

$$S_p(E, \theta) = \sum_{i=0}^{l_{\max}=2N} b_i^p(E) P_i(\cos(\theta)) \quad (1)$$

where $p = \pm 1$ is the light helicity, E is the photoelectron energy, θ its ejection angle with respect to the light propagation direction, and N the number of photons involved in the ionization process (see *e.g.* ref. 25). The expansion coefficients $b_i^p(E)$ are extracted by a least-squares fitting of the experimental distributions.⁴⁰ The first coefficient $b_0(E)$ is the angle-integrated photoelectron spectrum (PES). The odd coefficients reflect the forward/backward asymmetry along the optical axis in the photoelectron angular distribution. The angle-resolved photoelectron spectrum (ARPES) is calculated by:

$$\text{ARPES}(E, \theta) = \frac{S_{-1} + S_{+1}}{2} \quad (2)$$

The PECD, which quantifies the forward/backward asymmetry relative to the ARPES signal, is defined as

$$\text{PECD}(E, \theta) = \frac{S_{-1} - S_{+1}}{\text{ARPES}(E, \theta)} \quad (3)$$

The normalization procedure can strongly overestimate the PECD in areas where the ARPES is low (and noisy). It also modifies the angular distribution of the asymmetry, and does not directly reflect the shape of the antisymmetric part of the ARPES. To avoid this, in the following we will thus also use an alternative definition to monitor the absolute forward/backward asymmetry:

$$\text{APECD}(E, \theta) = \frac{S_{-1} - S_{+1}}{\max(\text{ARPES})} \quad (4)$$

Last, to evaluate the difference between the number of electrons emitted in the forward and backward hemispheres, we will use the general expression of multiphoton PECD:¹⁸

$$\text{MPPECD}(E) = \frac{1}{b_0} \left(2b_1 - \frac{1}{2}b_3 + \frac{1}{5}b_5 - \frac{5}{32}b_7 + \frac{6}{64}b_9 \dots \right) \quad (5)$$

which reduces to $2b_1/b_0$ in the single photon case.

Fig. 4 shows the ARPES (a) and PECD (b) obtained by ionizing fenchone by harmonics 3 (9.3 eV photon energy) and 5 (15.5 eV) of the 400 nm laser. This one-photon absorption case corresponds to $N = 1$ in eqn (1). The PES ($b_0(E)$, Fig. 4(c)) presents a sharp peak around 0.5 eV whose height is normalized to 1, followed by a broad bump from ~ 1 to ~ 5.5 eV. An additional (tiny) maximum is noticeable around 6.75 eV. In order to assign these features to ionization pathways, we performed Time-Dependent Density Functional Theory (TDDFT) calculations of the electronic spectra of the neutral and cationic fenchone using the GAMESS-US package.⁴¹ The geometry of fenchone has been optimized at the TDDFT level of theory, employing a 6-311++G** basis and CAMB3LYP hybrid exchange–correlation functional. The same geometry has been used for the cation, yielding a vertical ionization potential of 8.74 eV, in very good agreement