

This paper presents a classical molecular dynamics study of adsorption of a typical atmospheric gas molecule, SO₂, onto liquid water surface. The topic of the manuscript is suitable for J. Phys. Chem. The paper is interesting and provides new molecular-level details concerning gas-liquid interactions and the mass accommodation process, understanding of which is of critical importance for atmospheric and climate models. The calculations are performed carefully, employing well established methodology appropriate for the goals of this study. However, I find that there are several problems that need to be addressed by the authors before I can recommend publication of the manuscript.

Major issues:

1. The authors neglect a large body of literature that has already been devoted to molecular dynamics studies of adsorption/uptake of gas molecules onto liquid surfaces - see for example the pioneering work of Wilson and Pohorille (J. Phys. Chem. B 1997, 101, 3130) or the review by Garrett, Schenter and Morita (Chem. Rev., 2006, 106, 1355) and references therein. The main findings of these earlier studies should be at least briefly reviewed in the Introduction section. In addition, the authors should discuss what has been learned in the present study about the interaction of gas molecules with aqueous surfaces that was not known from previous simulation studies on closely related systems. One or two paragraphs concerning the simulation approach, system composition, analysis methods and, most importantly, the results and conclusions should be added to set this paper apart from previous work.
2. The main focus of the present study is on orientation preferences of water and SO₂ molecules in the interfacial region. These are analyzed in terms of two independent angular distributions for angles θ and ϕ defined in Fig. 4. However, it has been shown (see Jedlovsky et al, PCCP 2004,6,1874 and references therein) that the above distributions, while providing a full description of the orientational statistics of the corresponding molecule-fixed vectors, cannot describe unambiguously the orientation of the entire molecule. Rather, a bivariate joint distribution, such as $P(\cos \theta, \phi)$, is necessary to correctly describe the orientational statistics of a molecule with respect to an external direction. Using the monovariate distributions and simply combining them to infer the most probable orientation of a molecule (an approach applied in the present study) may lead to wrong conclusions. It is, therefore, critical that the authors perform the orientation analysis in terms of the bivariate joint distributions for several layers along the direction normal to the interface to make sure their conclusions regarding the molecular orientations are correct.

Other issues:

3. In the structure of the paper, description of methods should be clearly separated from the results and their analysis. Presently, everything is together in Section 2 entitled "Computational Approach", which is confusing for the reader.
4. It is important to distinguish clearly throughout the entire paper between adsorption onto/into a liquid surface and absorption into the liquid phase. In particular, the first sentence of the Abstract needs to be corrected adequately.

5. The force field for SO₂ has been taken from Baer et al., who developed (and tested) the SO₂ model to be used with the the Dang-Chang water model, whereas in the present study the POL3 model of water is employed. Without further testing, there is no guarantee that the SO₂ – water interactions will be accurately described when using a different water force field. The authors should provide some evidence of a satisfactory performance of their combination of force fields. Ideally, it should be demonstrated that the interaction energy and geometry of the SO₂:H₂O gas phase complex and the free energy of SO₂ hydration are well reproduced. The steered MD simulation in the "neat water" syste does in principle provide the free energy profile for SO₂ transport across the air/water interface (??), hence the hydration free energy should be readily available.
6. P. 3, l. 48-50: "The saturated system had 22 SO₂ molecules introduced to the water slab bulk in order to saturate it to a level coinciding with the Henry's law constant for SO₂ in water." Please provide values of the Henry's law constant and solubility of SO₂ in water for the comfort of the reader.
7. P. 3, l. 50-52: "Additionally, 50 SO₂ molecules were introduced into the gas phase outside of the saturated water slab to simulate an added SO₂ gas pressure." What gas pressure does this number of SO₂ molecules in the simulation box correspond to?
8. Important technical details about the MD simulations are missing: Cutoff? Treatment of long-range electrostatic forces? Temperature and pressure control? Which method was used to calculate the induced dipoles?
9. Section 2.1 mostly repeats what has been already said in the previous section. The relevant parts of text should be restructured.
10. P. 4, l. 27: I find the term "surface equilibrated method" confusing. Please rephrase.
11. Regarding the location of the water surface:
 - a. It is not quite clearly stated in the text, but it seems that the drift of the surface location was observed in all simulations, that is, not only in the steered MD, but also in the equilibrium runs. In the latter case, could the problem be remedied by removing the translation of the center of mass of the entire system at regular intervals (NSCM flag in Amber)?
 - b. A liquid slab has two surfaces. How exactly was the procedure for finding the surface location implemented? Was the position of the outermost water monolayer determined independently for the two surfaces?
12. p. 6, l. 25: "Gibbs dividing surface has a width of 3.77 Å..." In this statement, "Gibbs dividing surface" needs to be replaced by "intefacial region" of "interfacial layer". The Gibbs dividing surface is a plane (which corresponds to a line in Fig. 2A and B) that conveniently defines the position of the interface, not its width. Please specify how was the width determined.
13. p. 6, l. 45: "... 2.2 Å (the typical length of a bulk-water hydrogen bond)..." Please provide citation.

14. As regards the density distributions (Fig. 5):

- c. Only half of each slab is shown – were these density profiles obtained by taking an average over the two interfaces? If so, this should be stated.
- d. The width of the water interfacial region (i.e. the interval over which the density distribution decreases from its bulk value to zero) is significantly larger in the "saturated" system compared to the "neat water" one, which is a signature of water penetration between the SO₂ molecules forming the surface layer. This should be pointed out and discussed.

15. p. 12, l. 33-42: "This result agrees... less pronounced with the polarizable model".

While a detailed orientational analysis employing the bivariate distribution $P(\cos \theta, \phi)$ of molecules in the surface region has most likely not been performed for the POL3 water model, there is at least partial knowledge regarding orientational preferences of interfacial water molecules for this model available in the literature (for example Figs 3-5, Callahan et al, *J. Phys. Chem. A* **2010**, *114*, 8359–8368). How do the results of the present study compare with what has been known previously?

16. In my opinion, the first paragraph of Section 3 – Conclusions would better fit in the Introduction.