

----- Original Message -----

Subject: RE: PNAS publication "Water surface is acidic" (ms. no. 2006-11285)

From: "Salsbury, Daniel" <DSalsbur@nas.edu>

Date: Tue, June 12, 2007 4:51 pm

To: pavel.jungwirth@marge.uochb.cas.cz

Dr. Jungwirth,

The Editorial Board has considered your response to the Reader's comments. The Board finds your comments satisfactory and does not require any additional statements or changes to the paper. We appreciate you providing a prompt and detailed response.

Sincerely,

Daniel Salsbury

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Dear Dr. Salsbury,

Thank you for your e-mail and attached comment from the Reader of our PNAS article. We appreciate that our paper caught the attention of the Reader to the extent that he/she wrote such a detailed commentary. In general, the Reader seems to be less concerned about the scientific content of our work (and appears to have skipped significant parts of it) than about originality of our results and relation to previous literature.

Let us first note that the Reader seems to have overlooked that half of our PNAS paper is experimental with original spectroscopic results supporting the computational claims. New experimental data are presented showing enhanced proton activity at ice nanocrystal surfaces, as compared to the interior, as reflected by isotopic exchange. These results support the notion of proton surface preference for ice particles, in addition to water clusters and liquid. The structural connection between the three types of systems is due to the fact that ice nanocrystals have disordered surfaces. We have brought these systems into the argument for the first time.

Concerning the computational part of our paper the response is as follows: The title of our paper is "Water surface is acidic" which conveys our basic message that at the surface the concentration of hydronium ions is higher than that of hydroxide. None of the papers the reader mentions, no matter how pioneering and important they may be, deals with hydroxide ions, so in principle these could not have fully addressed the key issue of our paper. In other

words, for water surface to be acidic it is not enough to show that hydronium ions accumulate at the surface (as done previously by several groups including ours). One has to also demonstrate that hydroxide does not do the same, and we were the first to show and quantify in terms of surface pH and pOH this behavior of the ionic product of water. The conclusion reached in our paper is highly non-trivial; as a matter of fact a significant part of the colloid science community is still convinced that actually hydroxide accumulates at the surface more than hydronium and they claim that water surface is basic (Refs. 11-12 discussed in the Introduction and Conclusions of our PNAS paper).

Below we deal in more detail with the 8 points raised by the reader:

1. The paper the reader mentions is an important and pioneering one, therefore, we chose to cite it as a representative publication from the group of Voth on the topic of surface solvation of protons. As we mention in our paper it shows that protons have a propensity for the surface, however, it does not deal with the hydroxide ions and does not provide a quantitative estimate of the surface acidity. As stated clearly in our paper, proton surface propensity in the liquid phase is not presented as a *conclusion* of our present article, but as a *result of past literature*.
2. We are aware of the other papers related to Voth et al. work, but due to limited space we had to make a selection of papers we cited so that all key groups working on this subject are represented.
3. Again, saying that proton has a surface propensity and quantifying the surface acidity are two different things. We fairly discuss previous studies (including ours) on the former subject in the introduction to our PNAS paper. The fact that Voth et al. article was published before Mucha et al. article is quite clear from the citation list, in which the Voth article is cited first, and the years of publication are (evidently) noted.
4. Again, as stated in point 2, we do cite the important paper by Petersen et al. but we have to be fair also to other researchers involved in this field. Concerning citation of Ref. (7) in connection with n=20-21 cluster – this was in fact our inaccuracy, as Ref. (7) addresses a cluster with 1000 molecules. Our apologies to the author; however, we seriously doubt that other readers will ponder over this to the extent suggested by this Reader.
5. Both the methodology and the systems in the paper of Iyengar et al. are different from ours. We have both hydronium and hydroxide present and we combine BLYP and B3LYP DFT functionals to obtain primarily enthalpic information with classical

molecular dynamics, which is used primarily for the entropic data. For completeness, here is a summary of calculations which we did carry out, and which, as far as we know, are new: (a) on-the-fly simulation of zwitterionic slab and bulk systems which include both proton and hydroxide; (b) exhaustive search for low energy minima of a protonated cluster with 48 water molecules, with the objective to evaluate energy difference between the lowest minima with the proton at the surface, and in the interior; (c) evaluation of free energy difference between the surface and the bulk states, for a realistic slab geometry, for protonated water in the hydronium and Zundel states, and for the hydroxide.

