

Reviewer 1: The authors performed DFT MD to investigate the hydrogen bond situation at the water-air interface. The analysis used the Chandler's instantaneous interface definition + his hydrogen bond dynamics description. I found that the paper is not impactful in the community in the following two aspects; 1. no major physical insight. 2. very minor connection with experiment. For example, the hydrogen bond dynamics was investigated much more systematically and more intensively in J. Phys. Chem. Lett. 10, 4914 (2019) and the detailed comparison with experiment has been done, although it does not use the instantaneous liquid interface. I am not sure what is the selling point of the current manuscript, given that such a study has been done. Furthermore, no good connection with the experimental data is provided, despite the fact that some experiments (Ref. 7, Nature Comm. 11, 5344 (2020), J. Chem. Phys. 156, 224701 (2022)).

I do not recommend the editor to accept this manuscript for publication at the present stage. But, a simulation itself seems robust. If the authors can provide very good insight and very good angle for the physics and connection with experiments, the manuscript can be considered as a publication for ChemPhysChem, in my opinion.

Minor comment:

1. Ref. 36 provides the wrong SFG spectra (as is clear from J. Chem. Phys. 143, 124707 (2015) and Chem. Rev. 120, 3633 (2020)) and the number obtained based on the wrong data should not be trusted.
2. To obtain the good agreement with experimental data, a key is the definition of the free O-H. According to J. Chem. Theory Comput. 14, 357 (2018), the hydrogen bond definition the authors use cannot provide the good agreement between the simulation and experiment, because it is not good definition for a free O-H group.

## Report on Paper by Huang and Huang

The authors define a new descriptor based on intermolecular H-Bonds between water molecules in order to ultimately characterize the thickness of the interface of water with the air. The authors claim that this descriptor is parameter-free contrary to previous methods developed in the literature and applied for the same goal of finding the thickness of the air-water interfacial layer. This is an important project as chemical reactions are typically occurring in this specific interfacial layer that has very specific geometry and therefore very specific properties of relevance for chemical reactions.

I do not agree for the publication of this paper in its current form for several reasons, some of them are listed hereafter : 1) the descriptor used by the authors is based on H-bonds which are not parameter free, far from it ; 2) most of the data presented in the paper are already published in the literature without acknowledgements from the authors (citations and discussions in the paper that should compare results to literature) ; 3) the method described in the paper is too complicated to be applied by any group who would be willing to use such method to define an interface of an hydrogen bonded liquid on a routine basis. The Willard and Chandler (WC) definition of the interface based on the density of the liquid is nowadays well established to that end, and well known to be more accurate than the Gibbs dividing surface. The authors have to demonstrate that their method is far superior to the WC definition, including computational cost.

The definitions of H-bonds used by the authors to establish their method and descriptor of the interface are by construction using parameters for the H-bond distance as well as for the H-bond angle. The authors refer to the definitions and parameters of the paper by Luzar and Chandler, the numbers used are parameters chosen by these authors a long time ago, with numerous papers published since this reference paper making critics. The authors thus cannot write that their descriptor is parameter free.

In section II, the authors give 2 tables of values of their descriptors  $k$  and  $k'$  calculated over 2 very different periods of time over their trajectory of the air-water interface. Apart from commenting that these numbers are different, the authors never explain why such differences are obtained and what we should conclude from these differences.

In the same section, the authors define properties to be calculated in order to get the reactive flux. In these definitions, the authors tell us for instance that  $\langle h \rangle = 0$  and can be removed from the definitions because the probability that a pair of molecules being h-bonded is extremely small. This is incorrect at the air-water interface where a very specific 2D H-bonded network between the water molecules has been shown to exist (ref 38 for instance). So what is the point of this (wrong) assumption in this work?

There is also an assumption written in section II-B on the fact that each HB acts independently of the others. There again, literature (ref 38 and others) show the existence of this entangled 2D HBond network at the air-water interface, where the water molecules form a collective HBond network in which the HBonds are intertwined, hence not independent.

In section III, the authors use their descriptors of HBonds and the Willard-Chandler interface definition in order to get the instantaneous surface. This latter is then translated along the z-perpendicular direction of space in order to define an interface of a certain thickness. There are 2 critics here: 1) the authors at the start of their paper were telling us that they want to go beyond

this WC interface definition (because it uses a parameter, which by the way is partly incorrect), however they now include it here in order to find the interface thickness, I am lost ; 2) the translation made by the authors is incorrect. Indeed, the WC surface has a certain shape/rugosity (that can actually be seen in fig1) that reflects the specific surface of water in contact with the air. Translating this surface towards the liquid and use it for the properties calculations that the authors will use to draw conclusions is incorrect because the bottom of the hence defined interfacial layer has by construction a different shape/rugosity than the one at the interface with the air. If the authors want to define an interface layer with 2 WC definitions at the top and bottom, they need to change the density definition used in the WC method. With this, they will have the 2 correct boundaries of the interfacial layer.

This being said, I also believe that the minor differences seen in fig 4 are due to this wrong definition of the bottom of the interface layer.

Fig4 still: the authors have to include error bars on each point of the curve in order to account for the limited number of water molecules in the simulation box and within the layers used for the plot as well as for the limited time-length of the DFT-MD simulations. The authors are furthermore using only one trajectory in this investigation, which is far too low for a statistical descriptor as the one defined in this work.

Conclusions given in section III-B and C are already known from numerous papers in the literature, both for liquid water and for the air-water interface, see typically papers by Kuhne et al and by Pezzotti et al. and several other authors working on liquid water and the water interface with the air. What are the authors bringing new in the literature? I believe the authors have to rewrite this part of the paper.

I do not recommend publication of the paper in its current form, the paper has to be revised according to comments above before being considered for publication.