Hydrophobic hydration: water structure and dynamics as probed by Extended Depolarized Light Scattering (EDLS) and Raman spectroscopy

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The study of the molecular organization and structural dynamics of water around hydrophobic groups (hydrophobic hydration) is crucial to reach a molecular-based understanding of hydrophobic interactions, which are relevant in a wide variety of biochemical and biophysical phenomena occurring in the aqueous medium [1]. Despite the huge number of investigations on the subject, fundamental issues are still strongly debated, even for relatively simple molecular compounds.

Extended depolarized light scattering (EDLS) experiments were proven suitable to gain relevant insights on the molecular dynamics in aqueous solutions of biomolecules of different nature and complexity [2-7]. Using this approach - developed at the University of Perugia - the dynamical susceptibility is measured over a broad frequency range from 0.01 to 1200 cm^{-1} (from 0.3 GHz to 40 THz), by the combined use of a double monochromator and a multipass Fabry-Perrot interferometer. The method provides quantitative information on the molecular mobility of both solute and solvent in dynamical ranges going from fractions to hundreds of picoseconds [2-7].

Here, the fundamental aspects of the EDLS technique will be introduced, emphasizing the nature of the probed physical quantities, in connection with the observed spectral profiles and their analysis. Then, the results obtained by EDLS for the two biorelevant solutes, tert-butyl alcohol (TBA) and trimethylamine N-oxide (TMAO), will be illustrated and discussed [4,5]. TBA and TMAO are water-soluble small polar molecules with rather similar shape and volume. Despite their similarities, TBA is a denaturant that decreases the thermal stability of globular proteins, whereas TMAO stabilizes their native state [8]. Since a large fraction of their solvent-exposed surface area is related to the presence of three methyl groups, these molecules were often employed as simple models to study of hydrophobic hydration and interactions.

Finally, the dynamical picture obtained by EDLS will be discussed in connection with the structural information derived by analysis of the OH stretching signal in the IR and Raman spectrum. In this respect, a method was developed by Ben-Amotz and co-workers to extract the so-called solute-correlated (SC) spectrum, which contains specific features related to the organization of water in the solute hydration shell [9,10]. Inspired by this approach, we carried out a related analysis based on a direct subtraction procedure, as a simple way to obtain quantitative information about hydration features, including hydration numbers, aggregation effects and H-bond energy.

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