6. Concerning this point, may we propose the Reader to re-read the pertinent section of the article? Contrary to his claim, we actually do have both hydronium and hydroxide ions in our on-the-fly simulation, and we do observe recombination in the course of the simulation. As for the concentration problem – as in all on-the-fly studies, including the ones of Voth et al., the model system is of finite size due to computational limitations. Nevertheless the model is a reasonable representation of the two ions (the protonated water cation and the hydroxide) in water prior to recombination.
7. Within the ab initio molecular dynamics, which we performed in the first part of the computational work, hydronium and hydroxide can and actually do perform the Grotthuss shuffling and recombination. The empirical potential studies used to generate Fig. 2 addressed a thermodynamic quantity – the free energy difference ΔG for transfer of either the cation or the anion from the bulk to the surface. Two extreme forms of the cation (Zundel and hydronium) were examined. While inclusion of proton transfer in the simulation is crucial for studying proton dynamics, it is less important for sampling the solvation structures in the bulk and at the surface, as was done in the free energy simulations.
8. As stated above, the principal conclusion of our paper is that the water surface is acidic, i.e., there is more hydronium than hydroxide ions. We attempted to quantify this in terms of ΔG , and surface pH and pOH. The use of ΔG is undisputable and the use of surface pH and pOH is a straightforward extension of the classical 3D definition to 2D. As for the argument that one could have reached similar conclusion to ours from Ref. (7) alone – first, it was not done and, second, as noted above, it would not actually be possible due to lack of information on the hydroxide.

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Comment on “Water Surface is Acidic”, by V. Buch et al.

The originality of the research contained in the PNAS paper by Buch et al can be questioned for the

following reasons:

(1) The prediction repeatedly stated, e.g., in the title “Water surface is acidic,” in the abstract “However, pH of pure water surface is shown to be significantly lower, the reduction being caused by proton stabilization at the surface,” at the top of page 3 “We thus conclude that the surface of pure water is acidic” was clearly and unequivocally made three years ago and published by Peterson MK, Iyengar SS, Day T J F, Voth GA (2004) *J Phys Chem B* 108:14804. In particular, in the abstract of Petersen et al. it is clearly stated “It was found in our model that the hydrated excess proton displays a marked preference for water liquid/vapor interfaces.” In the conclusions (next to last sentence), it is further stated “Our simulations would also seem to suggest the existence of a negative pH gradient toward the water liquid/vapor interface.” Figure 1 of Petersen et al provides quantitative evidence to support this prediction, while Fig. 2 and the related discussion in the text depicts the physical reasons for the effect. These are all exactly the same conclusions as stated by Buch et al. now three years later.

(2) The finding of Petersen et al. published in 2004 is well known and widely recognized. It is even now described in review articles (e.g., Voth GA (2006) *Acc. Chem. Res.* 39:143; Swanson et al, (2007) *J. Phys. Chem. B* 111: 4300; Peterson PB, Saykally RJ (2006) *Annu Rev Phys Chem* 57:333).

(3) One may also look to the description by others of the work of Petersen et al in order to validate the historical discussion above. For example, the (uncited) work of Pegram and Record (2006) *PNAS* 103:14278, states on p. 14280 of their article “At the level of individual ions, our finding that the proton has an enhanced surface concentration relative to the bulk ($K_p = 1.5$) is consistent with the results of a recent molecular dynamics simulation in which a single hydronium ion (with a chloride counterion) was allowed to migrate through a water slab in a manner consistent with the Grothuss mechanism of proton transfer (32). The authors observed preferential distribution of the solvated proton at the air-water interface, which they attributed to the asymmetric hydrogen bonding of the ion. Other simulations of more concentrated acidic solutions also indicate that the proton is moderately accumulated at the surface (13).” Here, ref. 32 is Petersen et al, published in 2004, while ref. 13 is Mucha, et al., (ref. 8 of Buch et al.), published one year later in 2005. Mucha et al cite the Petersen et al work in their paper so they were clearly already aware of it even in 2005.

