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On the hexagonal ice-like model of structured water: Theoretical analysis of the low-lying excited states

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ABSTRACT

The *basic molecular unit* (**BMU**) of the hexameric ice-like model has been identified as the negatively charged radical species $[H_{19}O_{10}]^{\cdot-}$. On the basis of high-level *ab initio* computations, by means of using the CASPT2 methodology, the low-lying excited states of **BMU** and its π-stacked dimer are analysed. It is concluded that the **BMU** constitutes certainly a versatile unit having two spectroscopic features in the near infrared region, two in the visible range and two in the near ultraviolet zone. The main absorption feature is found however for the π-stacked dimer formed by two **BMUs**, the $H_{38}O_{20}$ system, which has a pronounced stabilization in the ground state with respect to the isolated **BMUs**. Most of the states of the π-stacked dimer, including the ground state, have a marked biradical character. In all the cases, the one- and two-electron promotions are located on the central O–H–O subunits of the fused hexagons. A total of twelve singlet → singlet electronic transitions have been computed for the $H_{38}O_{20}$ system, seven in the visible range and five in the near ultraviolet region. In the latter, the electronic transition $1^1A_g \rightarrow 2^1B_{1u}$ of π character is predicted at 4.58 eV (271 nm), with a computed oscillator strength of 0.29, in agreement with the experimental band maximum recorded at ∼270 nm (4.59 eV). The ability of water to build π-stacked aggregates under certain conditions is reinforced as the key feature to understand at the molecular level the intricacies of structured water.

1. Introduction

Structured water, also known as ordered water, has a number of distinct features as compared to bulk water [1–10]. Evidence that surfaces impact nearby water has been shown by using different experimental techniques, such as absorption spectroscopy [3], infrared absorption and emission [11], nuclear magnetic resonance [9], as well as from viscosity determinations [12], and optical measurements [13,14]. On the other hand, a number of structured layers are also clearly identified in carbon nanotubes containing water [15,16]. We shall focus in the present theoretical contribution on the absorption spectroscopy intrinsic to the presence of structured water.

The ∼4.59 eV absorption has been revealed to be a unique spectroscopic characteristic of water in contact with various charged systems. In fact, the absorption spectrum of structured water is characterized experimentally by a well-defined band maximum peaking at ∼270 nm (4.59 eV) in solutions of different substances and generic hydrophilic surfaces: salts, L-lysine, D-alanine, D-glucose and sucrose, similarly to that recorded in the "exclusion zone" EZ (solute-free) by using a Nafion 117 solution/film [3]. In addition, when ice melts, a transient 270-nm absorption has also been identified, which eventually leads to bulk water [17]. On the basis of high-level *ab initio* computations, we have recently reported that the spectroscopic absorption observed experimentally at ∼4.59 eV can be rationalized at the molecular level in terms of two π-stacked water molecules [18], which as far as we know, constitutes a completely novel concept within this context. Nevertheless, that simple scheme does not take into account the experimental fact that in the aqueous "exclusion zone" a local charge separation between the EZ and the regions beyond does exist, being the latter with abundant protons [15,19]. In this sense, the hexagonal ice-like model recently suggested by Pollack and co-workers looks much more appealing [1,17]. The multi-layer honeycomb-model proposed is consistent with the experimental evidence repeatedly offered by different labs leading essentially to the same conclusion: when water absorbs light, the absorbed energy builds structural order and drives charge separation [1,15]. Of the evidence showing hexagonality, it is worth noting that water hexamers have been observed next to diverse surfaces, including metals [20,21], protein subunits [22] and graphene [16,23]. Near-surface hexamers have also been found in

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supercooled water [24]. Therefore, the hexagonal ice-like model for structured water is largely supported experimentally.

A detailed analysis of the hexameric model for structured water at the molecular level may hopefully provide additional insights into the underlying properties responsible for the spectroscopic feature observed at ~270 nm, which serves indeed as a fingerprint to identify the presence of structured water. Within that spirit the present contribution is offered. As discussed in detail below, predictive high-level *ab initio* results fully support the presence of such a spectroscopic peak in the π-stacked system built from the most plausible *basic molecular unit* (**BMU** hereafter) of the hexagonal ice-like model, here identified as the negatively charged radical $[H_{19}O_{10}]^{\cdot -}$. Knowledge provided on theoretical grounds may be potentially relevant in the realms of biology, life-sciences and nanotechnology, where undoubtedly ordered water plays a fundamental role [1,21].

2. Computational details

Ground-state geometry optimisations for the **BMU** system and its π-stacked dimer have been performed at the MP2 level through the program GAUSSIAN 09 [25]. At the equilibrium structures so obtained, the corresponding vertical electronic transitions have been subsequently computed by using the CASPT2 approach [26,27], a well-established *ab initio* methodology especially suited for that purpose [26–31], as implemented in the MOLCAS-7 software package [32]. The basis set 6-31G** has been used throughout, as a compromise between accuracy and computational resources [26–31,33,34].

