Ultrafast Multiphoton Photoelectron Circular Dichroism in α-Pinene

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Introduction

Homochirality of life is well recognised, but no more understood than the origin of life itself.[1] Nevertheless, homochirality has profound everyday implications because the interaction of living organisms with their environment can be enantioselective at the molecular level, owing to chiral specificity in the recognition or interaction of one molecule with another. Pharmaceuticals, pheromones, and odorants all display chiral selectivity. Methods that distinguish between enantiomers, especially those that can determine absolute configuration of chiral molecules, are highly sought after because enantiomeric pairs share many properties which limit the opportunities for discrimination. Chiral identification by crystallography, NMR, mass spectrometry, and chromatography are all possible, but have limited capability. Very recently, a polarized double resonance microwave spectroscopy with phase sensitive detection for chiral discrimination was demonstrated.[2] The largest and most generic class of techniques are, however, chiroptical methods that exploit interaction with circularly polarized light (CPL) of definite handedness, or helicity.[3] The most common of these, conventional circular dichroism in absorption (CD), has its origin in a second order magnetic-electric dipole interaction and therefore suffers from the disadvantage of being rather weak (CD signals of $\sim 10^{-5} - 10^{-4}$). This requires measurements to be made in solution, which in turn introduces solvent cut-off restrictions on the useable wavelength ranges as well as uncertainties in the interpretation of data due to unquantified solvation shell-induced contributions.[4,5]

The alternative technique of one-photon photoelectron circular dichroism[6] (PECD) displays greatly enhanced sensitivity (10^3–10^4) to chirality and to both static (conformation) and dynamic (vibrational) structure. In recent years the use of ultrafast lasers has permitted demonstration of multiphoton (MP-)PECD measurements.[7] This combination of technology and technique offers many advantages for detailed probing of chiral chemistry in dilute environments, including time-resolved pump-probe experiments.[8] At the same time the increased accessibility of laser ionizing radiation opens up new opportunities for an enantioselective analytical method.[9]

The ultimate aim of this project was to perform a time-resolved MP-PECD study of the terpene odour molecule α-pinene to start to understand the evolution of PECD parameters with e.g. rotational dephasing in a non-reactive system, itself as a prelude to undertaking reaction dynamics type investigations. Due to instrumental problems with laser and electron detector we were so far unable to progress this far, but have succeeded to make a number of non-time resolved measurements laying the ground for achieving the stated aims in the future. These are described below.

Experimental Method

The PECD technique is based upon the observation of an asymmetry in the forward-backward emission of photoelectrons (relative to the light propagation direction) following photoionization of an initially randomly oriented chiral sample with circularly polarized light (CPL). This effect can be predicted in the pure electric dipole approximation for light-matter interactions,[10] and consequently the PECD asymmetry factors are in the range 1% – 40% — orders of magnitude greater than in conventional CD. The forward-backward asymmetry will reverse on exchange of either molecular enantiomer or the radiation helicity. In principle PECD may be determined from an angular distribution recorded by a single measurement with defined polarization, but in practice we prefer to record the dichroism by switching between left- and right-CPL.

The experiment was done in Artemis beamline of Central Laser Facility (CLF). An amplified femtosecond laser system (Red Dragon, KM Labs) generates 30 fs pulses of 800 nm light, with a pulse energy of up to 10 mJ and at a repetition rate of 1 kHz. The output of this system can either be used to generate 2nd–4th harmonics or be fed to an optical parametric amplifier (OPA, TOPAS Light Conversion) here to generate 370 nm pulses.

A molecular beam of R-α-pinene was generated after passing He (at ~0.6 bars) through a bubbler containing the sample at

room temperature and then expanding the seeded gas mixture through a 1 kHz pulsed nozzle with a 200 μm aperture. The resulting expansion passes through a 0.75 mm skimmer and enters the interaction region of the spectrometer through a hole in the centre of the repeller plate of the VMI. The typical pressure in the gas and ionization chamber were 1.36×10^{-5} mbar and 4.11×10^{-6} mbar, respectively. The detector consists of an 80 mm diameter microchannel plate (MCP) and a phosphor screen, which is imaged using a camera. VMI energy calibration was made using photoelectron spectra (PES) recordings of non-resonant Xe ionization and CS_2.

