

Effects of adsorbed OH on Pt(100)/water interfacial structures and potential



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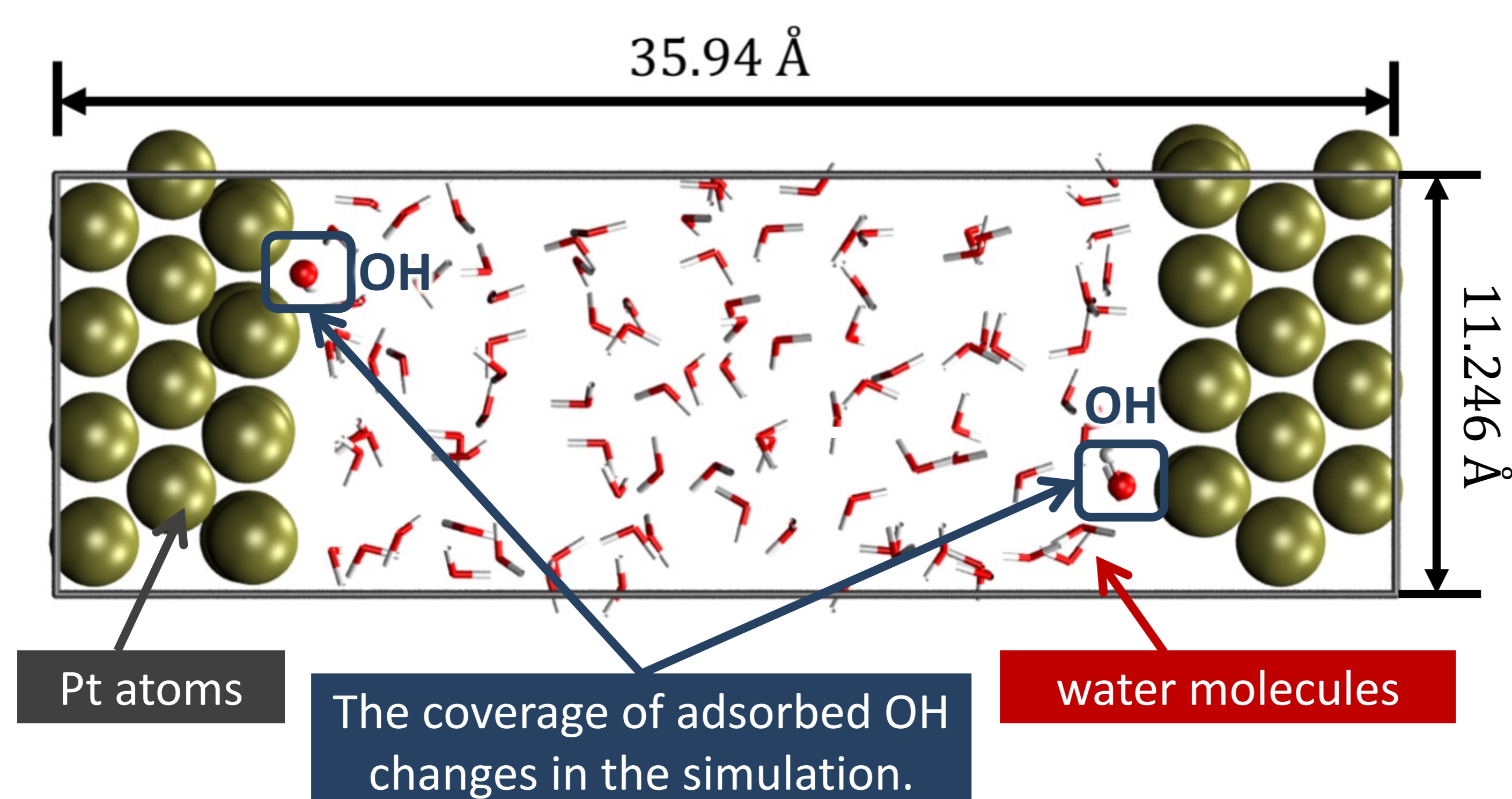
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Introduction

Adsorbates at the electrode change the structure of the electrode/electrolyte interface. Despite the important influence of the interfacial structure on electrochemical processes, computational investigations targeting this influence are still lacking. Even the impact of one of the most common adsorbates, namely adsorbed OH, is so far largely unknown. How will the adsorbed OH influence the interfacial properties?

