leads to an average value close to zero. The dichroism is further presented in Fig. 4 in terms of b_1/b_0 which represents, according to eqn (1), half the PECD along the light propagation axis. Remarkably b_1/b_0 does not maximize at the locations of the PES peaks, but on their falling edges. This could be due to several effects. First, for a given electronic and vibrational state of the cation, b_1 inherently depends on the kinetic energy of the electron.[10] Second, simulations have shown that vibrational excitation of the ion played an important role, with a dramatic b_1 change in the falling edge of the PES associated to vibrations that explore different parts of the potential.[11] Last, b_1 could be modified by the contributions from different ionic states, produced by adjacent H5($0 \rightarrow i^*$) channels with $16 \leq i \leq 20$. It should be noted that the harmonics used in the experiment are only elliptical, such that the extracted values of PECD and b_1 do not represent the asymmetry of the response of the molecule to a purely circular radiation as in synchrotron experiments.[17] Nevertheless, the PECD signal is strong, and this measurement demonstrates the possibility of using femtosecond pulses produced by resonant HHG to reveal the chiral response of a molecule.

2.2 Resonant-enhanced multiphoton ionization

The advantage of quasi-circular HHG is that it delivers XUV pulses capable of producing a PECD signal by single-photon absorption. This enables straightforward comparison with spectroscopic studies carried out at synchrotrons, and also

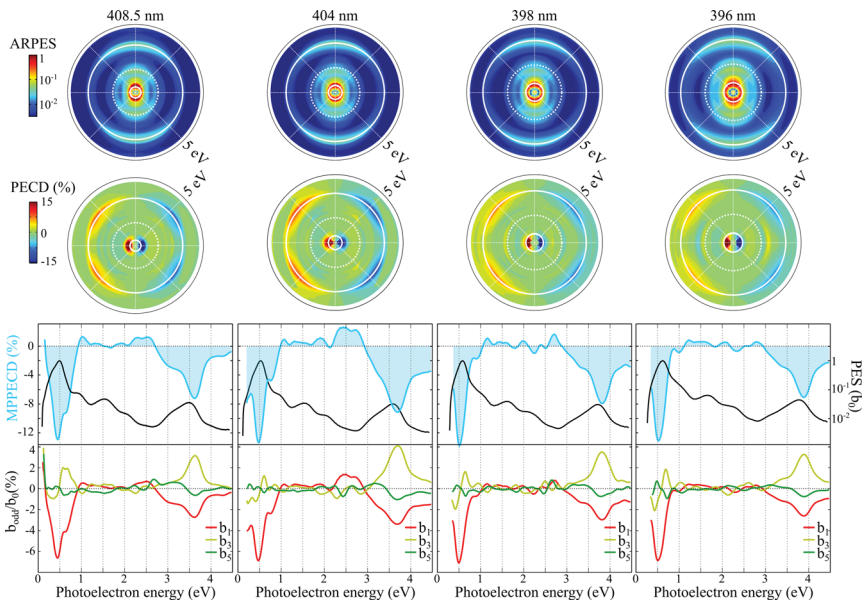

Fig. 5 Resonance-enhanced multiphoton ionization of (+)-fenchone. ARPES (top) and PECD (middle) for 408.5 nm 1×10^{13} W cm^{-2}, 404 nm 5×10^{12} W cm^{-2}, 398 nm 5×10^{12} W cm^{-2} and 396 nm 2×10^{13} W cm^{-2} pulses. The light propagation axis is horizontal and the radius extends from 0 to 5 eV. The continuous circle shows the expected electron energies for ionization from the HOMO, and the dashed circle from the HOMO−1. The PECD is set to zero when the ARPES is below 0.25% of its maximum. The associated PES, MPPECD and Legendre coefficients are plotted in the bottom graphs.