

What circular dichroism spectroscopy teach us about solvation

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ABSTRACT

Chiroptical spectroscopy, *i.e.* the uneven response of a chiral molecule to a circularly polarized light (CPL), is a unique tool for determining absolute configurations. It is also very sensitive to conformational isomerism and molecular interactions, such as hydrogen bond formation and solvation effects. These two aspects will be discussed for two different chiroptical spectroscopies, namely, Vibrational Circular Dichroism (VCD) in solution and Photoelectron Circular Dichroism (PECD) in jet-cooled molecules and complexes.

VCD is the very weak difference in absorption between left and right CPL in the IR range, for chiral molecules. Static quantum chemical methods are often sufficient for modeling the VCD spectra of rigid molecules in a non-interacting solvent. For flexible systems or those in strong interaction with their environment, anharmonicity and temperature effects, as well as solvation effects, must be considered carefully. Approaches resting on either static calculations, where the solvent is described as a cluster of limited size around the solute, or Force-Fields or First-Principles Molecular Dynamics simulations (FFMD or FPMD) will be described on the example of 1-indanol and 1-amino-2-indanol in non-polar or in DMSO solutions.¹⁻²

PECD is observed as a forward-backward asymmetry in the photoelectron angular distribution, with respect to the light axis, for randomly oriented chiral molecules photo-ionized by CPL.³⁻⁴ Recent results evidencing induced PECD from a chiral complexing agent to an achiral chromophore will be discussed.

Both examples illustrate the influence of hydrogen bond formation and solvation on the chiroptical response and will be discussed in terms of locality or non-locality of the observed signals.

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