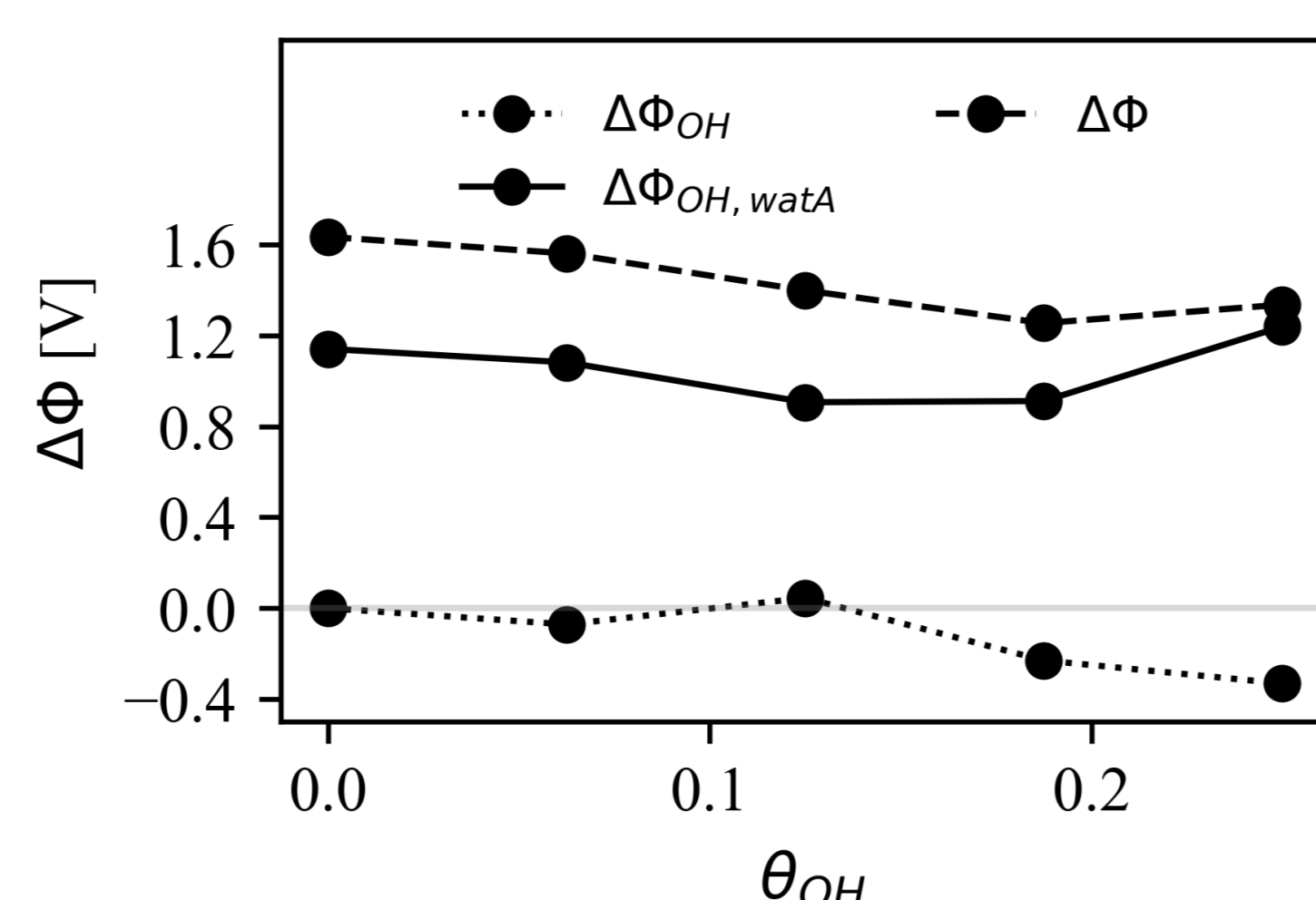
