



Fig. 4 Single-photon ionization of (+)-fenchone with harmonics 3 and 5 of a 400 nm,  $\pm 30\%$  ellipticity laser pulse. ARPES (a) and PECD (b); the light propagation axis is horizontal and the radius extends from 0 to 7 eV. (c):  $b_0$  (gray area) and normalized  $b_1/b_0$  (black line) Legendre coefficients as a function of electron kinetic energy; the positions of PES peaks expected from TDDFT calculations are marked by  $Hq(i^*)$ , which is a shortcut to the  $Hq(0 \rightarrow i^*)$  notation employed in the text.

with the experimental one, 8.72 eV. These calculations provide the vertical ionization potentials  $I_p^{0 \rightarrow i^*}$  from the ground state of fenchone (0) to the ground (0) and excited ( $i^*$ ) states of the associated cation. These ionization potentials ( $I_p$ ) are used in Fig. 4 to identify the different ionization channels  $0 \rightarrow i^*$  opened by the absorption of the  $q^{\text{th}}$  harmonic according to energy conservation  $E = q\hbar\omega_0 - I_p^{0 \rightarrow i^*}$ . The main and secondary maxima in the PES correspond to the  $H3(0 \rightarrow 0)$  and  $H5(0 \rightarrow 0)$  ionizing processes, respectively. The broad bump results from ionization leaving the cation in excited states,  $H5(0 \rightarrow i^*)$ . Within the Koopman's approximation, these processes would be understood as ionization of inner molecular orbitals. However for  $i > 11$  two-hole-one-particle configurations, *i.e.* ionization + excitation processes, come into play. Interestingly, the excited state contributions vanish in the PECD image which only shows peaks centered at  $H3(0 \rightarrow 0)$  and  $H5(0 \rightarrow 1^*)$ , with respective magnitudes of 10 and 3%. This indicates that the PECD associated to neighbouring  $0 \rightarrow i^*$  channels, with  $i$  in the range 4–12, alternates between positive and negative values so that their overlap