ON THE ICE-LIKE MODEL OF STRUCTURED WATER: A SPECTROSCOPIC ANALYSIS FROM QUANTUM-CHEMICAL COMPUTATIONS

Roca-Sanjuán D., Segarra-Martí J., and Merchán M.

Universitat de València, Instituto de Ciencia Molecular, P. O. Box 22805, ES-46071 València, Spain. E-mail: Daniel.Roca@uv.es, Manuela.Merchan@uv.es

Water structuring has been related experimentally to the intriguing feature around ~270 nm reported for the absorption spectrum of water [1]. A hexagonal ice-like arrangement of water molecules has been recently suggested as the most appealing model capable of fitting the experimental data [1, 2]. In the present contribution, we identify the basic molecular unit (BMU) of the model as the negatively charged radical species \([\text{H}_{19}\text{O}_{10}]^-\) formed by two fused water hexagons. On the basis of accurate complete active space second-order perturbation theory (CASPT2) computations [3, 4], the \(\pi\)-stacked dimer of BMUs, \(\text{H}_{38}\text{O}_{20}\), is shown to have an electronic transition \(1\text{A}_g \rightarrow 2\text{B}_{1u}\) of \(\pi\) character predicted vertically at 4.58 eV (271 nm), with a computed oscillator strength of 0.29, in agreement with the experimental band maximum [1]. Hence, the ability to build \(\pi\)-stacked aggregates under certain conditions is reinforced as the key to understand at the molecular level the intricacies of structured water [5]. In addition, since the DNA/RNA nucleobases and amino acids with aromatic rings absorb in the 270 nm region, they may easily resonate with \(\pi\)-stacked water. Therefore, certain characteristics such as the photostability properties of the genetic-code material, which are generally ascribed to the own intrinsic properties of the molecular system [6, 7], might also be intimately united to the presence \textit{in vivo} of \(\pi\)-stacked water.