

where b_1 is the so-called dichroic parameter. The corresponding asymmetry factors are large (up to a few tens of %) because PECD emerges in the pure electric-dipole approximation, and PECD is therefore orders of magnitude more intense than other chiroptical probes, such as circular dichroism in absorption, requiring interaction with weaker (magnetic and quadrupolar) terms.⁸ As found for other chiroptical parameters, b_1 is anti-symmetric with the switching of either enantiomers or light helicity.

In the context of molecular photoionization, b_1 depends on both the initial-state (orbital) and final state (continuum).^{9,10} However, unlike the usual cross section σ or the asymmetry parameter β , this new observable has a pure quantum origin in the scattering of the outgoing electron by an intrinsically chiral potential, being also fully dependent on the sine of the relative phase between adjacent outgoing partial wave continuum functions.⁵ This phase dependence makes b_1 a very sensitive probe of the whole molecular potential, much more so than σ or β , with a demonstrated dependence on conformers,^{11–15} chemical substitution,^{16,17} dimerization¹⁸ and clustering,^{19,20} and even vibrational-dynamics.^{21,22}

PECD possesses, therefore, a real analytical potential in the gas phase (*i.e.* in a solvent-free environment) which has recently been the driving force for a new emerging field of table-top PECD experiment based on fs laser ionization: UV-resonance-enhanced multi-photon ionization (REMPI) PECD^{23–28} or 1-photon VUV PECD by High Harmonic Generation (HHG).²⁹ These experiments are paving the way towards a potentially very sensitive analytic use of PECD for enantiomeric separation on mass-selected samples,³⁰ competing with other promising and emerging enantiomeric probes in the gas phase such as the one based upon phase-sensitive microwave spectroscopy.^{31–33} A natural step further will be the development of Time-Resolved (TR)-PECD to probe stereo-chemical reactions of chiral systems in real time.

Most of the pioneering SR-based experiments^{34–36} as well as the new generation of laser-based PECD experiments, were performed on the monoterpenes camphor and/or fenchone,^{24–26,30,37} two isomeric forms of a rigid, single-conformer, bi-cyclic ketone, quite easy to bring in the gas phase, and that can both be considered as showcases for molecular chirality. Note that fenchone has also been used to demonstrate a pioneering chiroptical method based upon High Harmonic Generation (HHG) from a chiral molecule,³⁸ and both isomers have been studied by REMPI-UV Ion Yield CD.³⁹ To be validated in sensitivity and reliability laser-based PECD experiments need benchmarking with data obtained with more well-established and controlled experiments such as the one that can be carried out with pure-CPL SR sources. This is one of the motivations for the present study, which provides for the first time complete and very accurate measurements of b_1 parameters for the two outermost orbitals of camphor and fenchone up to $h\nu \sim 16$ eV. Indeed, in the past some of us^{34,36,40} and other authors³⁵ published some data for these molecules but, because of technical SR light source limitations at the time, there were uncovered regions of the spectrum—notably in the crucial 10 to 15 eV

photon energy range for which theoretical models^{36,41} predict large oscillations of b_1 . The benchmarking of theory *versus* experiment, in this specific range, with very accurate data obtained with a state-of-the-art double imaging electron/ion coincidence (i²PEPICO) spectrometer set-up and quasi-perfect CPL is the second motivation of the present study, especially in a context where multi-photon/high field PECD modeling has just been initiated on these showcase molecules.^{42,43} The precision of the measurements we provide are such that departures from perfect enantiopurity in the sample we purchased could be detected, quantified, and corrections applied to the measured b_1 parameter, all perfectly corroborated by an independent analysis performed *via* chromatographic techniques. Establishing this new standard of accuracy, in terms of enantiomeric excess measurement *via* PECD, became an important issue that we also focused on in the course of the data analysis.

Finally, and this is an important goal of this work, the observation of PECD for various valence orbitals for both fenchone and camphor, which only differ by the position of two methyl groups, will allow us to expand our previous knowledge⁴⁰ on the sensitivity of valence-shell PECD to isomerism which in this case cannot be detected from the shape of the photoelectron spectra.

2. Experimental methods

Both *R*- and *S*-fenchone and *R*- and *S*-camphor were obtained from Sigma-Aldrich with a chemical purity above 98%. In the case of fenchone, the optical rotations quoted in the bottle labels for both enantiomers ($[\alpha]_D^{24} = -50.5^\circ$ for the *R* and $[\alpha]_D^{20} = +62^\circ$ for the *S*) suggested a difference in enantiopurity, with an *R/S* ratio of 0.81. For camphor, the optical rotations quoted in the chemical analysis of the particular lots used ($[\alpha]_D^{24} = +44.6^\circ$ for the *R* and $[\alpha]_D^{20} = -43.5^\circ$ for the *S*), led to an *R/S* ratio of 1.02. Therefore, we decided to analyze the exact enantiopurity of the purchased samples with multi-dimensional gas chromatography coupled to time-of-flight mass spectrometry (GC \times GC-TOFMS).⁴⁴ The GC \times GC column set consisted of a Chirasil-Dex CB (for fenchone) or Hydrodex- β -6-TBDM (for camphor) primary column modulator-coupled to a DB Wax secondary column. Temperature program was adapted to achieve maximum peak resolution. Secondary column was operated with 30 °C off-set. Modulation period of 3 s was applied. Helium was used as carrier gas at a constant flow of $\bar{u} = 1$ mL min⁻¹. Sample volumes of 1 μ L were injected in the split mode at an injector temperature of 230 °C. The TOF-MS was operated at a storage rate of 150 Hz, with a 25–500 amu mass range. Data were acquired and processed with LECO Corp ChromaTOF™ software. Samples of *S*- and *R*-enantiomers with the concentration 10⁻³ M were injected several times in order to obtain statistically relevant ee values.

PECD experiments were performed on the SAPHIRS end-station⁴⁵ of the VUV synchrotron beamline DESIRS,⁴⁶ at the French synchrotron facility SOLEIL. Each enantiomer of each molecule was directly placed into a temperature-controlled in-vacuum stainless steel oven. The reservoir was gently heated