

The Aqueous Liquid-Vapor Interface: New Insights from a Novel Car-Parrinello-like Approach to Born-Oppenheimer Molecular Dynamics

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Surface and interface properties of liquid water are of crucial importance for various processes in biology, chemistry and atmospheric sciences. However, studying the water surface is rather challenging due to the required system size to stabilize the surface, the 2D periodic boundary conditions and the hence reduced statistics in comparison to the bulk. Nevertheless, using the recently devised Car-Parrinello-like approach to Born-Oppenheimer molecular dynamics [1] it became now possible to study the aqueous liquid-water interface from first principles with great accuracy.

Applying a new hydrogen-bond definition [2], based on two-dimensional potentials of mean force, we find substantially less single-donor and acceptor-only moieties as in the groundbreaking study of Kuo and Mundy [3], but in good agreement with recent sum frequency generation experiments. Studying the orientational distribution of the water molecules near the surface we find that dangling OH bonds and lone pairs are not equally distributed, but that the dangling bonds are preferably protruding out of the water interface, while the lone pairs tend to point into the water phase. This leads to an asymmetry of the hydrogen-bond network near the surface, as can be seen by means of the spatial distribution function, and a shortening of the intramolecular OH bond lengths.

References

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