

at 40 °C and the resulting vapor was mixed with 0.5 bars of He and adiabatically expanded through a 70 μm nozzle. After traversing a differentially pumped chamber with two $\phi = 1$ mm skimmers, the collimated molecular beam crossed the synchrotron radiation at a right angle.

Tailored polarized light was provided by the HU640 electromagnetic undulator of DESIRS, set in the so-called “pure CPL-mode” and monochromatised with the 200 lines per mm grating of the 6.65 m normal incidence monochromator. For photon energies below 15 eV, a gas filter located upstream the monochromator was filled with Kr or Ar to remove the high harmonics from the undulator.⁴⁷ The monochromator slits were merely set to avoid saturation of the charged particle detectors, providing energy resolutions between 6 meV at the lowest photon energy, and 11 meV at the highest. The full polarization ellipse, including the unpolarized component, was measured *in situ* at the sample level with a dedicated polarimeter,⁴⁸ and was found to be quasi-purely circular, with absolute circular polarization rates (S_3) values of 0.99 ± 0.01 over the whole photon energy range⁴⁶ which we have used to normalize the experimental PECD values. Further and more complicated corrections to the PECD values due to S_1 and S_2 terms can be neglected in view of the polarization purity. In addition, the stability of S_3 over time is routinely confirmed by frequent polarimetry checks.

Electrons and ions formed in the interaction region are accelerated in opposite directions by a continuous electric field perpendicular to the molecular and synchrotron beams. A complete description of the DELICIOUS3 i²PEPICO spectrometer used in this work and its performances has been reported elsewhere.^{45,49} Briefly, it consists of an electron velocity map imaging (VMI) analyser coupled to a modified ion Wiley–McLaren imaging spectrometer. Electron and ion arrivals are correlated in time and therefore the photoelectron VMI images can be obtained and filtered as a function of ion mass and translational energy. Photoelectron spectra (PES) and angular parameters are then extracted from the Abel inversion of the VMI image using a least squares fitting of previously computed forward Abel functions.⁵⁰ For the PECD measurements, typically a total of around 20 images are obtained at a given fixed photon energy for a given enantiomer with alternating light helicities, switched every 15 min. The images are then summed according to the light helicity to provide a single pair composed of the left (LCP) and right (RCP) circularly polarized measurements. The PES is then obtained by Abel inversion of the LCP + RCP image with a kinetic energy resolution of 3% for the fastest electrons, while the b_0b_1 term, where b_0 is the total cross-section of ionization of a given electronic band as given by the integral of the PES, is obtained from the LCP–RCP difference, leading to the final PECD, $2b_1$, through normalization by b_0 (see ref. 36 for a complete description of the procedure). The statistical error bars are given as the standard error on the principle that each image pixel acts as an independent counter that follows a Poisson distribution, with the associated error properly propagated through all subsequent operations. Systematic errors are estimated by comparison of both enantiomers' data, which should exhibit perfect mirroring behavior.

3. Results and discussion

3.1 Camphor data

Fig. 1 shows the typical data recorded in these experiments, in this case for *R*- and *S*-camphor at 12.3 eV. Several features mentioned in the introduction can be readily observed in the figure. Indeed the large asymmetry observed with PECD up to 12% means that it is readily visible even in the raw non-inverted 2D-difference images shown in Fig. 1a and b. The strong initial orbital dependency is also appreciated with the sign and magnitude changing for different electronic bands across the image radius. Moreover, the PECD value in Fig. 1c oscillates several times between IE = 10 and 12 eV. These oscillations, although not seen in the VMI-PES concurrently recorded with our spectrometer, are real and exceed our error bars. They are perfectly mirrored in the *R*- and *S*-enantiomer curves as anticipated from the anti-symmetry of the b_1 coefficients for the two enantiomers,

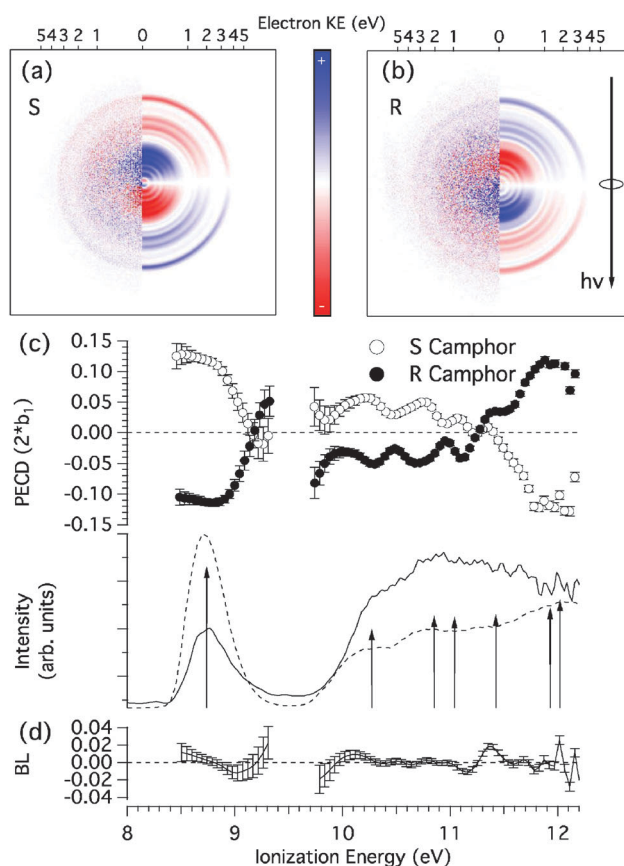


Fig. 1 VMI difference images (LCP–RCP) recorded at $h\nu = 12.3$ eV for 1S,4S-camphor (a) and 1R,4R-camphor (b) enantiomers. The left-half images show raw 2D-projections, and the right half the corresponding Abel inverted image (c) PECD (open and filled circles) and PES (solid line) extracted from inversion of the total and difference images. For clarity, the PECD is only shown for energies where the PES signal is higher than 10% of the maximum. The data have been normalized by S_3 and the ee measured by GC \times GC-TOFMS. (d) PECD baseline (BL) obtained as the mean value of the *S* and *R* PECD curves. Error bars are obtained according to the description written at the end of the experimental section. A higher resolution PES obtained at $h\nu = 95$ eV is also represented (dashed line) along with the calculated values (arrows), both taken from ref. 51.