Circular polarizations were achieved using achromatic λ/4
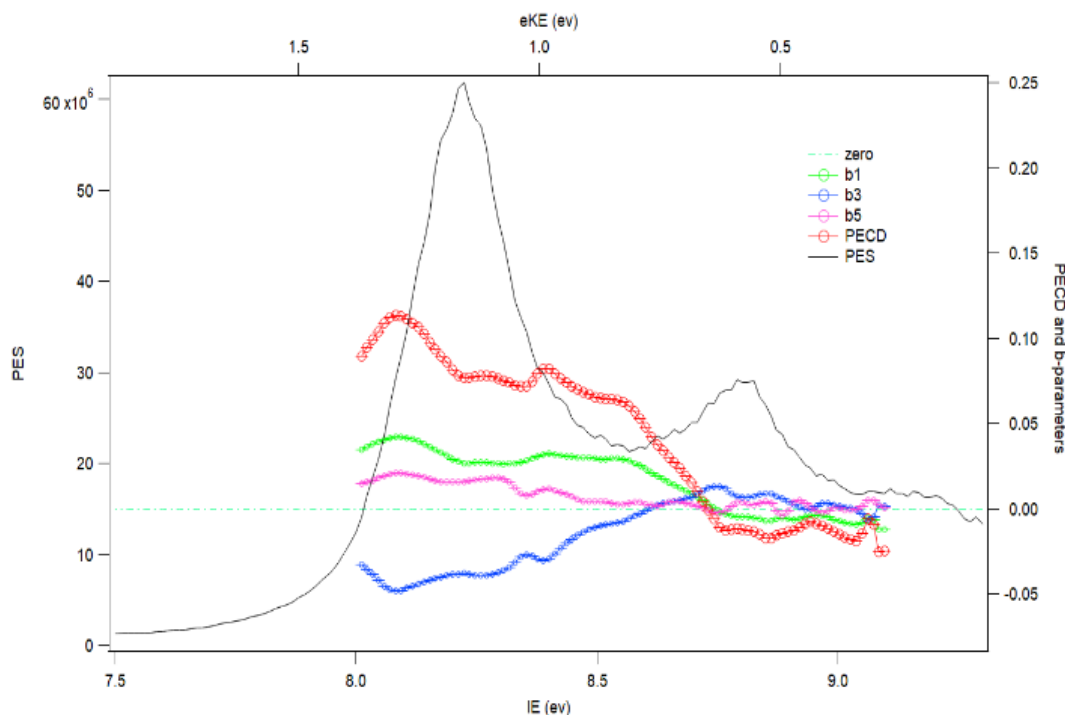
waveplates, and the degree of polarization checked using a rotating quarter-wave plate polarimeter.[11] At 400nm Stokes parameters $|S_3|$ were found to be in the range 0.86–0.977. We hope to improve this in future.

After accumulation for variable times VMI images were processed using the pBaseX algorithm,[12] recovering angular distribution parameters, b_j, and angle integrated PES.
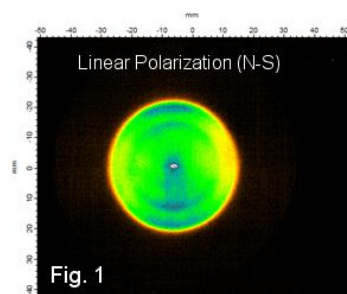
Results 396.52 nm

Fig. 1

Fig.1 shows a raw 2D VMI image of α-pinene recorded with linear horizontal polarization at 396.52 nm. This is a 3 photon transition to the cation, two-photon resonant via low-lying 3 s/p Ryberg states. At this level the rings reveal a structured PES with a parallel angular distribution.
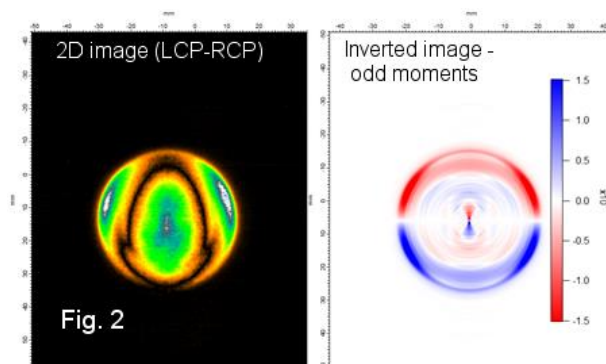