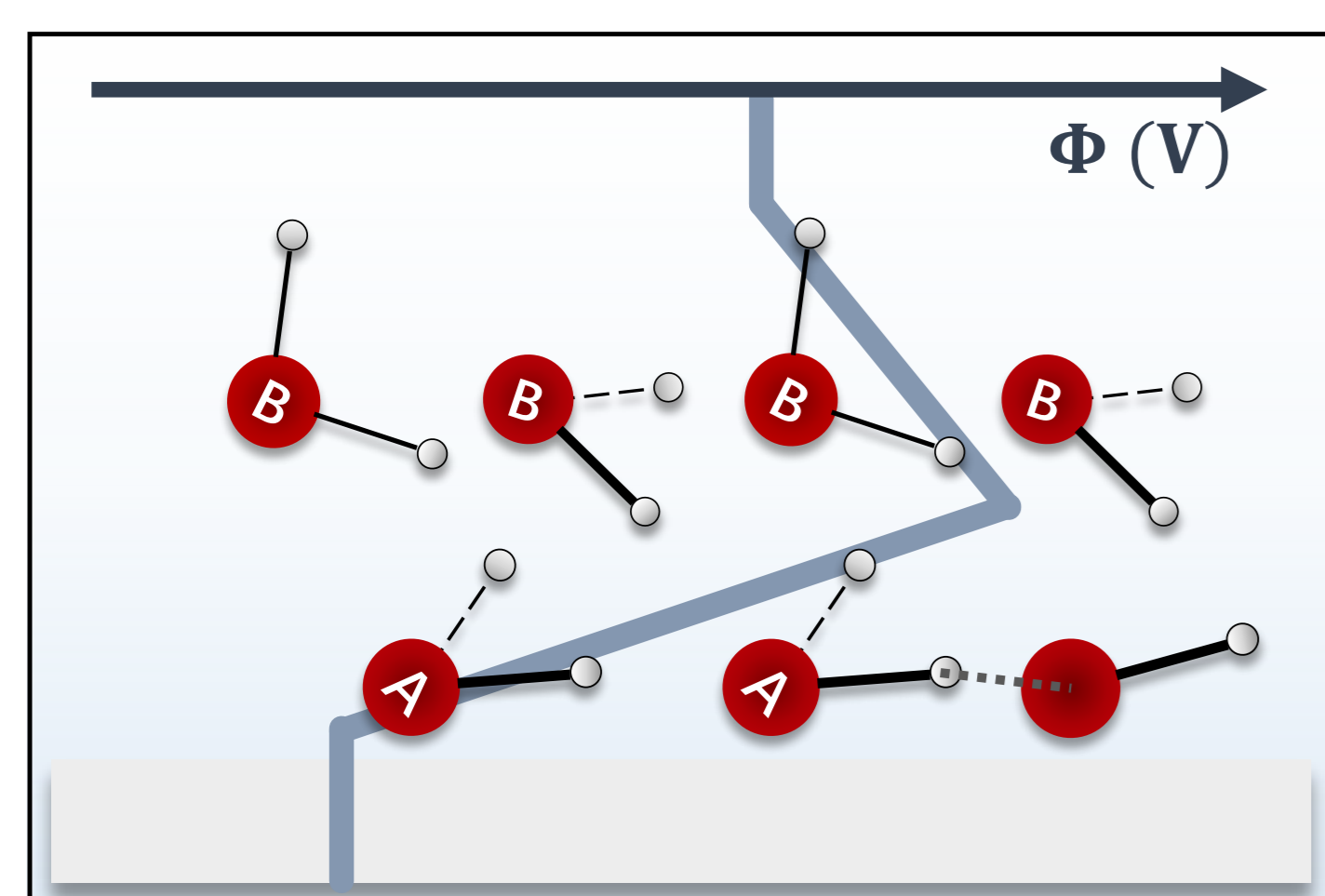
Computational setup

