The water/vapor interface is neutral with acidic surface and basic subsurface

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In our Invited Article[1] we highlighted the present controversy concerning the ionic composition of the surface of pure water. Namely, we discussed four possible scenarios for neat water: i) ion-free surface, ii) acidic surface, iii) basic surface, or iv) a combination of ii) and iii). The first picture is in accord with the traditional view of aqueous surfaces due to Onsager,[2] but it is not supported by modern simulations[3,4] or experiments.[5,6] The second option emerged from computational studies showing surface enhancement of H_3O^+ in aqueous clusters and slabs,[7-12] while no appreciable surface accumulation of OH^- was observed.[11,12] As is clear from the above references, we have neither been the only ones nor the first ones to predict surface propensity of hydronium; our primary goal has been to address and quantify the surface behavior of the complete ionic product of water. This picture of the surface is thus supported by a range of computational approaches (molecular dynamics with empirical and non-empirical force fields, effective valence bond method, and ab initio calculations), as well as by surface selective spectroscopies[5,6,13] and surface tension measurements.[14] The third possibility, advocated in the Comment, is supported by zeta-potential,[15] titration,[16,17] and disjoining pressure measurements,[18] which are interpreted in terms of surface adsorption of hydroxide. The last scenario, first suggested in our Invited Article[1] is discussed in more detail below.

For sake of clarity of the present discussion it is important to define several crucial terms. By surface we understand the topmost monomolecular layer of water molecules, while the water/vapor interface is the whole water region the properties of which differ from those in the bulk. The interface minus the surface is then denoted as subsurface which, depending somewhat on the property under scrutiny, is typically (sub)nanometer thick or wider. We denote a layer in the interface acidic (or basic) if the

concentration of hydronium there exceeds that of hydroxide (or *vice versa*).

Our view of the water/vapor interface (employing the above definitions) is schematically depicted in Figure 1. Here, the system is split into four layers – the bulk phase, water/vapour interface with subsurface and surface parts, and the vapour phase. The vapor phase is for all purpose ion-free due to the vanishing vapour pressure of ions. The bulk phase of neat water with pH = 7 is neutral and so is the interface as a whole (interface neutrality condition). We predict that the surface layer, i.e., the topmost water monolayer, is acidic - enriched by hydronium but depleted in hydroxide. Due to interfacial neutrality, the subsurface layer (the thickness of which is less precisely defined but clearly larger than that of the surface layer) must be then basic, i.e., enriched by OH^- and depleted in H_3O^+.

In the Comment the criticism toward our work is threefold. To the first point – most of the experimental evidence for surface enrichment of hydronium but not of hydroxide is indeed coming from relatively concentrated electrolytes. However, the picture persists over a broad concentration range. Moreover, surface selective spectroscopic experiments in neat water and very dilute (millimolar) electrolytes do not show enhancement of OH^-.[19,20] Second, it is a fact that it is technically impossible to simulate using molecular dynamics a single hydronium and hydroxide in $\sim 6 \cdot 10^8$ water molecules, corresponding to pH = 7. But, as in the spectroscopic experiments, the computational results are only weakly dependent on concentration and hold firm also for a single ion or ion pair in an aqueous slab or cluster, which is the best computational proxy to "infinite dilution". In addition, qualitatively similar results are obtained both from empirical force field simulations emplying relatively large slabs (~1000 water molecules) and nanosecond timescales and ab initio molecular dynamics for smaller

systems (~100 waters) and picosecond simulation times. The third point is a follow up of the second one. Unless a qualitatively new physics (beyond a gradual increase of the Debye-Huckel screening length) appears upon moving from a single ion or ion pair in ~100-1000 water molecules, typical in the calculations, to experimental ion dilutions in pure water the computational predictions hold. There can, of course, be quantitative changes but they should not alter the essential picture.

In an analogous way as in the Comment, one could speculate here about possible problems, namely with the interpretation of the macroscopic experiments which only indirectly infer the molecular character of the negative surface charge. For example, anionic surface active impurities or even electrons might confuse the interpretation. Also, titration experiments are not performed in pure water but in the presence of a buffer, moreover kinetic effects (such as stirring or motion of oil droplets and bubbles) may affect the measured pH.[21] Additionally, should OH^- strongly adsorb to water surface it sems counter-intuitive that polycation layers behave in contact with water more hydrophobically than polyanion ones.[22]

In summary, we attempted in our Invited Article[1] not only to present the computational and experimental results concerning the ionic composition of the water/vapor interface but also reconcile at least partially the conflicting views, in a way depicted here in Figure 1. A good part of the controversy might stem from "blindly touching the elephant from different sides." Namely, due to the neutrality of the whole interface, techniques scrutinizing it from the vapor side can see it as acidic, while approaching it from the aqueous bulk side it will appear as basic. Clearly, more work has to be done to fully resolve the existing controversy. On the computational side, larger systems should be studied without loosing atomistic resolution and accuracy in

the description of interactions. On the experimental side, it is imperative to establish

unambiguously the chemical nature of the observed charged species and the exact

region of the interface being probed.

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Figure captions

Fig. 1: A schematic picture of the distribution of hydronium and hydroxide ions across the water/vapor interface.

Figure 1: