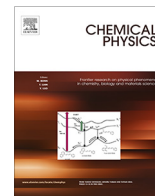




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The Lord Armstrong's experiment in the view of band theory of liquid water

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ABSTRACT

Liquid water considered in the band theory differs from the ice by localization of electrons in “tails” of the allowed energy bands separated by the wide band gap which defines electrochemical properties of water by means of the allowed energy levels above the middle of the band gap, $\epsilon_{\text{H}_2\text{O}}$, as electronic donors and below, ϵ_{OH} , as their acceptors. The population of electrons $[\text{H}_3\text{O}]/[\text{H}_3\text{O}^+]$ and holes $[\text{OH}]/[\text{OH}^-]$ on these levels depends on Fermi level in the band gap. This variable electrochemical potential (as a p-n boundary between the vacant impurity levels and the ones occupied by electrons) becomes the tool for changing physical and chemical properties of liquid water. It turned out that a noticeable shift of Fermi level (more than 1 eV) is possible in the band gap at the expense of an insignificant ($|z| < 10^{-10}$) deviation of the water composition H_2O_{1-z} from the stoichiometric water, H_2O . This deviation is easily homogenized in the bulk liquid. Then, one can introduce into pure water a negative charge $[\text{H}_3\text{O} + \text{OH}^-] \sim 10^{-7}$ M or the positive one $[\text{H}_3\text{O}^+ + \text{OH}] \sim 10^{-7}$ M by shifting Fermi level up to the donor or acceptor levels in the band gap. These charged molecular pairs $(\text{H}_2\text{O})_2^-$ and $(\text{H}_2\text{O})_2^+$ organize the two-way “traffic” in the aqueous “floating bridge” between two glass beakers with the pure liquid water under action of the high dc voltage in the Lord Armstrong's experiment.

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1. Introduction

In 1893, Lord Armstrong has demonstrated out the experiment with a cotton thread between two wine glasses filled with chemically pure water. When he has applied a high dc voltage to platinum electrodes in these wine glasses, the cotton thread has turned out in one of them by forming the stable water bridge between them when they are moved from each other. This bridge has consisted of two oppositely-charged and equal oppositely-directional water flows [1]. This experiment is described in details in the review [2].

An investigation of this phenomenon has not been carried out more the century up to the online experiment [3] which has been described in the article [4] and has been advertised by the Nature [5] later. The following publications [2,6–13] are considered as a first step in the explanation of this phenomenon.

At the same time, the effects of high voltage on dielectric liquids are studied a long ago from different points of view: classical physics and electrophoresis, electro-wetting and electro-spray, quantum physics and even quantum electro-dynamics. Moreover, one should note that the Lord Armstrong's phenomenon works

not only in water, it works in different molecular liquid dielectrics, for example, methanol [2,4].

The most outstanding feature of the floating bridge (between two glass beakers filled with pure water) is the geometric stability in spite of two water flows in opposite directions. The article [9] shows that the forces responsible for holding up the water bridge are formed by the strong electric field in liquid dielectric with the low concentration of charged particles ($[\text{H}_3\text{O}^+] \sim [\text{OH}^-] \sim 10^{-7}$ M). Therefore, just the pure water is needed for providing these dielectric effects [4]. However the explanations in [12] of experimentally found features (the oppositely-charged and equal oppositely-directional water flows as well as the double helix of these flows [4,11]) are doubtful.

The author's interpretation of the additional experimental results [14–16] only confirms such conclusion. As he asserts [15], the water bridges with currents of ~ 0.5 mA can be sustained for hours without the essential change of water quality in the glass beakers. Therefore the concept of only the proton transfer [14] from the anode beaker into the cathode one not stands up. In this symmetric task, one should suggest an “antiproton” (negative particle with equal mass) transfer from the cathode beaker into the anode one because the excess charge (positive or negative)

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and liquid mass remain stable in the beakers during for several hours in these experiments [16].

Taking into account only ions in liquid water [17], the charged transport is to be accompanied by its electrolysis. However the fact that this process can be absent when the electric current through the floating water bridge is small raise the question once again about the nature of the charged and mass flows in such system [4].

Thus, this matter should be the subject of further investigations including the check-up of suggestion [4,11,14] and a simpler explanation of this phenomenon because the X-ray diffraction experiments performed on a series of water bridges showed no anisotropic properties of liquid water [18]. It proves that water molecules and the proton transfer do not have any significant preferred orientation along the electric field. In the present work, we are using the electronic band theory of liquid dielectrics [19] for clearing these issues without application of quantum-electrohydrodynamic theory of water [11] and the proton band model [14–16].

