

In the case of the HOMO–1 orbital, as shown in Fig. 4, the new data in the 10–13 eV range display a reversed PECD asymmetry, as compared to the HOMO orbital, as the  $b_1$  parameter flips sign. This experimentally observed behavior is well reproduced by the CMS- $X\alpha$  model calculations until, in the first eV above threshold, the model predicts a spurious unobserved swing in  $b_1$ . Such low energy electrons will, of course be especially sensitive to the subtleties of the molecular potential, making this region especially challenging for calculation. Nevertheless, the overall experiment/theory is satisfactory.

### 3.2 Fenchone data

In Fig. 5 and 6 we present photon energy dependent PECD data for the HOMO and the HOMO–1 orbital ionizations of fenchone, obtained following a similar procedure outlined for camphor. In particular, the same PEPICO filtering treatment, to decipher the HOMO and HOMO–1 contribution has been applied to fenchone since the two molecules exhibit the same fragmentation pattern with HOMO orbital ionization leaving an intact molecular ion, while the inner orbitals leads to the cation fragmentation.

Pre-alerted by previous reports<sup>25,37</sup> that similarly sourced commercial fenchone samples may not be enantiopure, and by our own experience with camphor (above), we took additional steps to verify purity of our fenchone samples. The two different enantiomeric samples of fenchone were analyzed by GC  $\times$  GC-TOFMS to obtain a precise value of the ee. The results of the chromatographic analysis are shown in Table 1. While the *S*-fenchone sample was perfectly enantiopure, the nominal *R*-fenchone sample, had an ee of  $82.1 \pm 0.5\%$ . Note that here the error bars are given by the  $3\sigma$  statistical distribution analysis of the ee measurements over 10 injections into the GC  $\times$  GC-TOFMS apparatus.

While treating the fenchone PECD data we could infer such an enantiopurity difference between the two samples of fenchone

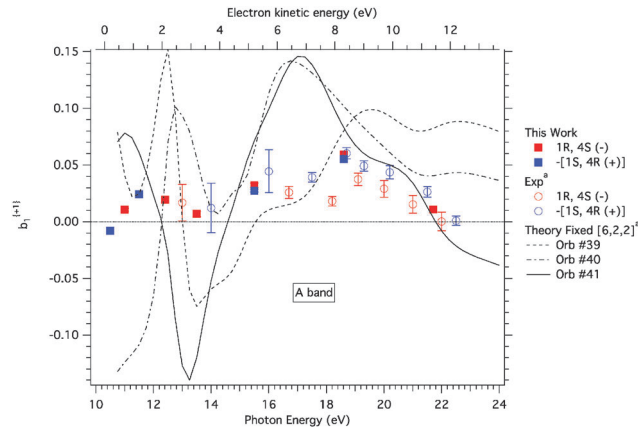


Fig. 6 Mean chiral parameter ( $b_1$ ) of the A band, corresponding to the binding energy region 10.05–10.61 eV of fenchone obtained at different photon energies. The data in this work are normalized to  $S_3$  and to the absolute ee as provided by GC  $\times$  GC-TOFMS. The markers represent experimental measurements while the lines correspond to two different CMS- $X\alpha$  models. The *S*-enantiomer data have been negated. For some of the data points, the statistical error bars are not visible because they are smaller than the point width (see Table S2, ESI<sup>†</sup>). <sup>a</sup> From ref. 40.

since at the three photon energies for which we had measured the PECD for both enantiomers (9.4, 15.5 and 18.6 eV) we observed systemically lower magnitudes for the  $b_1$  values of the *R*-sample. The average ratio of the  $b_1$  absolute values for the *R*-, *S*-enantiomer pairs at these three photon energies, weighted by the standard deviation, provides us with ee[R]/ee[S] ratio of  $0.82 \pm 0.01$ , as deduced from data presented in Fig. S1(b) (ESI<sup>†</sup>), in perfect agreement to the  $0.821 \pm 0.005$  obtained from the GC  $\times$  GC-TOFMS analysis (see Table 1). All the new data presented here in figures (and including Table S2, ESI<sup>†</sup>) have been corrected for the reduced sample enantiopurity, as was done earlier with our camphor data.

In a more extensive study using REMPI-PECD Kastner *et al.*<sup>52</sup> have similarly demonstrated relative ee determinations with better than 1% uncertainty for fenchone mixtures spanning the full range (0–100%). However, as compared to this latter method, the  $i^2$ PEPICO experiment provides the capability for ion mass-tagged PECD measurement. This allows for the simultaneous enantiomer specific analysis of multi-component mixtures which was proposed and demonstrated for a mixture of chiral and non-chiral species – spurious achiral decomposition product of alanine<sup>15</sup> – and for prepared mixtures of chiral compounds by Raffie Fanood *et al.*<sup>30</sup> In that later case an ee measurement on a component present in chiral mixture was made with 20% uncertainty, the limitation being the restricted data rate in that work. The present result confirms that this is not a fundamental restriction and that mass-selected PECD can be used for analyzing gas phase enantiomeric excess with precision in the  $\pm 1\%$  range. This is not far below chiral chromatographic measurement precision and very competitive with other gas phase chiroptical methods for relative ee determination, such as the one based upon microwave three-wave mixing.<sup>33,53</sup> Note that in addition, PECD-PICO may as well provide the chemical purity (by MS-TOF analysis of the coincident cation) at the

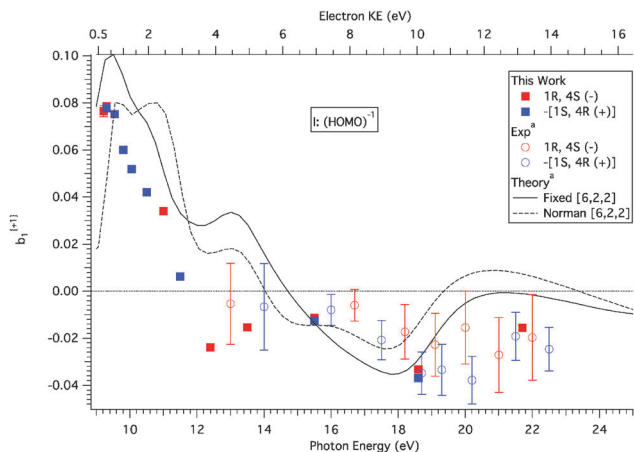


Fig. 5 Mean chiral parameter ( $b_1$ ) for ionization of the HOMO orbital of fenchone obtained at different photon energies. The values in this work are normalized to  $S_3$  and to the absolute ee as provided by GC  $\times$  GC-TOFMS. The markers represent experimental measurements while the lines correspond to two different CMS- $X\alpha$  models. The *S*-enantiomer data have been negated. For some of the data points, the statistical error bars are not visible because they are smaller than the point width (see Table S2, ESI<sup>†</sup>). <sup>a</sup> From ref. 40.