same time as the relative enantiopurity for each mass-selected species (by PECD).

The new measurements provide b_1 data for fenchone below 12 eV photon energy, where previously none had been published. The CMS-Xα modeling predicts for the HOMO orbital (Fig. 5) an intense asymmetry in the first few eV kinetic energy (KE) range, followed by a sign change of the asymmetry at increasing photon energies. These features are reproduced by the experimental data. However, and unlike the clearer case of camphor, the situation of the "HOMO−1" orbital in fenchone (Fig. 6) is more complex since due to our limited electron energy resolution and to the congestion of the PES, what we labeled as "HOMO−1" is in fact a mixture of several closely lying electronic orbitals such as the one labeled 39, 40 and 41 in ref. 40. In consequence the b_1 value observed in the A band (10.05–10.61 eV binding energy range) represents a blend of these individual ionizations. The comparison with the theoretical modelling of the various contributing orbitals is consequently not straightforward, although at high energy all calculations agree toward the same sign of b_1, corresponding to the experimental observations *i.e.* fixing the absolute configuration.

3.3 Camphor/fenchone comparison: sensitivity to isomerism

The sensitivity of PECD to chemical substitution in oxirane derivatives has been studied in the past theoretically[16] as well as experimentally[17] and strong effects upon substitution were reported even when the initial orbital appeared identical for all molecules and not centered onto the substituted chemical group. Even more spectacular are effects, as seen here, concerning pure isomers with the same chemical formula and the same localization of the HOMO orbitals as shown in Fig. S2 (ESI†). In this respect, Powis *et al.*[40] already commented on the different PECD values measured on camphor and fenchone, albeit in an energy range restricted to electron KE > 4 eV for the HOMO orbital. Here we can now extend this comparison to the threshold energy regions, which are known to be the most sensitive to the molecular potential.[7] The HOMO orbital in both molecules is a localized 2p lone pair of the carbonyl oxygen (see Fig. S2, ESI†). The corresponding hole in the unrelaxed cation potentials used for the CMS-Xα calculations is consequently similarly localized. The good CMS-Xα theory/experiment agreement that is evident, even within a few eV of the ionization threshold (Fig. 3 and 5) is then possibly attributable to relative accuracy with which the atomic-site partitioning of the multiple scattering potential model can reproduce this potential. Supporting this, ionization of the highly localized C1s orbital by soft X-ray SR in early studies of camphor and fenchone is similarly well described by the CMS-Xα calculations. In contrast, the more delocalized HOMO−1 ionizations give rise to PECD behavior which as discussed above is less well described by the CMS-Xα calculations in the low energy region.

Turning to a broader comparison of these molecules, both are rigid single-conformer structures whose isomerism can be reduced to the shift of two methyl groups (see Scheme 1) from a top position to a side one, none of them being directly connected to the asymmetric carbons (C1, C4) nor to the carbonyl
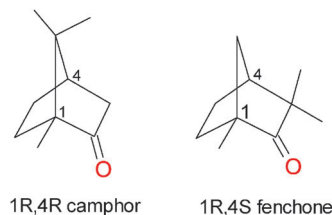
Scheme 1 Structure of the camphor and fenchone molecules.

group—in other words the isomeric changes are remote from the chiral centers and the localized HOMO orbitals. Fig. 7 shows the PES and PECD obtained at photon energies of 10.3 and 10.5 eV for 1R,4R-(+)-camphor and 1R,4S-(−)-fenchone respectively. The two photon energies are close enough so that dynamical effects would be marginal, so we can compare directly the data. The figure shows similar PES for both molecules, except for an energy shift due to the small ionization energy difference (fenchone is 180 meV lower than camphor[40,51]). The PECD curves, however, show a striking difference with opposite sign for the same absolute configuration of the two molecules. Here, note that absolute configuration of the C4 asymmetric carbon is fixed by the rigid cycle; the change in labelling from 4R (camphor) to 4S (fenchone) is due to a change in priority assigned by the Cahn–Ingold–Prelog nomenclature rules rather than a rearranged molecular configuration. Therefore, the natural comparison is shown in Fig. 7 and Scheme 1, *i.e.* between 1R,4R-(+)camphor and 1R,4S-(−)-fenchone. In this respect the quasi-mirroring of the PECD curves appearing in Fig. 3 is quite spectacular since it shows, that at 10.3/10.5 eV photon energy the two isomers behave nearly as opposite enantiomers while they have in fact the same absolute configuration!

A marked difference between REMPI-PECD measurements on fenchone and camphor at a single given energy was also reported by Lux *et al.*,[24,25] especially for the odd C_n ($n > 1$) parameters describing the high-order multi-photon electron angular distribution. Of course the role of the intermediate resonant state adds additional complexity to the interpretation of such results. Indeed, in the REMPI-PECD case, the origin
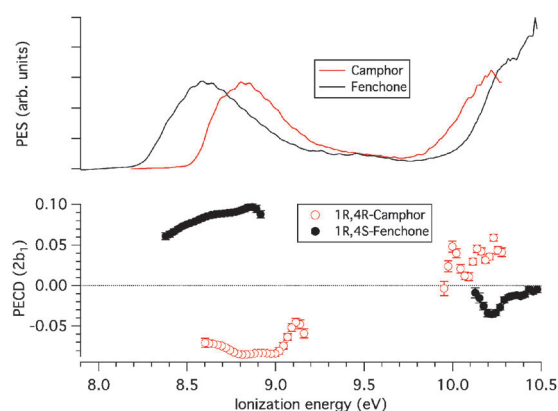

Fig. 7 PES and PECD for *R*-camphor (red) and *R*-fenchone (black) recorded at $h\nu$ = 10.3 eV and 10.5 eV respectively. The data have been normalized to S_3 and the absolute ee as provided by GC × GC-TOFMS.