Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Table S1: 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 1R,4R-(+)-camphor.

The Nahon et al. corresponds to Ref. [1] and Lischke et al. to Ref. [2].The table contains also the negated S enantiomer data. At photon energies where several b_1 values have been measured at the same photon energy and with the same experimental setup, the b_1 is presented as the weighted average of these measurements plus or minus its standard deviation. In this work, the binding energy region of the HOMO-1 orbital has been chosen as 10.15 ± 0.15 eV, whereas Lischke et al. use 10.45 eV. The values in this work have been normalized by S_3 and the e.e. measured by GCxGC-TOFMS.

HOMO			HOMO-1		
$b_1^{(+1)}$	$h\nu$	Ref.	$b_1^{(+1)}$	$h\nu$	Ref.
-0.011 ± 0.002	8.8	This Work	0.011 ± 0.003	10	Nahon et al.
-0.006 ± 0.004	8.8	Nahon et al.	0.0172 ± 0.0009	10.3	This Work
-0.010 ± 0.004	8.85	Nahon et al.	0.0209 ± 0.0009	10.3	Nahon et al.
-0.007 ± 0.002	9	Nahon et al.	0.010 ± 0.001	10.8	This Work
-0.013 ± 0.003	9.2	Garcia et al.	0.001 ± 0.001	11.05	This Work
-0.026 ± 0.006	9.2	Nahon et al.	-0.0024 ± 0.0009	11.3	This Work
-0.029 ± 0.005	9.6	Nahon et al.	-0.013 ± 0.001	11.8	This Work
-0.049 ± 0.001	10	Nahon et al.	-0.025 ± 0.005	12.3	This Work
-0.038 ± 0.004	10.3	Nahon et al.	-0.032 ± 0.004	12.8	This Work
-0.0396 ± 0.0007	10.3	This Work	-0.033 ± 0.006	13.2	Lischke et al.
-0.0289 ± 0.0009	10.8	This Work	-0.032 ± 0.004	14	This Work
-0.0278 ± 0.0007	11.05	This Work	-0.023 ± 0.006	14.2	Lischke et al.
-0.0273 ± 0.0007	11.3	This Work	-0.014 ± 0.003	15	This Work
-0.0515 ± 0.0009	11.8	This Work	0.01 ± 0.03	15.2	Nahon et al.
-0.0584 ± 0.0003	12.3	This Work	-0.001 ± 0.004	15.2	Lischke et al.
-0.044 ± 0.002	12.8	This Work	0.02 ± 0.02	16.2	Lischke et al.
-0.045 ± 0.006	13	Nahon et al.	0.027 ± 0.003	16.5	This Work
-0.030 ± 0.007	13.2	Lischke et al.	0.024 ± 0.005	17.2	Lischke et al.
-0.016 ± 0.001	14	This Work	0.022 ± 0.004	18.2	Lischke et al.
-0.019 ± 0.007	14.2	Lischke et al.	0.023 ± 0.007	18.2	Nahon et al.
-0.011 ± 0.001	15	This Work	0.018 ± 0.004	19.1	Nahon et al.
-0.02 ± 0.02	15.2	Nahon et al.	0.020 ± 0.006	19.2	Lischke et al.
-0.010 ± 0.005	15.2	Lischke et al.	0.02 ± 0.01	19.5	Nahon et al.
0.002 ± 0.006	16.2	Lischke et al.	0.015 ± 0.003	20	Nahon et al.
-0.0095 ± 0.0008	16.5	This Work	0.010 ± 0.004	20.2	Lischke et al.
-0.012 ± 0.009	17.2	Lischke et al.	0.02 ± 0.01	20.25	Nahon et al.
-0.027 ± 0.007	18.2	Nahon et al.	0.01 ± 0.01	20.5	Nahon et al.
-0.029 ± 0.006	18.2	Lischke et al.	0.01 ± 0.02	21.2	Nahon et al.
-0.07 ± 0.03	19.1	Nahon et al.	0.012 ± 0.005	21.2	Lischke et al.
-0.07 ± 0.01	19.2	Lischke et al.	0.000 ± 0.004	22	Nahon et al.
-0.077 ± 0.009	19.5	Nahon et al.	0.009 ± 0.005	22.2	Lischke et al.
-0.072 ± 0.008	20	Nahon et al.	0.005 ± 0.006	23.2	Lischke et al.
-0.08 ± 0.01	20.2	Lischke et al.	0.03 ± 0.01	24.2	Lischke et al.
-0.068 ± 0.009	20.25	Nahon et al.	0.006 ± 0.002	26	Nahon et al.

