

Valence-shell Photoelectron Circular Dichroism (PECD) on Chiral Halogenated Molecules in the Gas Phase

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Synopsis We measured and calculated the PECD of three different halogenated chiral molecules in order to study the role of the localization of the initial orbital of the outgoing electron with respect to the chiral center.

Photoelectron Circular Dichroism (PECD) is observed as a forward/backward asymmetry with respect to the photon axis, of the photoelectron angular distribution resulting from the CPL-induced photoionization of gas phase pure enantiomers of chiral species. This spectacular orbital-dependent chiroptical effect with intensities reaching up to the few tens of %, shows a rich photon energy dependence, and appears as a very sensitive probe of molecular conformations and of the chemical environment. [1] After the study of numerous organic compounds, we are interested here on unexplored questions, regarding to the role of the localization of the initial orbital of the outgoing electron with respect to the chiral center. Will the scattering phase of the outgoing electron be sensitive only to the nearby presence of a chiral center or is PECD a more global probe of the whole (chiral) molecular potential ?

Experiments were conducted on DESIRS beamline (Synchrotron SOLEIL, France) using the new electron/ion coincidence imaging spectrometer DELICIOUS 3, [2] which records Angle-Resolved photoelectron spectroscopy on mass-selected samples to extract the PECD. By alternating right- and left-handed circularly polarized radiation, the photoelectron circular dichroism (PECD) in the angular distribution was extracted from the photoelectron images obtained by coincidence with the ions corresponding to the parent and fragments, rejecting any spurious contribution from N₂ or H₂O for example.

Analysis of the photoelectron images of three well-chosen chiral halogenated molecules (Bromopropionic acid and Bromophenylethylamine isomers) on which the 4p Br orbitals are clearly localized (HOMO and HOMO-1 in the case of BPA, HOMO-3 and HOMO-4 in the case of BrPhEtA), allows us to observe and quantify the corresponding forward/backward asymmetry of the photoelectrons. Bromopropionic acid (BPA) possesses the Br atom directly bound to the chiral center whereas Bromophenylethylamine (BrPhEtA) isomers possess the Br atom localized far from the

chiral center. Interestingly, the highest asymmetry (on the HOMO orbital) is found for the 1,4-BrPhEtA molecule although it possesses the Br atom localized far from the chiral center. Sensitivity of the PECD to isomerism is also observed especially at 9 and 15.5 eV photon energies. Indeed, figure 1 shows the different experimental PECD values observed for the HOMO orbital on the two BrPhEtA isomers as well as a very good mirroring between the 1,3- BrPhEtA enantiomers. Recent Continuum Multiple Scattering (CMS-X α) calculations are then compared to experimental values at different photon energies and enable in some cases to determine the absolute configuration of the chiral molecule.

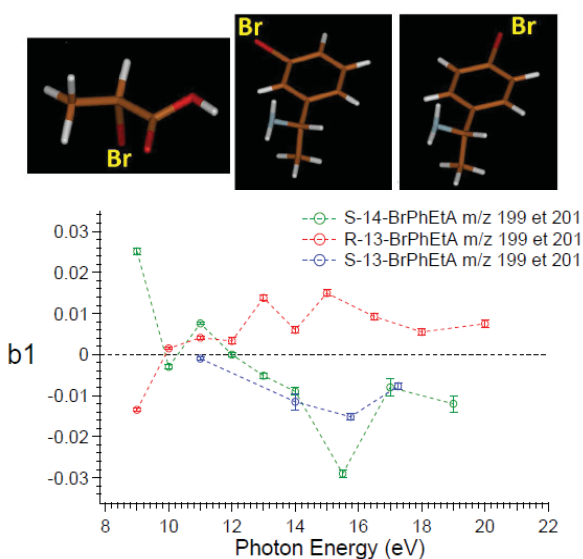


Figure 1. (up) Molecules corresponding to BPA and 1,3- and 1,4-BrPhEtA isomers. (bottom) Dichroic parameter extracted on the HOMO orbital as a function of the photon energy for the two isomers of BrPhEtA.

References

- [1] A. Zehnacker (ed.), *Chiral recognition in the gas phase* (CRC Press - Taylor & Francis, New York, 2010).
- [2] G. Garcia, B. Cunha de Miranda, M. Tia, S. Daly, and L. Nahon, 2013 Review of Scientific Instruments 84, 053112.

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