Multiconfigurational wave functions have been initially determined at the CASSCF level. In order to have enough flexibility in the employed wave functions to describe the low-lying excited states up to 5 eV, especial attention has been paid to the selection of the active space that has been based on a systematic number of calibration computations. For the **BMU** system, the active space comprises 13 electrons distributed in 12 active orbitals, hereafter denoted as the CASSCF(13,12). Accordingly, the respective results including electron dynamic correlation at the second-order level will be named as CASPT2(13,12). For the π-stacked dimer, the CASSCF(12,15) wave function has been used, where the second-order findings will be coined as CASPT2(12,15). The CASSCF and CASPT2 computations have been carried out within D_{2h} symmetry. Details on the wave functions will be next given as appropriate. The oxygen 1s electrons have been kept frozen in the perturbation step. In order to minimize weakly interacting intruder states, the imaginary level-shift technique, with a value of 0.2 au, has been employed. The CASPT2 method with the zeroth-order Hamiltonian as originally implemented has been used [35].

3. Results and discussion

The results are presented in three sections. Firstly, the hexameric model is introduced. Secondly, determination of the ground-state structure and the low-lying vertical excited states for the basic molecular unit, the negatively charged radical species $[H_{19}O_{10}]^{\cdot -}$ formed by two fused hexagons, is considered. Thirdly, the interaction of the π-stacked dimer constituted by two basic molecular units is analysed, both for the ground and excited states.

3.1. On the hexagonal multi-layer model

The hexagonal ice-like multi-layer model of structured water is formed by a network of fused hexagonal units [1,36]. An illustrative scheme of the model is shown in Fig. 1.

The net charge of the six-hexagon structural diagram drawn in Fig. 1 is −5. It can be easily checked that, in general, for N-fused hexagons, the charge acquired by the global system is 1-N [36]. Therefore, for the hexagonal water model, the *basic molecular unit* corresponds to the negatively charged radical species $[H_{19}O_{10}]^{\cdot -}$ constituted by two-fused hexagons, denoted above as **BMU**. In order to fulfil the empirical formula $(H_2O)_n$, for each couple of fused hexagons built, a proton is assumed to be released, which is consistent with the local charge separation observed between the EZs and the regions beyond observed by Chai et al. [19] using pH measurements. As stated in the introduction, water next to many surfaces is evidently hexagonal [21], which agrees with the proposed model. It is however worth noting that the hexagonal model proposed here is different from previous suggestions [1,36], although the three proposals emphasize that the planes themselves are negatively charged. In 1969, Lippincot et al. [36] suggested the hexagonal model of water in the generic form depicted in Fig. 1, assuming that an appropriate number of hydronium ions, protons or tetra-coordinate hydrogen-bonded oxygen atoms would be required to maintain the empirical formula $(H_2O)_n$. A year later, Allen and Kollman [37] supported the "anomalous water" by quantum-mechanical calculations concluding that a cyclic, symmetrically bonded form of water and related species have stabilities comparable to the liquid. On the other hand, in the Pollack's model [1], proposed forty-four years later, the net charge of the hexagon is −1, which corresponds to the infinite lattice. In our proposal, two-fused hexagons, the **BMU** system, bear the negative charge. Of course, as larger becomes the number of fused hexagons considered (N), the charge per hexagon (1-N)/N gets closer to −1. As shall see below, the π-stacking of two **BMUs** leads already to the characteristic spectroscopic fingerprint of structured water. The two protons (one for each **BMU** considered) required to fulfil the empirical formula $(H_2O)_n$ are not directly involved in the model. It would be interesting to actually verify whether the larger number of $[H_{19}O_{10}]^{\cdot -}$ plus H^+ systems potentially generated by light irradiation is consistent with the experimental evidence of the growing size of the EZ region in relation to the decrease of pH measurements just beyond it, as it seems to be the case [19]. It is anticipated that the electronic transitions of the π-stacked **BMU** dimer are locally centred in the central O–H–O subunits, being responsible for the unique spectroscopic signature of structured water. According to the conclusions derived from the present computational research, the O–H–O subunit is essentially the key to understand the spectroscopic and photochemical properties of ordered water.

3.2. The low-lying excited states of the basic molecular unit

The ground-state equilibrium geometry obtained for the **BMU** system at the MP2(UHF)/6-31G** level is shown in Fig. 2. As

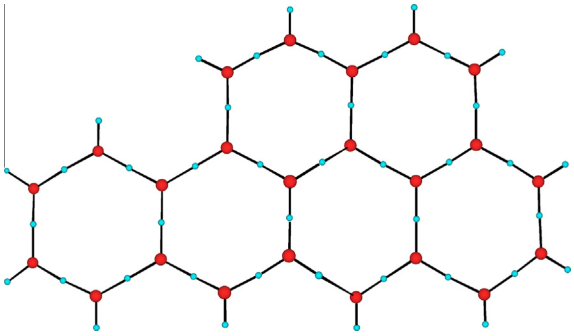

Fig. 1. Scheme for the ice-like multi-layer model of structured water formed by hexagonal units. The system is negatively charged (see text).

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