-0.07 ± 0.01	20.5	Nahon et al.
-0.06 ± 0.02	21.2	Nahon et al.
-0.06 ± 0.01	21.2	Lischke et al.
-0.054 ± 0.002	22	Nahon et al.
-0.05 ± 0.01	22.2	Lischke et al.
-0.05 ± 0.01	23.2	Lischke et al.
-0.02 ± 0.02	24.2	Lischke et al.
-0.012 ± 0.003	26	Nahon et al.

Table S2: 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 1R,4S-(–)-fenchone. The Powis et al. corresponds to Ref.[3] .The table contains also the negated S enantiomer data. At photon energies where several b_1 values have been measured at the same photon energy and with the same experimental setup, the b_1 is presented as the weighted average of these measurements plus or minus its standard deviation. In this work, the binding energy boundaries of the A region have been chosen as 10.05–10.61 eV, whereas Powis *et al*. used 9.9–11.0 eV. The values in this work have been normalized by S_3 and the e.e. measured by GCxGC-TOFMS.

HOMO			**A band**		
$b_1^{(+1)}$	$h\nu$	**Ref.**	$b_1^{(+1)}$	$h\nu$	**Ref.**
0.077 ± 0.002	9.22	This Work	-0.0082 ± 0.0007	10.5	This Work
0.078 ± 0.001	9.3	This Work	0.011 ± 0.001	11	This Work
0.0753 ± 0.0009	9.54	This Work	0.0242 ± 0.0007	11.5	This Work
0.0601 ± 0.0007	9.8	This Work	0.019 ± 0.001	12.4	This Work
0.0519 ± 0.0006	10.05	This Work	0.02 ± 0.02	13	Powis et al.
0.0420 ± 0.0006	10.5	This Work	0.007 ± 0.003	13.5	This Work
0.034 ± 0.001	11	This Work	0.01 ± 0.02	14	Powis et al.
0.0063 ± 0.0006	11.5	This Work	0.031 ± 0.003	15.5	This Work
-0.0239 ± 0.0008	12.4	This Work	0.04 ± 0.02	16	Powis et al.
-0.01 ± 0.02	13	Powis et al.	0.026 ± 0.005	16.7	Powis et al.
-0.015 ± 0.001	13.5	This Work	0.039 ± 0.004	17.5	Powis et al.
-0.01 ± 0.02	14	Powis et al.	0.018 ± 0.004	18.2	Powis et al.
-0.0118 ± 0.0009	15.5	This Work	0.058 ± 0.003	18.6	This Work
-0.008 ± 0.007	16	Powis et al.	0.060 ± 0.005	18.7	Powis et al.
-0.006 ± 0.007	16.7	Powis et al.	0.038 ± 0.006	19.1	Powis et al.
-0.021 ± 0.008	17.5	Powis et al.	0.049 ± 0.004	19.3	Powis et al.
-0.02 ± 0.01	18.2	Powis et al.	0.029 ± 0.007	20	Powis et al.
-0.035 ± 0.003	18.6	This Work	0.044 ± 0.006	20.2	Powis et al.
-0.035 ± 0.009	18.7	Powis et al.	0.015 ± 0.008	21	Powis et al.
-0.02 ± 0.01	19.1	Powis et al.	0.026 ± 0.005	21.5	Powis et al.
-0.03 ± 0.01	19.3	Powis et al.	0.011 ± 0.001	21.7	This Work
-0.02 ± 0.02	20	Powis et al.	0.000 ± 0.008	22	Powis et al.
-0.04 ± 0.01	20.2	Powis et al.	0.001 ± 0.004	22.5	Powis et al.
-0.03 ± 0.02	21	Powis et al.			

-0.02 ± 0.01	21.5	Powis et al.
-0.016 ± 0.001	21.7	This Work
-0.02 ± 0.02	22	Powis et al.
-0.025 ± 0.009	22.5	Powis et al.

