. In this study, we show how these asymmetries in the ketones camphor and fenchone depend upon the ellipticity of the laser pulses and the enantiomeric excess of the sample. By using a high repetition rate femtosecond laser, enantiomer excesses with uncertainties at the few-percent level could be measured in close to real-time. As the instrument is compact, and commercial turnkey femtosecond lasers are readily available, the development of a stand-alone chiral analysis instrument for a range of applications is now possible.

1. Introduction

Many molecules exhibit a specific handedness or chirality, a property which extends to biologically essential molecules such as amino acids and sugars. Molecular handedness directly influences

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* Corresponding author.
E-mail address: j.greenwood@qub.ac.uk (J.B. Greenwood).

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organism response to the specific molecule since it determines how the molecule binds to a particular site on a receptor. Applications of advanced chemicals and pharmaceuticals necessitates the use of a pure active isomer, making the development of enantiomerically pure synthesis processes a persistent and extremely active research area. Detection of chiral excess post-reaction is an equally important but challenging proposition. Currently, there is not a simple, quick, and cost-effective method for chiral excess analysis that can be universally applied on a regular basis.

The difficulty is that the physical properties of enantiomeric pairs are almost identical or have very small differences, so that existing techniques such as optical rotation, circular dichroism (CD) and NMR peak height spectroscopy usually lack the speed, sensitivity and selectivity typically expected in analytical chemistry. Meanwhile, finding suitable host chiral compounds for identification by complexation or for the stationary phase in chiral chromatography usually has to be undertaken empirically on a case-by-case basis. As a result, there is considerable current research into alternative approaches which could be faster, more sensitive, and can be used on mixtures of compounds.

The discovery of a phenomenon known as photoelectron circular dichroism (PECD) has dramatically altered this landscape. Whereas conventional CD relies on very small differences in the excitation rates of electronic transitions between enantiomers (usually < 0.1%), the asymmetry in photoelectron angular emission relative to the direction of light propagation from chiral enantiomers has been found to be orders of magnitude higher (typically 10%). Since PECD is also measured with particle counting techniques in the gas phase, it potentially offers a route to chiral analysis with sensitivity and speed on a par or better than mass spectrometric chemical analysis. This PECD asymmetry has been investigated for single photon and multi-photon ionization through sophisticated velocity map imaging and analysis.

Asymmetry in the angular distribution of electrons is manifested via electric dipole transitions in the ionization process, hence it is orders of magnitude larger than conventional CD which depends on the weak contribution from the magnetic dipole moment in the transition matrix [1–3]. The multiphoton PECD angular distributions are described by a partial wave expansion of the photoelectron wavefunction which results in an angular distribution with $2N$ terms (where N is the number of photons absorbed and P_i are Legendre polynomials).

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

It is the odd coefficients of this expansion b_i which produce the asymmetry in the forward-to-backward electron emission with respect to the light propagation direction. They are non-zero only for chiral molecules irradiated with circularly polarized light. Theoretical calculations and experimental verification of PECD were first conducted around the year 2000 for single photon ionization with vacuum ultraviolet radiation [4–6]. Subsequent studies have demonstrated PECD in a range of chiral molecules and for ionization of valence and core electrons [7–13]. The origin of the PECD asymmetry is attributed to the scattering of the outgoing electron wavefunction by the chiral potential of the molecule which, due to interferences, is sensitive to the emission energy, the initial orbital ionized, and small structural variations. However, the inherent asymmetry is primarily manifested through the simple ratio of photoemission into the forward and backward hemispheres, largely due to the b_1 coefficient. Therefore, we have developed a simple and elegant stereo-detection method by which the forward and backward emission rates are directly measured.

Many previous studies have been undertaken at synchrotron beamlines with adjustable helical undulators, which can produce left- or right-handed circularly polarized light [14,15]. Elliptically polarized light produced from high harmonics of optical lasers has also been successfully used for PECD measurements [16]. However, direct application of femtosecond lasers via multi-photon ionization PECD (MP-PECD) has also been established recently, which has opened up the possibility of a table-top analysis device.

By acquiring 2D projections with a velocity map imager and reconstructing the electron angular distribution, in 2012 Lux et al. were able to show a substantial asymmetry for the enantiomers of camphor via resonant $2+1$ photon ionization at 398 nm[17]. Similar results were acquired by Lehmann et al. [18] using a set-up for which the 3D distribution was obtained directly using a delay-line imaging detector. These groups have demonstrated PECD in a few other molecules, and by fitting the distributions with Legendre polynomials, the odd coefficients b_i arising from the chirality of the target were obtained [19–25]. The sensitivity of these parameters to molecular structure is evident for the isomers camphor and fenchone for which the b_1 coefficient has opposite signs.

From these formative studies it can be concluded that molecular chirality can be sensitively probed by the PECD b_i parameters through acquisition of the photoelectron's angular and energy distributions. However, such detailed information is not essential for identification of enantiomeric proportions or observing ultrafast chiral changes when a single parameter would be more expedient. Such a parameter (G) can be expressed through the ratio of the forward F (0°–90° to the laser propagation) to backward B (90°–180°) emission obtained from the integrated electron yields. In practice results are acquired for both left-(L) and right-hand(R) circularly polarized pulses to remove any instrumental asymmetries, so that G is defined as [18].

$$G = \frac{F_L - F_R}{(F_L + F_R)/2} - \frac{B_L - B_R}{(B_L + B_R)/2} \tag{2}$$

This definition benefits from the fact that any instrumental asymmetry, such as differences in the detector efficiencies, is eliminated. As a result, it is not necessary to use sophisticated image detection and analysis to characterize the chirality of a sample when a simple stereo electron detection scheme could be just as effective. To this end we have developed a novel instrument which has been specifically designed to measure G values integrated over all electron energies of the forward and backward emitted electrons.

2. Experimental

A schematic of the experimental design is shown in Fig. 1 [26]. Femtosecond laser pulses are focused through apertures into an interaction region which is sandwiched between two grounded rectangular plates where they intersect an effusive gas jet at room temperature. A magnetic field of 30–40 gauss is applied along the laser propagation direction, so that photoelectrons spiral along the field lines with a net motion parallel or anti-parallel to the laser direction depending on whether they are emitted at less than or greater than 90°. Once the electrons have passed through grounded apertures at the entrance and exit of the interaction region, they are accelerated by a positive electric potential into $\mathbf{E} \times \mathbf{B}$ deflection plates which separate the electrons from the laser beam and direct them onto separate channel electron multipliers. In this way all the electrons emitted in each hemisphere are steered into their respective detectors regardless of their initial angle or energy.

The instrument can also be configured as a mass spectrometer with the two plates in the interaction region used to repel and