We choose the Pt(100)/water interface as a model system to investigate the interfacial structures at various OH coverage with *ab initio* molecular dynamics (AIMD)^[1].



With the AIMD trajectories, additional calculations are performed to determine the interfacial potential shifts in the presence of adsorbed species^{[2][3]}.

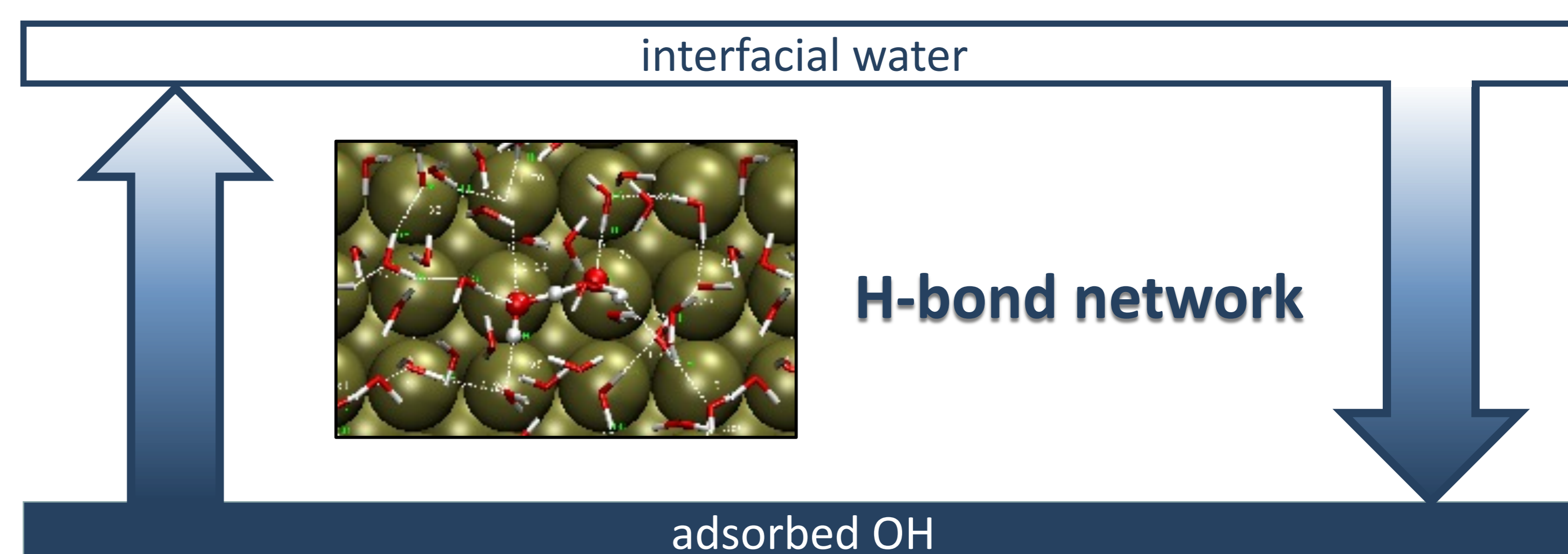
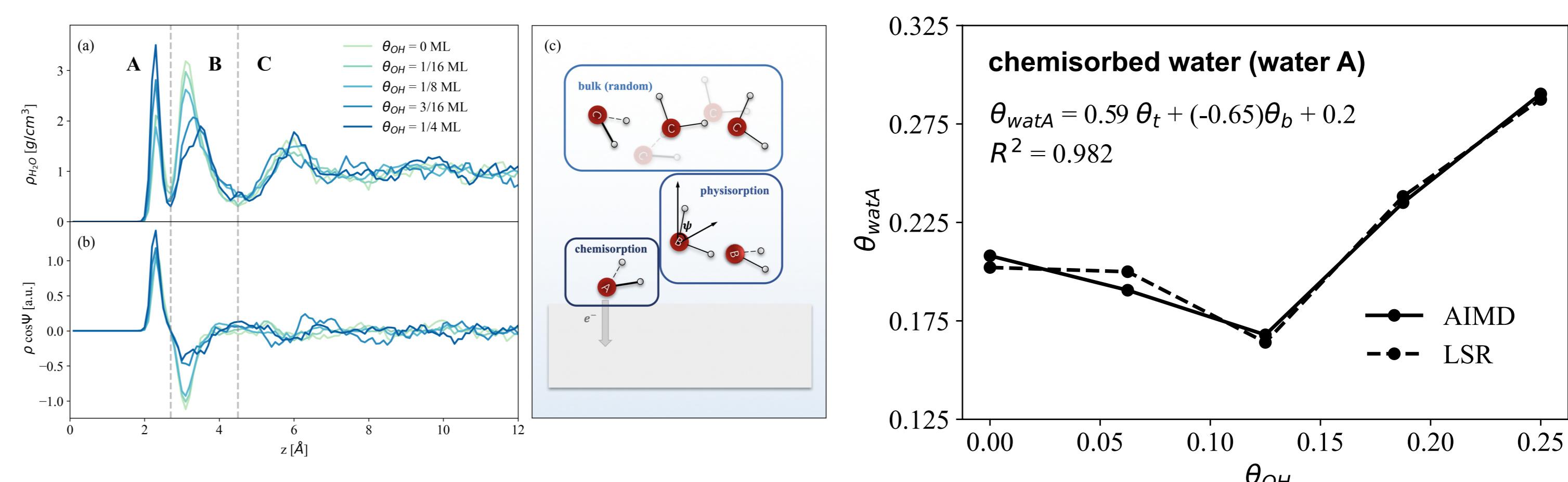
Interfacial potential



