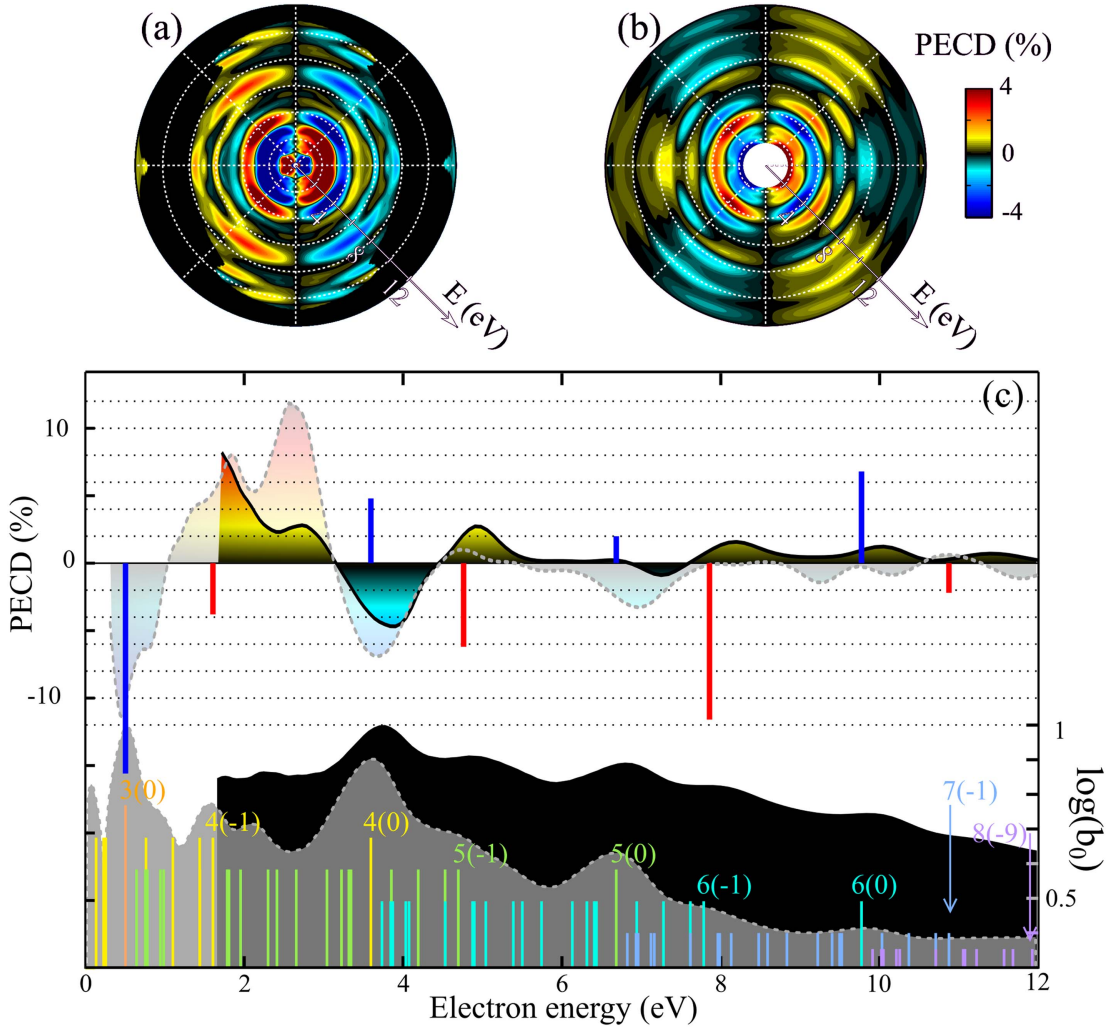

Figure 2. MPI and ATI of (+)-fenchone by 402 nm pulses. PECDs for $I \sim 5 \times 10^{12}$ (a) and 4×10^{13} W cm^{-2} (b). The light propagation axis is horizontal and the radius extends from 0 to 12 eV. (c): corresponding PES and MP-PECD for $I \sim 5 \times 10^{12}$ W cm^{-2} (lightest shaded area) and $I \sim 4 \times 10^{13}$ W cm^{-2} (darkest shaded area); the dark (blue) and light (red) thick vertical lines are the one-photon PECD values from the HOMO and HOMO-1,2, respectively, measured in [20]; the thin lines labeled $k(i)$ indicate the positions of PES peaks expected from our calculations.

ion left in $\nu = 1$ excited state, and the associated PECD sign is again opposite to that corresponding to $\nu = 0$. The magnitude of the PECD increases to reach a maximum around $E = 0.57$ eV, which roughly corresponds to the electron kinetic energy release for a limonene cation in the $\nu = 2$ state. In addition electron kinetic energy effects between the $3\hbar\omega\,(0 \rightarrow 0)$ and $3\hbar\omega\,(0 \rightarrow 1)$ thresholds might also play a role. Sign reversals in PECD from vibrationally excited ions have recently been observed in one XUV-photon absorption and intepreted as a signature of non Frank-Condon transitions [5, 19]. Our present findings generalize this observation in the MPI regime and show that PECD enables resolving vibrational features invisible in PADs.

2.2. PECD in the ATI regime

We now turn to the investigation of high-order ATI by increasing the laser intensity I while keeping the wavelength fixed at 402 nm. We consider a different chiral species, (1S,4R)-fenchan-2-one, referred to as (+)-fenchone, in which two-photon absorption of 402 nm pulses resonantly excites Rydberg states. Figures 2(a) and (b) show the PECD images obtained at 402 nm for $I \sim 5 \times 10^{12}$ and 4×10^{13} W cm^{-2}, respectively. The associated PES are displayed in figure 2(c), together with the so-called multiphoton PECD defined as MP-PECD $(E) = \frac{1}{b_0}\left(2b_1 - \frac{1}{2}b_3 + \frac{1}{4}b_5 - \frac{5}{32}b_7\right)$ [10, 12]. This quantity corresponds to difference between electron emission in the forward and backward hemispheres, normalized by the average number of electrons per hemisphere. At low intensity, the PES presents two series of ATI peaks equally spaced by the energy of one photon, $\hbar\omega = 3.09$ eV. The two series begin at $E = 0.53$ and 1.57 eV, respectively. According to time-dependent