density functional theory (TDDFT) calculations of the electronic spectra of neutral and cationic fenchone[4], these two series correspond to the ionization channels $k\hbar\omega\,(0 \rightarrow 0)$, with k ranging from 3 to 6, and $k'\hbar\omega\,(0 \rightarrow 1,\ 2)$, with $k' \leqslant 7$. Our TDDFT calculations validate the Koopmans approximation for $i < 11$, so that the two series can safely be interpreted as ionization from the HOMO and HOMO-1,2, respectively[5]. The angle-resolved PECD (figure 2(a)) shows that the PECD is maximum about $\theta = 0°$ at threshold and maximizes around higher θ values as the ATI order increases. This is due to the additional absorption of photons which results in the increase of the maximum order in the Legendre decomposition. The MP-PECD from the HOMO is negative and decays from $\sim -12\%$ at threshold ($k = 3$) to $\sim -1\%$ for 6-photon ionization (figure 2(c)). This reflects the fact that as the electron gets more energy through sequential absorption of photons, it is less sensitive to the molecular chiral potential. The values of the PECD obtained by a single-photon XUV ionization experiments [20] are reported in the same figure. While the results are remarkably similar for the 3-photon ($3\ \hbar\omega = 9.3$ eV) and single-photon ($\hbar\omega = 9.3$ eV) ionization of the HOMO, the single-photon PECD switches sign above this energy, while it remains negative in the multiphoton regime. Well above threshold, the single-photon PECD is much stronger than the multiphoton one. This could be the signature of a better isolation of the HOMO contribution by coincidence electron-ion detection in the single-photon experiment, while background from other channels may decrease the multiphotonic PECD.

As the laser intensity increases, the overal value of the PECD diminishes (figure 2(b)). This is the signature of the stronger influence of the laser field on the electron dynamics compared to that of the chiral molecular potential. Deeper observation of the PECD plot reveals significant changes, especially for $E \geqslant 4$ eV. This can be understood by monitoring the PES in figure 2(c): it still consists of two series of ATI peaks, but they appear upshifted in energy with respect to the lower intensity case. The series that was attributed to HOMO-1,2 now maximize around the neighbor $k''\hbar\omega\,(0 \rightarrow i)$ transitions, with $i = 12$–14 and $k'' = 6$–8. Interestingly, TDDFT associates $i > 11$ excited states of the cation to two-hole-one-particle configurations which are accessible from the ground state of the neutral through excitation + ionization processes. Similar processes, with even higher i in the range 16–20, may also come into play in the close neighborhood of the main HOMO peaks. In both cases, the juxtaposition of one-electron direct ionization and higher-order (excitation + ionization) processes leads to the observed shift of the PES peaks. It also leads to modifications of the PECD picture, inducing sign changes in the high-E range where the magnitude of the high-order ATI peaks associated to one-electron direct ionizations is low. Thus, tuning the laser intensity enables probing different responses of the molecule: the pure one-electron PECD response at low intensity, and higher order processes, beyond the Koopmans theorem, at higher intensity.

2.3. From ATI to tunnel ionization

The ionization regime is not only defined by the laser intensity but also by its wavelength. A recent study of molecular strong field ionization showed that ionization to excited cationic states was significantly suppressed if the gap between the ground and excited states was higher than the photon energy [25]. In other words, ionization from orbitals deeper than $\hbar\omega$ from the HOMO is unfavored. Since the HOMO and HOMO-1 channels are separated by ~ 2 eV, using 800 nm photons (1.55 eV energy) should enable isolating the response of the HOMO. That is what we show in figures 3(a), (b) which display the $\overline{\text{PAD}}$s obtained for $\lambda = 800$ nm and $I \sim 0.9$ and 1.2×10^{13} W cm^{-2}, respectively. The $\overline{\text{PAD}}$s exhibit three ATI peaks associated to 7-, 8- and 9-photon absorption, all of them leaving the fenchone cation in its ground state. The contributions of excited ionic states, mainly located about the $7\hbar\omega\,(0 \rightarrow 0)$ peak, are extremely weak. The peaks show a global downshift in energy with respect to the positions inferred from field-free TDDFT calculations. This is the signature of the laser-induced ponderomotive shift, which is a typical feature of non-resonant MPI. The PECD presents very significant values, reaching $\sim 8\%$ in figure 3(d), and exhibits repeatedly regular features associated to ionization from the HOMO in the ATI range. However, as I is increased to 1.2×10^{13} W.cm^{-2} the PECD picture becomes blurred (see figure 3(e)). In fact these last irradiation conditions correspond to a Keldysh parameter $\gamma \sim 1.9$ which is rather close to the limiting value of 1 that signs the entrance to the tunneling regime.

2.4. PECD in the tunneling regime

This last observation led us to investigate PECD in genuine tunneling regime. We employed 1850 nm, $I \sim 4 \times 10^{13}$ W cm^{-2} pulses, corresponding to $\gamma \approx 0.6$. We present in figures 3(c) and (f) the raw experimental 2D projections of the $\overline{\text{PAD}}$ and PECD. The shape of the $\overline{\text{PAD}}$, strongly peaked about 90°, is typical of tunnel-ionized electron distributions. It extends up to energies corresponding to the absorption of more than 30

[4] We have optimized the geometry of fenchone at the TDDFT level of theory, employing the GAMESS-US package [21] with a 6-311++G** basis [22] and CAMB3LYP hybrid exchange-correlation functional [23, 24]. The same geometry has been used for the cation, yielding all necessary vetical ionization potentials $IP_{0\rightarrow i}$. The computed $IP_{0\rightarrow 0}$ is 8.74 eV, in very good agreement with the experimental one, 8.72 eV.

[5] The penultimate (HOMO-1) and third-to-last (HOMO-2) occupied molecular orbitals of fenchone lie too close on the energy scale to be experimentally distinguished.