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Asymmetric photoelectron emission from chiral molecules using a high repetition rate laser

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Abstract. In the chiro-optical phenomenon known as photoelectron circular dichroism, the angular distribution of electrons ionized from chiral molecules by circularly polarized light pulses has been found to be anti-symmetric with respect to the direction of the light propagation. To study this phenomenon, chiral molecules were multiphoton ionized with a femtosecond laser in our laboratory. Using a simple stereo-detection setup, direct measurements of the asymmetry for the exemplar aromatic chiral molecule 1-phenylethanol were made using 260 nm pulses produced at a rate of 1 MHz. It was found that the asymmetry had a linear dependence on Stokes' S₃ parameter indicating that the photoelectron circular dichroism is due to a single photon process from the excited state of the molecule. This is in contrast to previous and new results for camphor where a more complex dependence on S₃ suggested that selective excitation of molecules with certain orientations was influential.

1. Introduction

For more than 150 years chirality has fascinated scientists, with the two enantiomers being indistinguishable apart from when they interact with another chiral medium (either other chiral molecules or circularly polarized light). Since 2000 a new, highly sensitive method for enantiomer identification called the Photoelectron Circular Dichroism (PECD) effect has been investigated[1].

When a chiral molecule is ionized with circularly polarized photons there will be an asymmetry in the number of electrons emitted in the forward hemisphere (F) to the backward hemisphere (B) with respect to the laser propagation direction. This asymmetry reverses when switching between right circular polarized light (RCP) and left circularly polarized light (LCP). This allows for an asymmetry parameter G to be calculated, $G = 2(F^L - B^L)/(F^L + B^L) - 2(F^R - B^R)/(F^R + B^R)$, with G having the opposite sign for the other enantiomer. The PECD effect boasts asymmetries on the order of 10% [2–4] making it potentially a highly sensitive detection method. The use of femtosecond laser systems to measure this effect allows for the exploitation of resonances inside these aromatic molecules to create efficient ionization on a rapid time scale, allowing a wide range of interesting organic molecules to be investigated.

The ellipticity dependence of the PECD has already been investigated in [3,5] for camphor at 398nm and 400nm respectively. These results showed a near linear dependence on the Stokes' S₃ parameter until $S_3 > 0.95$ at which point there was a drastic change. This suggests that the molecular orientation plays a vital role in the measured PECD as the excitation of intermediate states is dependent on the direction of the transition dipole moment. For linearly polarized light, molecules with their transition moment aligned along the electric field oscillation axis are preferential excited



whereas for circular polarization molecules with transition moments in the oscillation plane are more likely to be excited. These differences in the ensemble of excited molecules results in different values of G as the asymmetric scattering of the photoelectron in the chiral potential is strongly dependent on the molecular orientation.

2. Experimental Setup

A full description of the device created at Queen's University Belfast (QUB) to measure the PECD effect has been presented by Miles, et al.[5], however a brief overview of this stereo-electron detection system is given. An effusive molecular gas is generated, the laser beam is focussed at that position to ionise the molecules. The resulting photoelectrons are constrained in a helical path by a small applied magnetic field ($\mathbf{B} \approx 30$ Gauss). The electrons from the forward and backward emission hemispheres are separated due to the initial component of their emission velocity along the laser axis. They are then deflected by applied electric fields (\mathbf{E}), creating an $\mathbf{E} \times \mathbf{B}$ deflection, away from the laser's path and into two separate detectors.

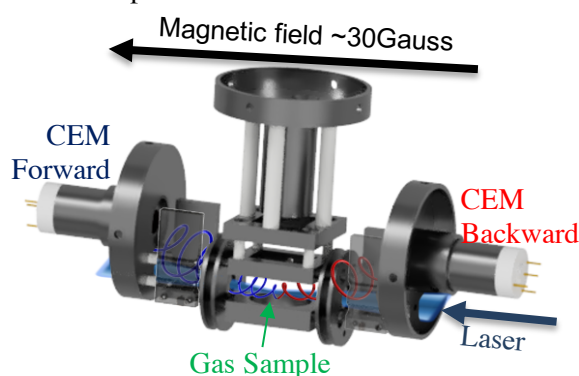


Figure 1. CAD drawing of electrodes inside the experiment, created using Fusion 360. The blue helix represents a trajectory for a forward emitted electron, whilst the red helix represents a backward emitted electron.

