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Toward Elucidating Solvation Effects in Photoelectron Circular Dichroism

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Photoelectron circular dichroism (PECD) —the forward-backward asymmetry in photoemission from chiral molecules photoionized by circularly polarized light —is an exquisitely sensitive experimental probe, capable of determining enantiomeric excess and electronic and molecular structures in chiral samples. Although the use of PECD to study chiral biomolecules under physiologically relevant conditions promises to reveal otherwise inaccessible interactions, for example the nature of chirality transfer between the chiral solute and the solvent shell, PECD has until now been exclusively demonstrated in the gas phase. PECD is a threshold effect, with effect magnitude increasing as photoelectron kinetic energy decreases. However, scattering of photoelectrons in liquids increases commensurately at low energies, thereby leading to unavoidable convolution of PECD signals with the low-energy secondary electron background.[2] Despite these challenges, we have recently successfully measured core-level PECD in neat liquid fenchone, and in aqueous solutions of alanine, the latter under both neutral and basic conditions. These results constitute the first measurements of PECD in the liquid phase. We will discuss recent developments that have enabled these measurements, and will highlight our recent efforts to draw connections between gas- and liquid-phase experiments, with the aim of resolving solvation-based effects in PECD from biomolecules.

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