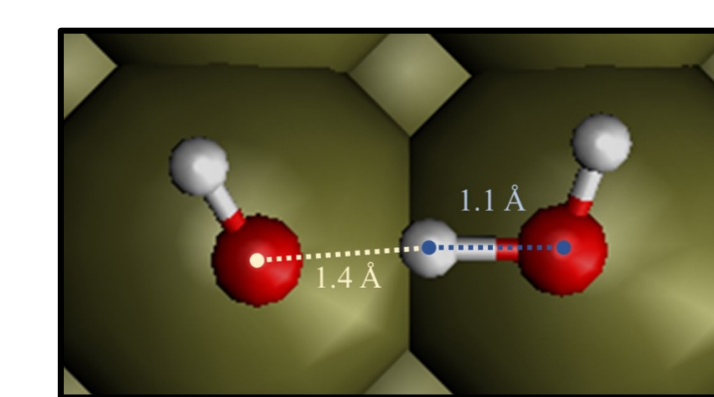
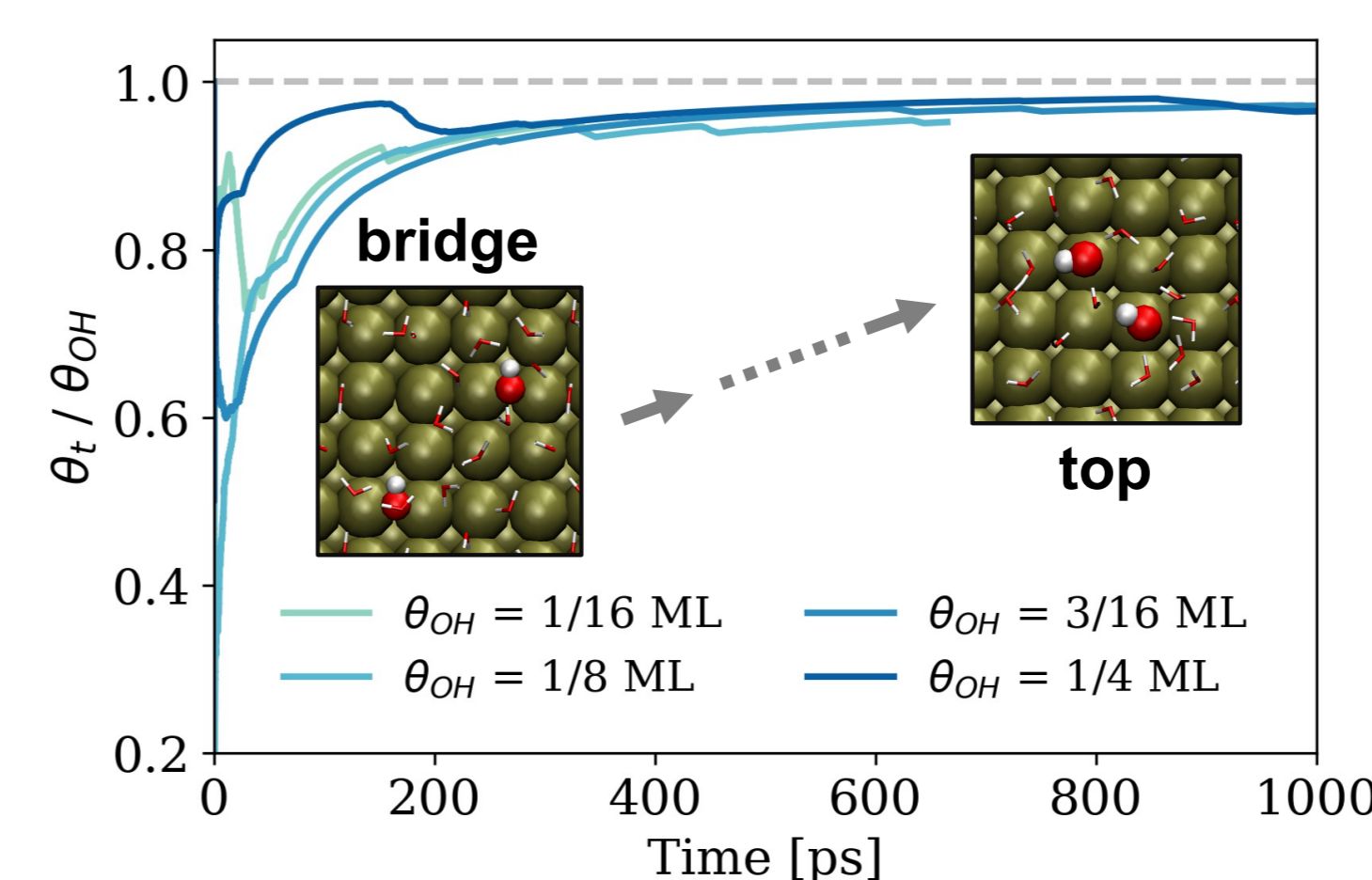
The interfacial potential difference as a function of OH coverage is clearly governed by a complicated interplay of the OH present at the surface and the interfacial water, especially the chemisorbed water (water A).

Interfacial structures

On Pt(100)/water interfaces, the coverage and orientation of water change strongly with changing coverage of adsorbed OH.



The presence of water influences the adsorption site of OH at the interface due to solvation effects.



	$E_{ad}(vac)$	$E_{ad}(with\ 1\ water)$
top	-2.374	-2.902
bridge	-2.776	-2.954

Conclusions

On Pt(100)/water interfaces, the structures of interfacial water and OH are correlated due to a strong H-bond network. This H-bond network results in a complicated dependence of the interfacial potential on the OH coverage, which is governed not only by the OH directly, but also by the influence the OH species have on the interfacial water structure.

Bibliography

- [1] Zhu J-X, Le J-B, Doblhoff-Dier K, et al. to be submitted
 [2] Cheng, Jun, and Michiel Sprik. *Physical Chemistry Chemical Physics* 2012, 14:32: 11245-11267.
 [3] Le J-B, Iannuzzi M, Cuesta A, et al. *Phys. Rev. Lett.* 2017, 119.1: 016801.