



Cite this: *Phys. Chem. Chem. Phys.*,
2016, 18, 12696

Determination of accurate electron chiral asymmetries in fenchone and camphor in the VUV range: sensitivity to isomerism and enantiomeric purity†

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Photoelectron circular dichroism (PECD) manifests itself as an intense forward/backward asymmetry in the angular distribution of photoelectrons produced from randomly-oriented enantiomers by photoionization with circularly-polarized light (CPL). As a sensitive probe of both photoionization dynamics and of the chiral molecular potential, PECD attracts much interest especially with the recent performance of related experiments with visible and VUV laser sources. Here we report, by use of quasi-perfect CPL VUV synchrotron radiation and using a double imaging photoelectron/photoion coincidence (*i*²PEPICO) spectrometer, new and very accurate values of the corresponding asymmetries on showcase chiral isomers: camphor and fenchone. These data have additionally been normalized to the absolute enantiopurity of the sample as measured by a chromatographic technique. They can therefore be used as benchmarking data for new PECD experiments, as well as for theoretical models. In particular we found, especially for the outermost orbital of both molecules, a good agreement with CMS-X α PECD modeling over the whole VUV range. We also report a spectacular sensitivity of PECD to isomerism for slow electrons, showing large and opposite asymmetries when comparing *R*-camphor to *R*-fenchone (respectively -10% and $+16\%$ around 10 eV). In the course of this study, we could also assess the analytical potential of PECD. Indeed, the accuracy of the data we provide are such that limited departure from perfect enantiopurity in the sample we purchased could be detected and estimated in excellent agreement with the analysis performed in parallel *via* a chromatographic technique, establishing a new standard of accuracy, in the $\pm 1\%$ range, for enantiomeric excess measurement *via* PECD. The *i*²PEPICO technique allows correlating PECD measurements to specific parent ion masses, which would allow its application to analysis of complex mixtures.

Received 25th February 2016,
Accepted 6th April 2016

DOI: 10.1039/c6cp01293k

www.rsc.org/pccp

1. Introduction

Since its formal prediction in 1976,¹ its first precise calculated values in 2000,^{2,3} and its first experimental evidence in 2001,⁴ Photoelectron Circular Dichroism (PECD) has been the subject of a large number of both theoretical and experimental studies,^{5–7} mainly carried out with Synchrotron Radiation (SR), for valence and core-shell ionization. PECD is an orbital-specific chiroptical effect which manifests itself as a forward/backward asymmetry, with respect to the photon axis, of the electron angular distribution produced by the photoionization with Circularly Polarized Light (CPL) of randomly-oriented pure enantiomers of a chiral system. More precisely, PECD asymmetry can be defined, for a given light helicity and molecular handedness, as the normalized difference between the electron flux in the forward *vs.* backward direction which will equal $2b_1$ in the case of one-photon ionization,

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† Electronic supplementary information (ESI) available: Compilation of literature values, and those obtained in this work of the mean $b_1^{(+1)}$ values for ionization from the HOMO and HOMO–1 orbitals of 1*R*-4*R*(+)-camphor; compilation of literature values, and those obtained in this work of the mean $b_1^{(+1)}$ values for ionization from the HOMO orbital and A band of 1*R*-4*S*(–)-fenchone; observed enantiomeric excesses ratio for camphor and fenchone at the photon energies where both enantiomers were measured; computed isosurface plots showing the electronic density for the HOMO orbitals of 1*R*,4*R*-camphor and 1*R*,4*S*-fenchone. See DOI: 10.1039/c6cp01293k