Photoelectron Circular Dichroism Of Liquid Samples

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ABSTRACT

Photoelectron Circular Dichroism (PECD) is an intense chiroptical effect defined as the forward/backward asymmetry along the light propagation axis upon photoionization of a chiral molecule by circularly polarized light. PECD is particularly sensitive to molecular and electronic structure, and benefits from the intrinsic strengths of photoelectron spectroscopy (PES), which for core-level ionization include surface, atomic-site, and chemical-state sensitivity. Despite these strengths, PECD has until recently been applied almost exclusively to molecules in the gas phase. Using our custom liquid-jet photoelectron spectroscopy apparatus,[1] we previously performed PECD experiments for neat liquid fenchone.[2] This work confirmed the feasibility of applying PECD to liquid samples, but also laid bare a number of experimental challenges inherent to this method. PECD is most intense for low kinetic energy (< 20 eV) photoelectrons, which for condensed-phase systems means that the primary photoelectrons of interest will be subject to scattering events and will become unavoidably convoluted with the high-intensity background signal comprised of scattered and secondary electrons.[3,4] The former effect will result in a loss in measured angular anisotropy, while the latter complicates data analysis. Here, we report on our experimental efforts to circumvent these effects by focusing on the surface-active molecule α-methylbenzylamine (MBA), and we compare our results for this molecule with our recent work on the bulk-soluble amino acid alanine,[5] thereby exploring PECD's sensitivity to protonation state and solvation conditions.

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