2. The band structure of liquid water

The pure liquid water is recognized as the amorphous dielectric [19] with the wide band gap of ~ 6.9 eV and the work function of water equal to 6.45 eV [20,21]. Here it is important to note that the authors of the work [22] mistake the electron affinity of water (a statistical magnitude) with the bottom of conduction band which should be defined by the energy of solvated electron.

We have shown in [23] that band gap of liquid water contains the allowed local energy levels like the impurity levels in a solid dielectric. The molecular bearers of these electronic levels are inherent species in liquid water as the occupied-by-electron hydroxyl, OH^- , and the vacant hydroxonium ion, H_3O^+ , that is obtained by the chemical reaction of dissociation [24]:



when their mole concentrations $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ satisfy the ratio [25]

$$[\text{H}_3\text{O}^+] \cdot [\text{OH}^-] = K_w \quad (2)$$

with the dissociation constant $K_w = 10^{-14} \text{ M}^2$ at $T = 298 \text{ K}$.

These ions are associated with the vacant electron level, $\varepsilon_{\text{H}_3\text{O}^+}$, and the one, $\varepsilon_{\text{OH}^-}$, occupied by electron. They lie symmetrically to the band-gap middle which is Fermi level, ε_{Fs} , of stoichiometric water, H_2O , as shown in Fig. 1a [23].

One can see that Fermi level, $\varepsilon_{\text{F}(6)}$, in hypo-stoichiometric water (H_2O_{1-z} , $z > 0$) is defined by the electron population of the donor level, $\varepsilon_{\text{H}_3\text{O}}$, as the concentration, $[\text{H}_3\text{O}] = \sqrt{K_{\text{H}_2}[\text{H}_2]}$, where K_{H_2} is the constant of H_2 dissociation in water for forming hydroxonium radical, H_3O , as hydrated hydrogen atom, $\text{H} \cdot \text{H}_2\text{O}$, by reaction



Fermi level, $\varepsilon_{\text{F}(7)}$, in hyper-stoichiometric water ($z < 0$) is defined by a hole population of the acceptor level, ε_{OH} , as the hydroxyl concentration, $[\text{OH}] = \sqrt{K_{\text{H}_2\text{O}_2} \sqrt{K_{\text{O}_2} [\text{O}_2]}}$, where K_{O_2} and $K_{\text{H}_2\text{O}_2}$ are the constants of O_2 dissociation in water with forming hydrated oxygen atom, $\text{O} \cdot \text{H}_2\text{O}$ and the dissociation of hydrogen peroxide H_2O_2 :



The electrochemical states of liquid water in Fig. 1b with Fermi levels: $\varepsilon_{\text{F}(6)}$ and $\varepsilon_{\text{F}(7)}$, are realized by the standard reactions [24]:

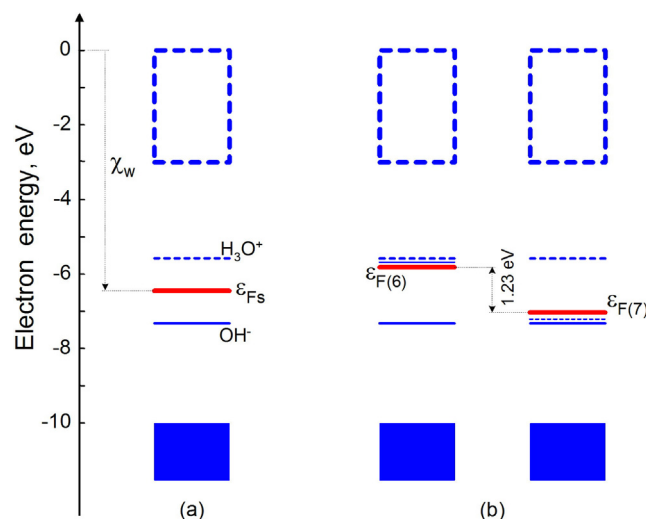
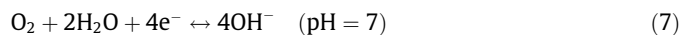
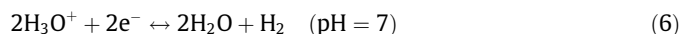


