

We expect these data to be useful for the development and benchmarking of new PECD experiments, especially those involving VUV radiation based upon HHG and probably in the near future Free Electron Lasers (FELs).

In addition, in the context of a growing development of VUV/XUV CPL sources from FELs,⁵⁷ HHG,^{29,58,59} plasma-based laser⁶⁰ and associated polarizing optics,⁶¹ PECD could, like other dichroic effects,⁶² be used as a “molecular polarimeter template”, especially when either the β parameter is null or known, or when the linear polarization components of light (S_1 and S_2) are negligible, in which case accurate PECD benchmarking with the present data would allow the disentangling of the unpolarized component (S_4) from the circular one (S_3). This would be a complementary approach from the molecular polarimetry data deduced from molecular-frame photoelectron angular distributions (MF-PADs), recently demonstrated⁶³ and valid in the dissociative ionization continuum range of small molecules, *i.e.*, above 20 eV or so. We therefore hope in this context, to contribute to the expansion of the active field of polarization dependent short wavelength photodynamics with short pulses.

In the more fundamental context of the understanding of the PECD process itself, we found a remarkable agreement between the experimental data and the CMS- $X\alpha$ modeling of the HOMO orbital of both camphor and fenchone, even in the challenging low KE energy range. On the other hand some clear discrepancies remain. Owing to the size and lack of symmetry simplifications in these molecules, current methods rely on solving independent electron dynamics in single reference derived potential (either semi-empirical as in CMS- $X\alpha$ or DFT as in the B-spline method).⁴¹ Future developments are likely to introduce electron correlations into the $N - 1$ electron potential model, and the current experimental data could serve as a benchmark for judging performance of such developments. Equally, there is accumulating evidence of the need to take fuller account of vibrational motions in refining our understanding of PECD,²¹ something which is absent from the current capabilities of fixed-geometry computations.

Besides, the accuracy of the data we provide is such that limited departure from perfect enantiopurity in the samples we purchased could be detected, by the non-perfect mirroring of the R/S PECD data. The benchmarking *versus* a conventional chromatographic analytical method, highlights the interest and high accuracy, in the % range, of PECD as a precise enantiomeric analytical tool in the gas phase. Especially when combined in with TOF mass spectrometry of the photoions, recorded in coincidence with the photoelectrons, *via* the so-called PECD-PICO scheme, we stress the ability to analyze a mixture of compounds simultaneously and to provide highly accurate relative ee measurement of each of these compounds, now with significantly improved accuracy over the first demonstrations of this capability.^{15,30} As compared to the well-established GC type of technique, PECD is a direct method with no derivatization, nor use of reagents, directly applicable in the gas phase, and which provides additional electronic information, as a multi-dimensional chiroptical probe (photon energy, electron energy, coincident ion mass).

Also as compared to the REMPI-PECD-PICO technique, there is no need here, in the VUV one-photon PECD-PICO approach for any chromophore absorbing in the UV range, so that the method is genuinely universal. We intend therefore in the near future to apply such a PECD-PICO scheme to disentangle the enantiomeric composition of a complex mixture of samples.

Finally, our experimental data show a very striking signature of the profound sensitivity of PECD to isomerism with large and opposite asymmetries measured on the HOMO orbital of the same enantiomers of camphor and fenchone. This feature, especially marked for slow electrons, is very well reproduced by theory, while the same theory shows that the two isomers have similar anisotropy parameter β . This ability of PECD could be applied in the future in the field of gas phase chemical reactivity, in order to probe and disentangle isomers in chemical reactions involving chiral products, as for instance in combustion of biofuels. PECD, with its exquisite sensitivity to isomers would be, in this context of gas phase chemical reactions probed by photoionization, an additional observable to products appearance energies,⁶⁴ or even to the full PES of mass-selected species.^{65,66}

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