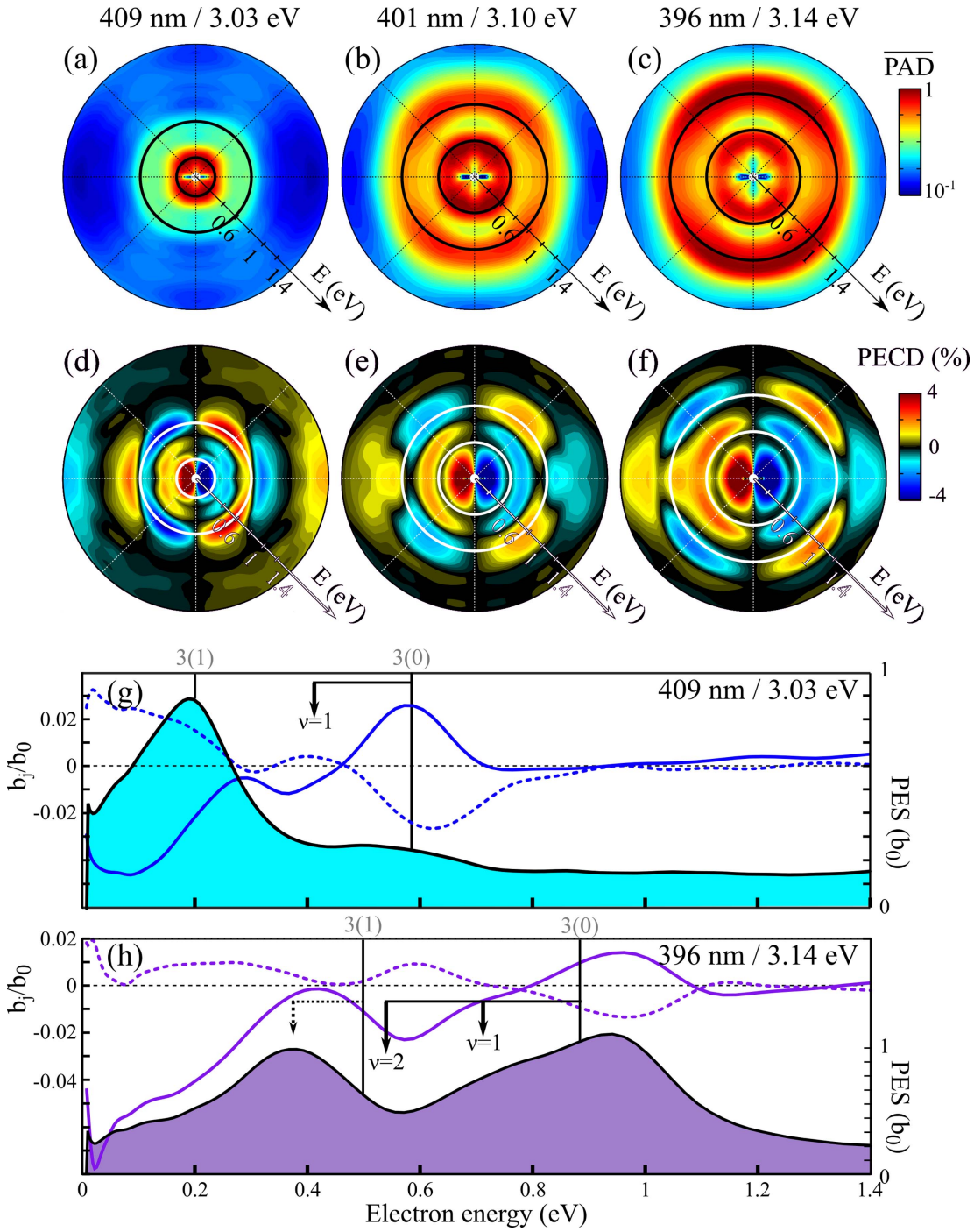


**Figure 1.** MPI of (+)-limonene molecules. $\overline{\text{PAD}}$s (a)–(c) and PECD images (d)–(f) for $\lambda = 409$ (a), (d), 401 (b), (e) and 396 nm (c), (f). The light propagation axis is horizontal and the radius extends from 0 to 1.4 eV. (g), (h): PESs (shaded area) and normalized $b_1/b_0$ (solid line) and $b_3/b_0$ (dashed line) as functions of $E$, for $\lambda = 409$ nm (g) and 396 nm (h). The theoretical positions of the PES peaks are marked by $k(i)$, as a shortcut of the notation $k\hbar\omega\,(0 \rightarrow i)$ employed in the text; the arrow combs refer to vibrational quanta of energy.

trace of vibrational excitation of the cation. At 409 nm the $3\hbar\omega\,(0 \rightarrow 0)$ pathway shows a nice maximization of the asymmetric coefficients $b_1$ and $b_3$ at the expected electron energy 0.6 eV (figure 1(g)). As the electron energy decreases, the PECD coefficients switch sign and maximize at 0.17 eV lower from the main peak (gray arrow). This 0.17 eV shifted band corresponds to one quantum of vibrational energy in the ground electronic state of the ion [18]. The detected structures are thus most likely associated to $3\hbar\omega\,(0 \rightarrow 0)$ ionization producing ions with some population in the $\nu = 1$ state. Signatures of vibrational excitation also show up in the $3\hbar\omega\,(0 \rightarrow 0)$ ionizing process at 396 nm (figure 1(h)). The PES shows a shoulder around the expected electron energy for an