

Supporting Information for “Hydrogen-Bond Dynamics of Water at the Interface with InP(001) and GaP(001) and the Implications for Photoelectrochemistry”

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Simulation cell

Figure 1 shows a schematic of the initial surface configuration of hydroxylated InP/GaP(001) used in the molecular dynamics simulations. A surface coverage of 1.5 ML was used, with both exposed surfaces terminated identically. Hydroxyls initially occupied every other bridge site along $[\bar{1}10]$, and every atop site. The chosen surface coverage and adsorbate arrangement were based on the minimum-energy configuration obtained from the convex hull of cluster expansion calculations.^{1,2} The complete simulation supercell, which is periodically repeated in the simulations, is shown in Fig. 2.

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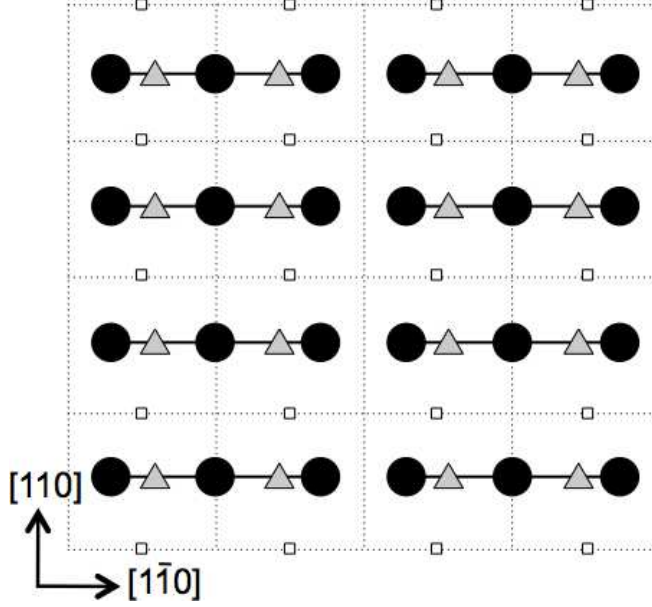


Figure 1: Surface structural model used for the initial configuration of hydroxylated InP/GaP(001) in the molecular dynamics simulations. Triangles and squares represent In/Ga and P atoms, respectively. Circles are hydroxyl groups. Larger size and darker color indicates closer atoms.

Interface equilibration

In order to generate the initial interface configuration, bulk water was first independently equilibrated using classical molecular dynamics with the TIP4P interatomic potential.³ The water was then placed in contact with the semiconductor surface, and *ab initio* dynamics were run for 1 ps with all semiconductor and adsorbate degrees of freedom frozen. The interface was then equilibrated for an additional 3 ps using full *ab initio* dynamics, after which statistics were gathered for 20 ps production runs. In each case, statistics were averaged over both exposed interfaces.

During the runs, temperatures were maintained using a chain of four Nosé-Hoover thermostats⁴ with frequencies of 10, 20, 35, and 50 THz. Simulations were run at 400 K, since the elevated temperature has been shown to be necessary for properly reproducing the structural properties of ambient liquid water.⁵