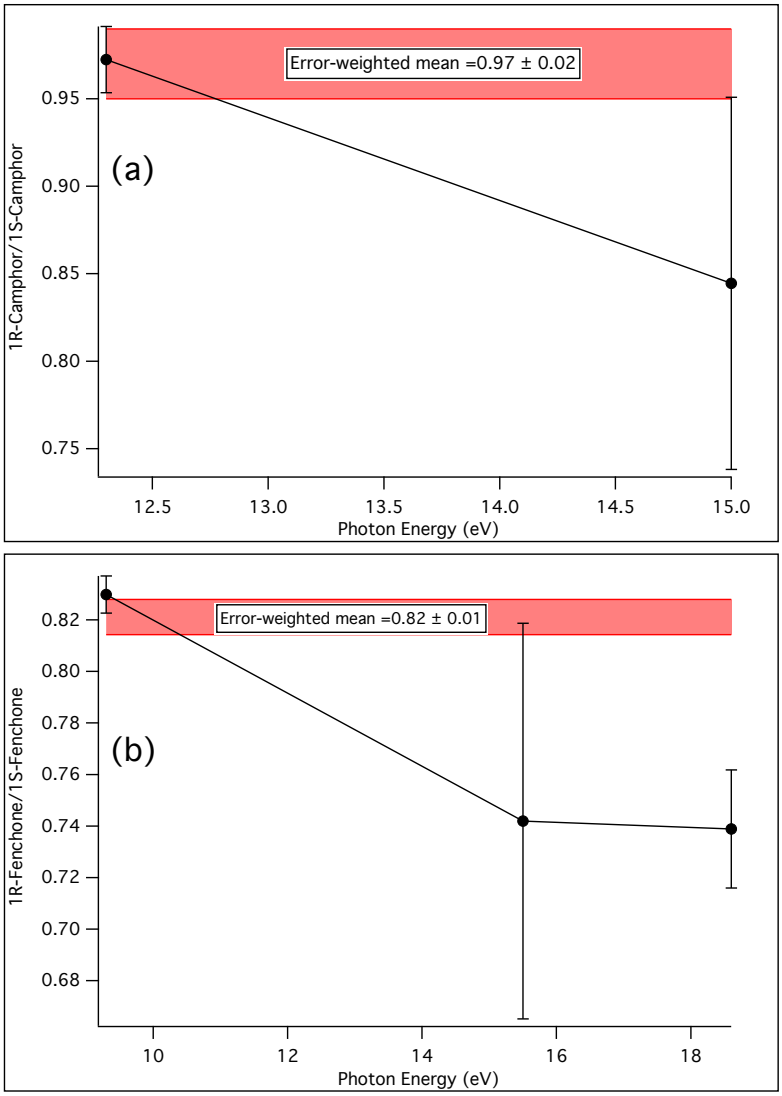

Figure S1: Observed $\frac{\mathrm{PECD_R}}{\mathrm{PECD_S}}$ ratio for (a) camphor and (b) fenchone at the photon energies where both enantiomers were measured. The error-weighted mean values are given as red transparent band. Note that the error bars will increase for small absolute values of b_1, and for increasing photon energies where the HOMO relative cross-section is smaller, so that the more precise values are generally obtained at low photon energies.

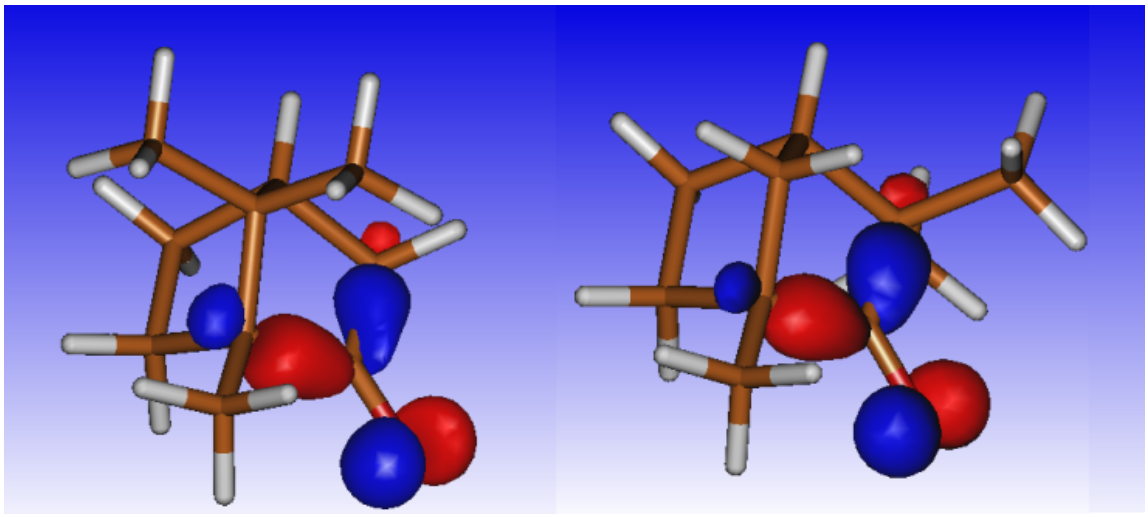

Figure S2: Computed (HF/6-31G**) isosurface plots showing the electronic density for the HOMO orbitals of 1R,4R-camphor (left) and 1R,4S-fenchone (right).

1. L. Nahon, G. A. Garcia, C. J. Harding, E. A. Mikajlo and I. Powis, *J. Chem. Phys.*, 2006, **125**, 114309.
2. T. Lischke, N. Böwering, B. Schmidtke, N. Muller, T. Khalil and U. Heinzmann, *Phys. Rev. A*, 2004, **70**, 022507.
3. I. Powis, C. J. Harding, G. Garcia and L. Nahon, *ChemPhysChem*, 2008, **9**, 475-483.