(4) The key paper described above by Petersen et al is only cited in passing by Buch et al. (their ref. 7) and it is never discussed. Instead, it is wrongly referred to at the end of page 2 along with ref. 6, which concerns results on largely unrelated small protonated water clusters. Here the Buch et al. say “This energy preference for surface structures is consistent with the values obtained by other authors (6, 7) for smaller $(\text{H}_2\text{O})_{n-20,21}\text{H}^+$ clusters, which, however, acquire a rather special cage-like geometry.” The reader is therefore lead to believe that ref. 7 is about small protonated water clusters when in fact it contains essentially the same simulations and exactly the same conclusions as Buch et al. In another example, the explanation for the surface stabilization of hydronium (acid) given in the last paragraph of the introduction of Buch et al. is improperly attributed to the authors of ref. 10, but this important explanation originates with Petersen et al. (ref 7). In fact, one can actually read ref. 10 and there it is stated from the figure caption of their fig. 7: “Surface hydrogen bonding network predicted by Voth and co-workers.”²

(5) Key additional evidence for the surface acidification of water is presented by Buch et al. in the form of *ab initio* molecular dynamics computer simulations of protonated water clusters. However, essentially the same (uncited by Buch et al) results were already published two years ago and presented many of the same results and conclusions. See, for example, the paper by Iyengar *et al.*, (2005) *Int. J. Mass Spectrom.* 241:197 in which they used even a higher level of *ab initio* molecular dynamics to explore the dynamics of several water clusters with the same results and very similar analysis. Likewise, the dynamical and structural considerations of larger water clusters were also previously addressed in the (uncited) paper

by Burnham *et al.*, (2006) *J. Chem. Phys.* **124**: 024327 where the hydronium surface enhancement was reported for the protonated 100 water cluster across a range of temperatures, including below cluster freezing.

(6) Buch *et al.* claim to be discussing “pure water”. (Petersen *et al.* describe a dilute acidic solution at 0.055 mole/liter concentration.) The reader is further led to believe that a computer simulation is presented in Buch *et al.* of a hydronium (H_3O^+) cation and hydroxide (OH^-) anion in a water “slab” geometry (compare fig. 2 of Buch *et al.* with fig. 2 of Petersen *et al.*). However, this simulation is *not the real system* and nowhere is this clearly stated in the manuscript. In particular, in their simulation the hydronium and hydroxide do not have the possibility of chemically recombining into a water molecule as they do in Nature. If one included chemical recombination of hydronium and hydroxide into water molecules as actually happens in Nature, the simulation would have to be of an astonishing magnitude. In fact, to reliably simulate the thermodynamics of a pure water system of pH 7, having an interfacial pH gradient to 5 or lower, one would need a slab geometry as shown in fig. 2 of Buch *et al.* with more than 500 *million* water molecules. The empirical simulation of Buch *et al.* is therefore actually a dilute acid solution no different than the simulation presented by Petersen *et al.* (in fact it is of a higher effective acid concentration at 0.13 mole/liter).

(7) Furthermore, the hydronium cation in the empirical simulation of Buch *et al.* cannot participate in the well known Grotthuss shuttling (published first in 1806 and widely celebrated last year) which delocalizes protons and transports them across multiple water molecules via an interchange of hydrogen and chemical bonds. Also, their hydroxide anion does not have the possibility of “inverse” Grotthuss shuttling. Both of these effects occur in Nature and have been shown in ref. 13 of Buch *et al.* to be extremely important in the autoionization and ion recombination process in water. The simulation in fig. 2. of Buch *et al.* is in fact just a classical hydronium cation in a simulation with a model classical anion at a concentration of 0.13 mole/liter. By contrast, the simulation model utilized by Petersen *et al.* *includes Grotthuss shuttling*, so their simulation published three years earlier is considerably more physically accurate than that of Buch *et al.*

(8) It might be argued that Buch *et al.* have provided a “quantitative” result on the “surface pH” of water and that Petersen *et al.* did not do so. However, the pH is a bulk thermodynamic quantity (defined as $\text{pH} = -\log[\text{H}^+]$, where $[\text{H}^+]$ is the 3-dimensional concentration of acid). It has no meaning, and cannot even be defined, as an interfacial quantity. Instead, Petersen *et al.* provided a quantitative *distribution function* that can be related to possible interfacial experimental measurements. While they did not convert this probability function into a free energy difference via the well-known formula $\Delta G(z) = kT \ln P(z)$, it is trivial to do so and the result for the free energy difference between bulk and surface will be the same as estimated by Buch *et al.* (around 2-4 kcal/mole, depending on the treatment of the statistics). The two different ways of plotting the Petersen *et al.* data is essentially no different than plotting data in a regular versus semilogarithmic fashion. Petersen *et al.* have therefore presented essentially the *same quantitative data* three years earlier.