Fig. 2

Fig 2 shows the dichroism image (obtained as LCP-RCP difference) in the 2D projection form (left) and after inversion by pBaseX (right). The CPL laser light propagates vertically in these images. The data inversion assumes only odd (chiral) coefficients $b_{1,3,5}$ in the angular distribution. A strong forward backward asymmetry is evident as nett +ve to -ve colour coded regions. Moreover, the angular distribution clearly has a four-lobed structure that qualitative indicates a significant b_3 parameter. However, visual comparison reveals that despite the subtraction of normalized LCP/RCP images, the raw dichroism image still contains some *symmetric* component that is removed in the inversion. While we have never previously encountered this it was evident in recordings reported by Baumert et al.[13] Our preliminary examination reveals that this is due to differences in PES intensities between RCP and LCP measurements for reasons that are not yet clear, with further investigation required.

Figure 3 shows VMI 396.5 nm PES. Comparison with the HOMO band VUV (1-photon) PES of α-pinene[14] reveals that the two peaks evident here correspond to the first and fourth vibrational structures in the single photon ionization. We can attribute the modified vibrational structure to influence of the resonant intermediate Rydberg states in the laser experiments.

Also shown in Fig. 3 are the nett PECD asymmetry and individual chiral distribution parameters $b_{1,3,5}$ overplotted on the PES. The PECD reaches 10% indicating that the large chiral
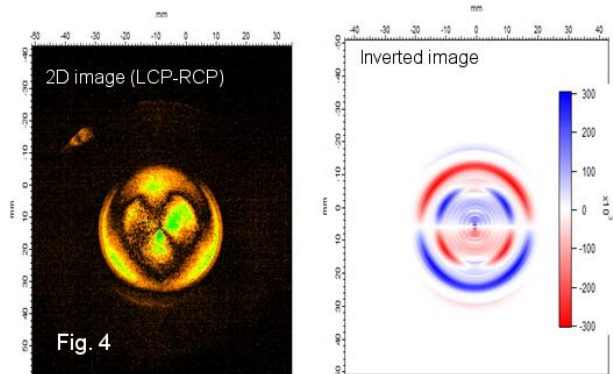

Fig. 4

in Fig. 3 switching in relative intensity. At the same time the PECD is much weaker at this excitation wavelength.

Results 200.66 nm

On the final day at Artemis we succeeded in generating sufficient 4th harmonic 200 nm light to make two-photon (1+1) REMPI measurements with α-pinene. Unfortunately, there was insufficient time to adequately isolate the residual fundamental and third harmonic, 266 nm, required in the mixing scheme. The total laser power was 0.27 mW but it was estimated that of this 0.02 mW was 266 nm, 0.07 mW was 800 nm fundamental, with the remainder, 0.18 mW, being the desired 200.66 nm. So while (1+1) single colour (200.66+200.66) can be expected (1+1') two colour ionization is also possible. In either case, as there is no absorption >240 nm, the pump photon should be unambiguously from the 200.66 nm beam. On the other hand for PECD measurement any (1+1') ionization creates additional uncertainties going beyond the ionization energetics, and unknown relative ionization cross-sections. This is because of the differing polarizations of the harmonics passing through the final quarter waveplate. With these caveats in mind, we present
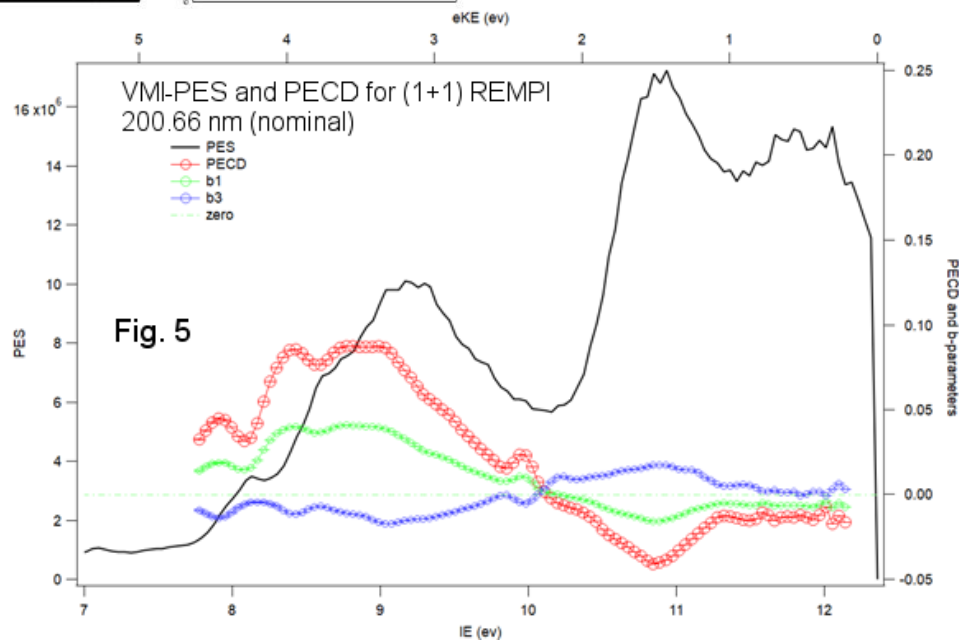

Fig. 5

asymmetries typical of VUV PECD, may also be expected in laser MP-PECD. The PECD also switches sign (direction) between the two vibrational peaks.

Because of angular momentum restrictions the higher terms b_3, b_5 are only possible in a 3-photon ionization. Nevertheless, to now these higher terms have been found to make only a minor contribution to MP-PECD, with the b_1 term remaining dominant. Clearly, from Figs. 2 and 3 this is no longer the case here, with the b_3 term particularly dominant.

Results 371.02 nm

The measurement sequence was repeated using 371.02 nm light generated by the Topas. The length and geometry of the beam path into the VMI chamber created some problems, and overall there were stability issues with this source that compromised our measurements. Nevertheless, a VMI-PES and PECD measurement were acquired. Inevitably the PES is extended due to the higher 3-photon equivalent energy (~10 eV), but the vibrational distribution is also changed; the two peaks evident

Fig. 3: VMI-PES and PECD of *R*-α-pinene with 5mW 396.52 nm CPL. Also included are the chiral angular parameters, b_{1-5}, that comprise the PECD asymmetry. Error bars are smaller than the marker size and cannot be seen in the figure

the raw and inverted dichroism images in Fig. 4. Visually the latter indicates that the PECD (forward-backward) asymmetry reverses between the inner and outer rings of the image, and that the balance between b_1 (2-lobed) and b_3 (4-lobed) terms also changes. (Note no b_5 term is expected for this nett 2-photon excitation). Finally, Fig. 5 shows the PES, PECD, and $b_{1,3}$ parameters extracted from this image.

Forward Look

These are preliminary measurements, made in conditions that were, as yet, sub-optimal, so that drawing firm conclusions would be premature. Nevertheless, these results do represent some degree of success in achieving a preliminary part of our objectives, and partially validate the underpinning hypotheses.

The magnitude and significance of the b_3 angular distribution parameter is already an interesting finding from these preliminary measurements. This has not been noted in the small number of previous MP-PECD measurements, made either by ourselves or others. Large $|b_3|$ is indicative of a significant contribution to the overall asymmetry made by molecular alignment, created via optical pumping to the resonant intermediate state. Control of this is anticipated to provide means to further enhance the chiral asymmetry (sensitivity).

It is intended that, well prepared from the experience gained here, a future opportunity will deliver on the overall goals. In the meantime, work is in hand to re-record, at higher resolution than current literature provides, and interpret the VUV absorption and REMPI spectra of α-pinene to better facilitate understanding of the role of the resonant intermediate state. This will in turn permit full modelling of the PECD under these t_0 conditions. Synchrotron works is already scheduled to obtain comparative single photon PECD measurements; these will help validate and calibrate theoretical efforts prior to our proposed extension to examine time-resolved dynamics.

Acknowledgements

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