

Here we first show that PECD is rather insensitive to the electronic character and oscillator strength of resonances involved in MPI of limonene in the UV range. Switching to fenchone samples, we further demonstrate by increasing the laser intensity and wavelength that PECD exists in very high-order ATI peaks, up to the tunneling ionization regime. We interpret this universality using a classical analysis of the ionization process, which gives an intuitive picture of the ongoing electron dynamics.

2. PECD measurements

The experiments were conducted using the Aurore laser at CELIA, which provides 7 mJ-25 fs pulses at 800 nm with a 1 kHz repetition rate. The laser pulses are frequency doubled in a 200 μm thick type I BBO crystal, whose orientation was adjusted to tune the central frequency of the pulses between 396 nm and 409 nm. For long wavelength experiments, an optical parametric amplifier (HE-TOPAS) was used to convert pulses of 4.5 mJ at 800 nm to 500 μJ ones at 1850 nm with ~ 100 nm FWHM bandwidth. The pulses were focused by a 50 cm focal lens into a velocity map imaging spectrometer. The chiral molecules were heated in an oven and introduced as a continuous flow through a 200 μm capillary 7 cm away from the laser focus. The pressure in the interaction chamber was typically 2×10^{-6} mbar, with a background pressure of 5×10^{-8} mbar. The PECD was measured by recording the photoelectron spectra with left (LCP, $p = +1$) and right (RCP, $p = -1$) circular laser polarizations, defined from the point of view of the observer. In order to remove the influence of slow drifts in the experiments, the polarization state was switched every 10 seconds. Typically 7×10^5 laser shots were accumulated to obtain each of the LCP and RCP images.

The velocity map imaging spectrometer measures 2D projections of the 3D photoelectron angular distributions (PADs). The PAD can be decomposed as a sum of Legendre polynomials $S_p(E, \theta) = \sum_{i=0}^{2N} b_i^p(E) P_i(\cos(\theta))$ 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 ionizing photons. The even expansion coefficients $b_{i=2n}^p(E)$ fulfill $b_{i=2n}^{+1}(E) = b_{i=2n}^{-1}(E)$ while $b_{i=2n+1}^{+1}(E) = -b_{i=2n+1}^{-1}(E)$ for the odd ones (see e.g. [12]). The former ones are therefore obtained by least-square fitting the experimental projection of the averaged PAD, $\overline{\text{PAD}}(E, \theta) = (S_{+1} + S_{-1})/2$, while the odd coefficients are retrieved from the fit of the dichroism image $(S_{+1} - S_{-1})/2$ [17]. The PECD is then defined as $\text{PECD}(E, \theta) = 2(S_{+1} - S_{-1})/(S_{+1} + S_{-1})$, and the angular-integrated $\overline{\text{PAD}}$ provides the photoelectron spectrum (PES) $b_0(E)$.

2.1. MPI- and REMPI-PECD

2.1.1. Role of resonant enhancement in REMPI-PECD

First, we studied the photoionization of (4R)-1-methyl-4-(prop-1-en-2-yl)cyclohex-1-ene, referred to as (+)-limonene, by absorption of 3 photons where the central wavelength λ was varied between 409 and 396 nm, at intensity $I \sim 10^{12} \text{ W cm}^{-2}$. Figures 1(a)–(c) shows the measured PADs, and figures 1(d)–(f) the PECD. Using the ionization potentials $\text{IP}_{0 \rightarrow i}$ from the ground state of limonene (0) to the ground (0) and excited (i) states of the associated cation given in [18], we calculate the expected positions of the $3\hbar\omega$ ($0 \rightarrow 1$) and $3\hbar\omega$ ($0 \rightarrow 0$) ionization pathways, depicted as continuous circles. Within the Koopmans approximation, they correspond to the removal of one electron from the highest occupied molecular orbital (HOMO, outer circle) and the HOMO-1 (inner circle) respectively. The most striking feature is a strong change of the intensity of the HOMO peak as the photon wavelength decreases: the signal increases by around one order of magnitude when the wavelength changes from 409 to 396 nm. In addition, the angular distribution of the photoelectrons ejected from the HOMO is modified, with a sign change of the b_2 Legendre coefficient from positive to negative. This indicates a clear modification of the ionization scheme. Indeed, changing λ from 409 to 396 nm brings different Rydberg states of limonene into resonance with $2\hbar\omega$ absorption from the HOMO: from 3s to the lowest 3p state according to the assignment made in [18], or from the lowest 3p to the intermediate 3p state according to [11]. Comparison of figures 1(d) and (f) unambiguously shows that similar PECDs are obtained at both wavelengths for the HOMO, with the same sign and in the 4% range. Furthermore, (2 + 1)-REMPI at 420 nm, involving vibrationally excited 3s state as the intermediate step, also led to $\sim 4\%$ PECD [11]. All of this proves that PECD is not sensitive to either the electronic character or the strength of the intermediate resonance involved in UV-MPI of limonene. Further investigations on different systems are required to determine whether limonene is an exceptional case or if this is a general trend of REMPI-PECD.

2.1.2. Vibrational features in MPI-PECD

A more advanced assignment of the different structures can be performed by plotting the Legendre coefficients (figures 1(g) and (h)). The lower peak in the PES is associated to the $3\hbar\omega$ ($0 \rightarrow 1$) pathway which involves the 3s(HOMO-1) resonance encountered around 6.1 eV [11]. As the laser wavelength increases, this peaks shifts up in energy, but not as much as expected. At 396 nm it is 0.1 eV below the expected position, which is probably a