Conformational landscape in floppy chiral systems explored by one-photon Photoelectron Circular Dichroism (PECD)

Content

Chirality plays a fundamental role in molecular recognition processes. Molecular flexibility is also crucial in molecular recognition, allowing the interacting molecules to adjust their structures and hence optimize the interaction. Methods probing simultaneously chirality and molecular conformation are therefore crucially needed.

This is the case of a newly introduced chiroptical effect called Photoelectron Circular Dichroism (PECD) leading to very intense (up to 35 %) forward/backward asymmetries, with respect to the photon axis, in the angular distribution of photoelectrons produced by circularly-polarized light ionization of gas phase pure enantiomers. PECD happens to be an orbital-specific, photon energy dependent chiroptical effect and is a subtle probe of the molecular potential being very sensitive to static molecular structures such as conformers, isomers, clusters, as well as to vibrational motion, much more so than other observables in photoionization such as the cross section (Photoelectron Spectrum-PES) or the usual (achiral) asymmetry parameter (for a reviews see [1] [2]).

After an introduction to PECD stressing the universality of the effect in terms of chirality type as well as in terms of targets, ranging from free chiral molecules to clusters and complexes, up to nanoparticles [3], several recent results regarding one VUV-photon valence-shell PECD on various floppy systems will be presented:

- Alanine, for which a Boltzmann-averaged global PECD response could be measured.[4, 5]
- Proline, for which owing to a large binding energy difference between two types of conformers, we could observed directly and rationalize with the help of theoretical calculation a conformer-specific PECD.[6]
- 1-Indanol, for which by changing the carrier gas of the molecular beam we could control the conformer distribution and observe a dramatic conformer inversion of PECD, while the PES and asymmetry parameters are completely insensitive to conformational isomerism.[7]

Such a sensitivity to conformation is both an asset and a challenge for the ongoing developments of laser-based PECD techniques as a sensitive chiral (bio)chemical analytical tool in the gas phase.

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[4] M. Tia et al. , "Chiral asymmetry in the photoionization of gas-phase amino-acid alanine at Lyman-a radiation wavelength", J. Phys. Chem. Lett. 4, 2698-2704 (2013).
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