

offers *a priori* an easier comparison with calculations, avoiding effects due to the transition *via* intermediate states and their possible alignment. On the other hand, multiphoton ionization makes PECD measurements possible directly using femtosecond laser pulses without the need of the intermediate HHG step, offering an interesting alternative. In order to compare the two techniques, we studied the multiphoton ionization of fenchone by the same 400 nm laser pulses as the ones used in HHG. We focused the circularly polarized laser pulses with a 50 cm focal lens into the VMIS. Two-photon absorption resonantly excites the molecules into a 3s-Rydberg state (of energy 6.11 eV according to TDDFT calculations and 5.9 eV according to absorption measurements²¹), facilitating subsequent ionization. The acquisition procedure was similar to that used for XUV ionization. The images were analyzed by setting $N = 5$ in eqn (1) in order to account for absorption of up to 5 photons in above-threshold ionization.

In order to evaluate the influence of the resonance in the PECD signal, we performed measurements at different laser wavelengths. Fig. 5 shows the ARPES and PECD obtained using laser pulses at 408.5 nm (3.04 eV) and $1 \times 10^{13} \text{ W cm}^{-2}$, 404 nm (3.07 eV) and $5 \times 10^{12} \text{ W cm}^{-2}$, 398 nm (3.12 eV) and $5 \times 10^{12} \text{ W cm}^{-2}$, 396 nm (3.14 eV) and $2 \times 10^{13} \text{ W cm}^{-2}$. The laser intensities are slightly different but we have observed that at fixed wavelength, the PECD remains independent of the laser intensity within the 0.5 to $2 \times 10^{13} \text{ W cm}^{-2}$ range, in good agreement with previous measurements.²⁰ The ARPES is constituted of three main peaks, corresponding to 3- and 4-photon ionization of the HOMO ($4\omega_0(0 \rightarrow 0)$ and $4\omega_0(0 \rightarrow 0)$, around 0.5 eV and 3.5 eV electron energy respectively), and 4-photon ionization of the HOMO–1 ($3\omega_0(0 \rightarrow 1^*)$ around 1.5 eV). These peaks shift to higher energy as the laser wavelength decreases, as expected. Apart from that, the ARPES does not show strong sensitivity to the laser wavelength within the scanned range. This indicates that the electron spectrum is not very sensitive to the details of the Rydberg excitation. At 408.5 nm, the two-photon absorption excites the fenchone molecules in the lower part of the 3s band, while at 396 nm the excitation lies in the upper part of the 3s, inducing about 200 meV of vibrational excitation, and overlaps with the beginning of the 3p band calculated at 6.56 eV and measured at 6.25 eV.²¹ Stark shifts may bring the 3p band out of the photoexcitation spectrum, such that the wavelength scan that we performed may not enable changing the electronic character of the resonance. Our measurements show that the level of vibrational excitation of the resonant intermediate state does not affect the ARPES. The Rydberg and ionic potential energy surfaces are generally quasi-parallel. The vibrational distribution of the ionic populations thus tends to be the same as the Rydberg states, following the propensity rule $\Delta v = 0$. As a consequence, the photoelectron associated to different vibrational states of the ion all have the same kinetic energy, whatever the level of vibrational excitation of the Rydberg states.⁴² This prevents the resolution of vibrational effects in REMPI photoelectron spectra. Changing the photon energy by δE thus does not result in a shift of the photoelectron spectrum by $3\delta E$, as in a direct 3-photon ionization, but by δE , since only the last photon of the $2 + 1$ process plays a role. The photon energy difference between 396 nm and 408.5 nm is $\delta E = 92 \text{ meV}$, which agrees reasonably well with the measured energy shift of the $2 + 1$ peak ($\delta E^{\text{exp}} = 115 \text{ meV}$) and $2 + 2$ peaks ($\delta E^{\text{exp}} = 250 \text{ meV}$). Since PECD is *a priori* very sensitive to vibrational excitation of the cation, one can wonder if it will reveal any feature connected to deviations of the $\Delta v = 0$ propensity rule in the REMPI process.