

may also lie in the resonant excited intermediate state which can also differently select, and align, the two isomers. Such a structure-specificity in REMPI experiments is a well known process which has been recently applied to measure conformer-specific response in absorption CD.⁵⁴ In the present work, the b_1 sign inversion makes this isomerism phenomenologically quite striking but its origin is also very clear being, in a one-photon ionization regime, purely due to the multiple scattering of the outgoing electron in the chiral potential of the molecule.

The comparison between 1*R*-camphor and 1*R*-fenchone PECD spectra is shown across the full photon energy range studied in Fig. 8 and 9 for respectively the first (HOMO–1 channel) and second PES bands. In a previous study carried out with photon energies above 13 eV,⁴⁰ a difference between the b_1 curve for the HOMO orbitals of fenchone *versus* camphor was observed mainly as a difference in amplitude in the 18–22 eV range, *i.e.* KE of \sim 9–13 eV, corresponding to a shape resonance. These are known to be sensitive to molecular structures. Here (Fig. 8) the new PECD data show a far more striking signature of isomerism, in the KE = 0–5 eV region. Although it is also quite evident in the A band PECD (Fig. 9), this enhanced sensitivity is especially marked for electrons ejected from the HOMO orbital. There is a totally different behavior of the b_1 parameter, in terms of oscillation pattern and sign, for the same absolute configuration. With caveats discussed above, b_1 is very well reproduced by the CMS-X α modeling.

In a more general context the enhanced sensitivity of the chiral parameter b_1 to the molecular potential—and thus to effects such as isomerism, chemical substitution, conformers, vibrational dynamics, clustering—has been discussed previously^{3,6,7} and arises from the strong dependence on the phase shifts of the different outgoing partial waves that interfere in the scattering process.⁵ This dependency has been shown to be much more marked in the dichroic parameter b_1 than in the anisotropy parameter β or in the cross section,¹⁶ so that tiny changes in the

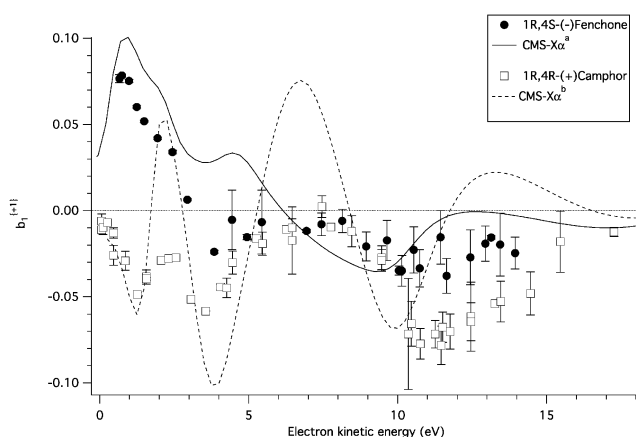


Fig. 8 Chiral parameter ($b_1^{(+1)}$) for ionization from the HOMO orbital of *R*-fenchone and *R*-camphor (*S* enantiomers negated). The points represent all the available experimental data in the literature, including the present work, while the lines correspond to CMS-X α calculations. The data have been normalized to the absolute ee as provided by GC \times GC-TOFMS. ^a From ref. 40. ^b From ref. 36.

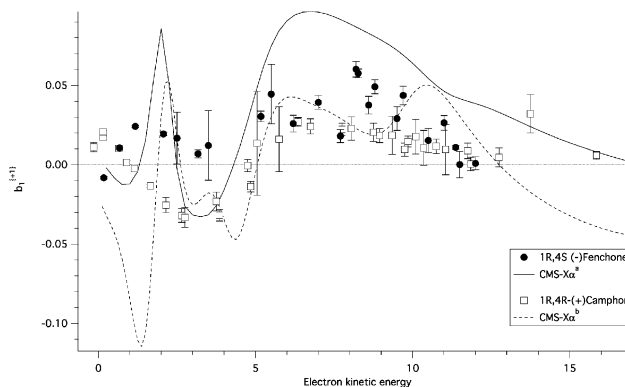


Fig. 9 Chiral parameter (b_1) for the A region of *R*-fenchone and ionization from the HOMO–1 orbital of *R*-camphor. The points represent all the available experimental data in the literature (*S* enantiomers negated), including the present work, while the lines correspond to CMS-X α calculations. In the case of fenchone, an average theoretical curve of three orbitals (#39, #40 and #41) weighted by their cross sections is shown. The data have been normalized to the absolute ee as provided by GC \times GC-TOFMS. ^a From ref. 40. ^b From ref. 36.

molecular potential will have a much larger effect on this new observable (b_1) accessible on randomly-oriented chiral targets. In contrast to b_1 , numerical computations of the β parameter of fenchone⁴⁰ and camphor⁴¹ lead to very similar, non-distinguishable behaviour with photon energy. The present results also confirm that the enhanced sensitivity of PECD to the molecular potential is especially marked for slow electrons as already pointed out in the case of conformers^{14,15} and dimers.¹⁸ Finally, this sensitivity to isomerism confirms also that PECD is a long-range effect, at least for slow electrons, since in the case of camphor the methyl groups are localized quite far from the site of the ionized orbital.

Because PECD happens during the scattering process, it also observed upon inner-shell ionization from spherical orbitals, and some difference have also been found in the PECD from C1s ionization of camphor and fenchone.⁵⁵ However these differences, mainly observed along the shape resonance above 10 eV KE, are much smaller than what is observed here for outer valence shell electrons. This difference of sensitivity to isomerism between core and valence ionization, clearly observed experimentally and simulated by theory, is *a priori* unexpected since in both cases the initial orbital is very localized, and in the same area in the molecule.

In a broader context of chiroptical spectroscopies, note that the micro-wave 3 wave-mixing technique has been shown to be also sensitive to isomerism able for instance to distinguish menthone from isomenthone.⁵⁶

4. Conclusions and future prospects

In this work we have experimentally studied the chiroptical PECD effect induced by one-photon valence-shell ionization in the VUV range of randomly-oriented enantiomers. We provide b_1 values on showcase chiral isomers camphor and fenchone with high accuracy since sources of systematic errors such as imperfect CPL or enantiopurity have been taken into account.