The laser used in the experiment was a Spectra-Physics Spirit 1040-16-SHG laser, operating at 1 MHz creating 300fs long pulses. The 4th harmonic 260nm was generated by twice doubling the fundamental wavelength of 1040nm. The linearly polarised pulse was passed through a QWP which could be rotated to control the ellipticity of the polarisation. This allowed the PECD G asymmetries to be measured as a function of the Stokes S_3 parameter. This Stokes parameter was measured for each waveplate using the method described in Schaefer, et al., 2007 [6]. The laser was then passed through a 30cm focal length lens to achieve a pulse intensity of 1.4×10^{10} Wcm⁻².

3. Results and Discussion

To demonstrate the application of this new laser system, we have used the aromatic chiral molecule 1-(R)-phenylethanol as an exemplar. The 4th harmonic at 260 nm is resonant with the $\pi^* - \pi$ absorption band of the molecule and hence there is an efficient (1+1) resonantly enhanced multiphoton ionization (REMPI) process. This produces a strong PECD asymmetry which increases linearly as the degree of circular polarization increases, reaching a maximum at fully circularly polarized light, Figure 2. As expected, the asymmetry also switches between right ($S_3 > 0$) and left ($S_3 < 0$) circular polarization. This indicates that the asymmetry is solely a result of the single photon ionization out of the intermediate excited state. Similar results have been found for single photon ionization [7], but this behaviour is unlike the results for camphor at 398nm & 400nm given in [3,5] which showed linearity until close to circular polarisation followed by a nonlinear trend. The cause of the nonlinear trend was assumed to be due to the preferential ionisation of molecules relative to the preferred direction in space. The linear trend for phenylethanol shown here suggests that there is no preferential molecular orientation in the excitation process or that the PECD does not depend strongly on the orientation of the molecule. This (1+1)-REMPI ionisation scheme is simpler than the (2+1) scheme used to ionize camphor at 398nm & 400nm, so the excitation step may not be as strongly dependent on the molecular orientation.

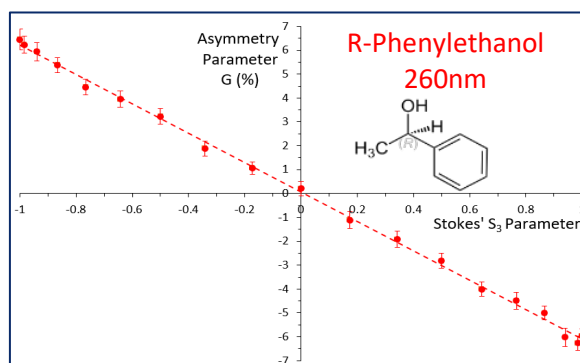


Figure 2. PECD asymmetry G as Stokes' S_3 parameter is varied for (R)-phenylethanol, shows a linear trend between the asymmetry and the degree of circular polarisation. From the linear fit to this data the gradient gives a value of $G = -6.16 \pm 0.06$ %.

4. Conclusion

In this paper, we have demonstrated multiphoton photoelectron circular dichroism in an exemplar aromatic chiral molecule for the first time. The observed asymmetry of more than 6% is much larger than that achievable with conventional circular dichroism, even when the molecules have been supersonically cooled and individual ro-vibrational transitions are excited by a narrowband laser [8]. By exploiting the UV absorption band using laser pulses at 260 nm, the molecule was also efficiently ionized at an intensity of 10^{10} Wcm² using only a few nanojoules of pulse energy. Therefore, this technique holds considerable promise for the analysis of chiral pharmaceuticals, pesticides, and fragrances (many of which are aromatic), at high speed and sensitivity by using small commercially available femtosecond laser oscillator modules.

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