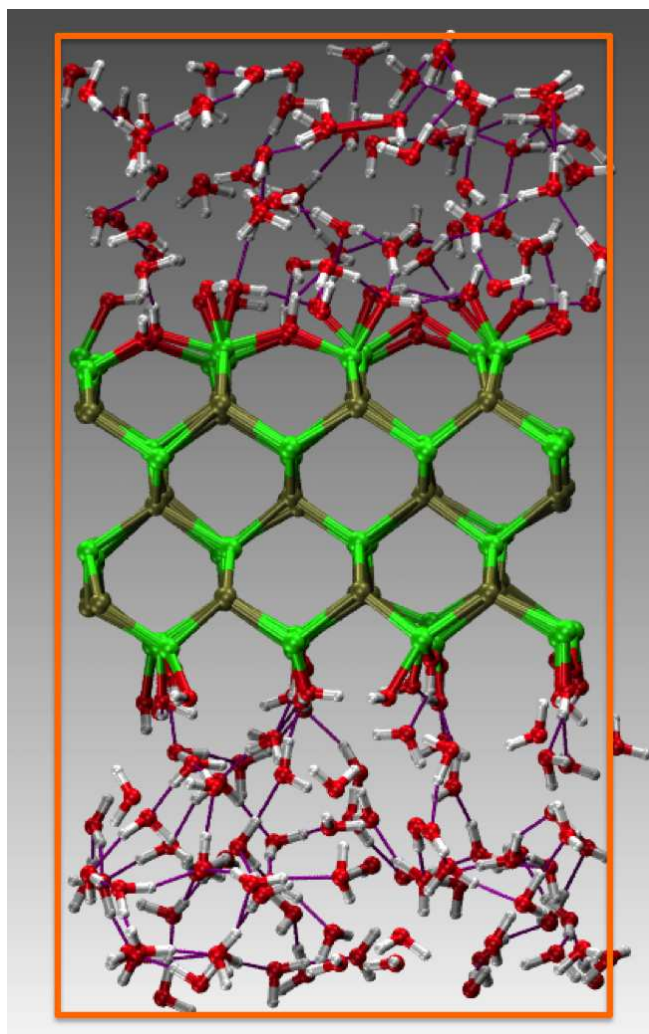


Figure 2: Simulation cell of hydroxylated InP/GaP(001). In/Ga, P, O, and H atoms are shown in green, brown, red, and white. Supercell edges are outlined in orange.

Choice of time step

In order to verify that our chosen Car-Parrinello time step ($\Delta t = 12$ a.u.) is sufficiently small to properly reproduce the properties of water at the interface, we have calculated the oxygen-oxygen radial pair distribution function ($g(r)$) for liquid water using the same parameters. Figure 3 compares the resulting $g(r)$ is compared with the $g(r)$ for a smaller time step ($\Delta t = 6$ a.u.), and with the $g(r)$ from the Born-Oppenheimer molecular dynamics simulations from Ref.⁶ The high level of agreement in each case (even using different pseudopotential descriptions) affirms the choice of simulation parameters.

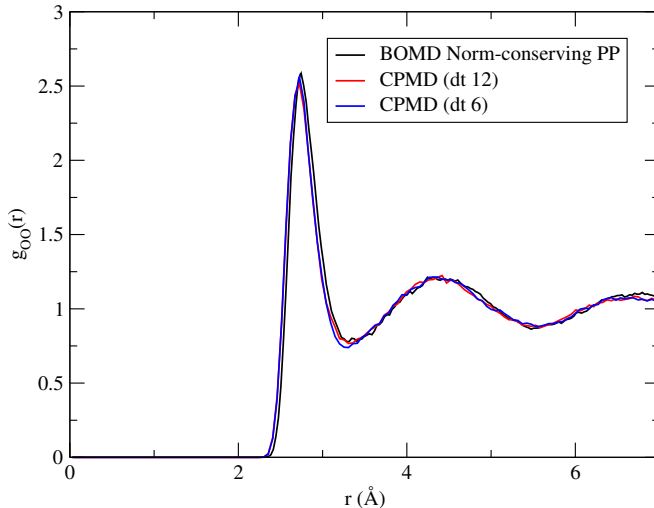


Figure 3: Oxygen-oxygen radial pair distribution function $g_{OO}(r)$ for liquid water using Born-Oppenheimer molecular dynamics and norm-conserving pseudopotentials (from Ref.⁶), compared with values obtained using Car-Parrinello molecular dynamics with ultrasoft pseudopotentials and time steps of 12 a.u. (this work) and 6 a.u.

Bond existence criteria

For evaluating the existence of an O–H chemical bond, a history-dependent hysteresis was applied. If a bond already existed at the previous time step, then it was considered to break once the interatomic distance $d(\text{O–H}) \geq 1.40$ Å. However, if the bond did not exist at the previous time step, then the distance criterion for new O–H bond formation was $d(\text{O–H}) \leq 1.15$ Å. This way of

accounting for the chemical bonds prevents overcounting of bond breaking events due to thermal bond stretching.

For oxygen-hydrogen bonds too long to be considered chemically bound, the existence of an $\text{O}\cdots\text{H}$ hydrogen bond was determined by a strict distance criterion of $d(\text{O}\cdots\text{H}) \leq 2.46 \text{ \AA}$.

In each case, values were based on close examination of the oxygen-oxygen radial pair distribution function, shown in Fig. 3.

References

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