Fig. 1. The band structure of liquid water for the stoichiometric state (a) with Fermi level, ε_{Fs} , in the middle of band gap and for the non-stoichiometric ones (b) with Fermi levels, $\varepsilon_{\text{F}(6)}$ and $\varepsilon_{\text{F}(7)}$, as confines of water stability defined by reactions (6) and (7); the blue full lines denote energy levels $\varepsilon_{\text{H}_3\text{O}}$ and ε_{OH} occupied by electrons as hydroxide ion, OH^- , and hydroxonium radical, H_3O ; the blue dotted lines are the vacant levels of hydroxonium ion, H_3O^+ , and hydroxyl, OH ; χ_w is the work function of liquid water equal to 6.45 eV [21].



at conditions: $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 10^{-7} \text{ M}$, $K_{\text{H}_2} \sim 2 \cdot 10^{-19} \text{ M}$, $K_{\text{O}_2} \sim 6 \cdot 10^{-33} \text{ M}$, and $K_{\text{H}_2\text{O}_2} \sim 6 \cdot 10^{-7} \text{ M}$, $[\text{H}_2] = 1.6 \cdot 10^{-3} \text{ M}$, $[\text{O}_2] = 2.7 \cdot 10^{-4} \text{ M}$, $P_{\text{H}_2} = P_{\text{O}_2} = 1 \text{ atm}$, $T = 298 \text{ K}$ [26].

Then, we find $[\text{H}_3\text{O}] \sim 2 \cdot 10^{-11} \text{ M}$ for the reaction (6) and $[\text{OH}] \sim 8 \cdot 10^{-13} \text{ M}$ for (7), i.e. the electron level, $\varepsilon_{\text{H}_3\text{O}}$, is mostly vacant as hydroxonium ions, H_3O^+ , due to $\varepsilon_{\text{F}(6)}$ is below $\varepsilon_{\text{H}_3\text{O}}$ (see Fig. 1b, left) and the energy level, ε_{OH} , is fully occupied by electrons as hydroxide ions since this Fermi level is essentially above ε_{OH} . Fermi level, $\varepsilon_{\text{F}(7)}$, is slightly above the electron level, ε_{OH} . Therefore it contains holes (the thin blue dotted line in Fig. 1b, right) as hydroxyls (OH) but the energy level, $\varepsilon_{\text{H}_3\text{O}}$, is fully vacant as hydroxonium ions, H_3O^+ , since $\varepsilon_{\text{F}(7)}$ is essentially below $\varepsilon_{\text{H}_3\text{O}}$. The forcedly shifted Fermi level, ε_{F} , in the band gap of liquid water is determined rigorously by the proportions of concentrations: $[\text{H}_3\text{O}^+]/[\text{H}_3\text{O}]$ and $[\text{OH}]/[\text{OH}^-]$, of the vacant species (H_3O^+ , OH) and the occupied-by-electrons ones (H_3O , OH^-) with the energy levels, $\varepsilon_{\text{H}_3\text{O}}$ and ε_{OH} , in the band gap of liquid water. These proportions are given by Fermi–Dirac statistics which can be simplified to Maxwell–Boltzmann distribution of electrons and holes in the corresponding energy levels [27] where k_B is Boltzmann constant

$$[\text{H}_3\text{O}^+]/[\text{H}_3\text{O}] = \exp[(\varepsilon_{\text{H}_3\text{O}} - \varepsilon_{\text{F}})/k_B T] \quad (8)$$

$$[\text{OH}]/[\text{OH}^-] = \exp[(\varepsilon_{\text{OH}} - \varepsilon_{\text{F}})/k_B T] \quad (9)$$

From this and the chemical stability of liquid water: $\varepsilon_{\text{F}(6)} - \varepsilon_{\text{F}(7)} = 1.23 \text{ eV}$ [24], we have found in [23]: $\varepsilon_{\text{H}_3\text{O}} - \varepsilon_{\text{OH}} = 1.75 \text{ eV}$. Then, the electron levels of inherent water constituents are

$$\varepsilon_{\text{H}_3\text{O}} = -\chi_w + 0.875 \text{ eV} = -5.575 \text{ eV} \quad (10)$$

$$\varepsilon_{\text{OH}} = -\chi_w - 0.875 \text{ eV} = -7.325 \text{ eV} \quad (11)$$

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