The angular resolved PECD shows a remarkable stability as a function of the laser wavelength. The PECD is strong for the $3\omega_0(0 \rightarrow 0)$ and $4\omega_0(0 \rightarrow 0)$ channels. By contrast, no measurable PECD is detected from the HOMO-1 despite the presence of a significant $4\omega_0(0 \rightarrow 1^*)$ peak in the ARPES. The PECD associated to the 3 and 4 photon ionization of the HOMO have different angular distributions. This is reflected by the evolution of the Legendre coefficients with electron energy (Fig. 5, bottom). The $3\omega_0(0 \rightarrow 0)$ component has a dominant b_1 character (maximum around $0°$) while the $4\omega_0(0 \rightarrow 0)$ shows stronger b_3 with an opposite sign (maximum around $45°$). These results could be interpreted as an indication that PECD in fenchone is mainly imprinted by the absorption of a single or two photons from the excited state. However, this is not a general effect, since previously reported $2 + 1$ REMPI measurements in camphor, an isomer of fenchone with very similar structure of the HOMO, showed a strong b_3 component.[25]

The maximum MPPECD of the $3\omega_0(0 \rightarrow 0)$ transition is around -13% at all wavelengths. It thus has a similar amplitude and the same sign as the one recorded in single photon absorption (see Fig 4). While the photoelectron peak shifts linearly with photon energy, the MPPECD remains maximized at 0.5 eV, with a sign change of b_3 around this energy. This insensitivity to the ionizing photon wavelength indicates that the strong peak of the MPPECD between 0 and 1 eV is the effect of the electron kinetic energy, as established in near threshold single-photon absorption.[17] There is no signature of vibrational excitation with an alternating asymmetry like the ones we recently observed in limonene molecules.[43] This indicates that the $\Delta\nu = 0$ propensity rule for ionization from the 3s Rydberg states is maintained in the MPPECD of fenchone, and that the magnitude of this MPPECD is mainly fixed by the kinetic energy of the photoelectron and not affected by the variation of the chiral potential induced by the vibrational excitation in the cation.

For the $4\omega_0(0 \rightarrow 0)$ transition, the MPPECD maxima are upshifted by 100–200 meV with respect to the PES peaks. The MPPECD reaches -8% at 404 nm, while it is only -6% at 408.5 nm and 398 nm. These values, which are peak values of the MPPECD, are slightly higher than those previously reported, which were averaged over the FWHM of the electron energy distribution.[44] They can be compared to the $+4.78\%$ PECD recorded in single absorption of a 12.4 eV photon ionizing the HOMO.[17] The MPPECD at $4\omega_0$ is stronger, with an opposite sign. Obviously, although the photoelectron has the same kinetic energy and is associated to the same ionic state, it does not experience the same scattering in the chiral potential. In the ATI picture, the absorption of the fourth photon occurs when the electron is already slightly away from the ionic core, when most of the scattering into the molecular potential has happened. Since this scattering, and the associated interference of the outgoing partial waves, is what sets the value of the PECD, the MPPECD is mostly determined by the $2 + 1$ process, and only slightly modified by the absorption of one additional photon. We have observed a similar sign change of the MPPECD relative to the single photon PECD in the $2 + 1$ and $2 + 2$ ATI peak in limonene.[43] Theoretical investigations are required to confirm this hypothesis as well as to establish the sensitivity of MPPECD to vibrational excitation.

2.3   Above-threshold and tunnel ionization

By enabling direct measurements with femtosecond laser pulses, resonance-enhanced multiphoton ionization provides a valuable alternative to single-photon