

Online Supporting Information for:

**Insights on the Structural and Dynamic Properties of Corundum–Water Interfaces from
First Principle Molecular Dynamics**

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Validation of Simulation Procedure

As discussed in the main text, all *NVT* ensemble FPMD calculations were completed at 400 K using the Nosé thermostat. The choice of temperature followed the work of Cheng and Sprik,¹ Huang et al.,² Leung et al.³⁻⁵ and VandeVondele et al.⁶, as 400 K with the PBE functional⁷ yields the structure and dynamics of liquid water at 300 K. Additional simulations were conducted at 300, 350 and 400 K on the (001) surface. For these calculations, the surface cut, surface site hydroxylation and slab thickness were identical to that used in the main text. The slab surface area was set at the unit cell dimensions in the *a*- and *b*-directions ($4.18 \times 4.825 \text{ \AA}^2$). All calculations followed the approach outlined in the main text. At 400 K, an additional set of simulations included dispersion corrections, specifically the D3 method by Grimme et al.⁸

As described in the main text, a system comprising only water molecules was prepared (H_2O system). As for all water slabs, the H_2O system was constructed using the program Packmol,⁹ thus comprised randomly orientated water molecules. The simulation cell was a cube of $16 \times 16 \times 16 \text{ \AA}^3$; similarly in dimension to the *b*-direction of the (113) surface (15.58 \AA , Table 1 main text). The H_2O system comprised 136 water molecules, imposing a 1.0 g/cc density. All calculations (i.e., *NVT* and *NVE* ensembles) followed the procedures outlined for the alumina-water systems.

Following the *NVE* ensemble calculations, partial vibrational density of states (PVDOS) were calculated using *nMoldyn* and interpreted in the $2500\text{--}4500 \text{ cm}^{-1}$ region. For the water slab of the alumina-water systems, PVDOS were obtained for two sublayers above the (001) surface: the first layer comprised interfacial first solvation layer water molecules (Figure S1, upper plot), and the second layer contained the rest of the water molecules, extended interfacial layer and bulk-like water molecules (Figure S1, middle plot). For the extended interfacial layer plus bulk-like water above the alumina slabs, each spectra comprises a broad asymmetric band; the maxima of the bands blue shift from 3300 to 3500 cm^{-1} as temperature increases from 300 to 400 K, respectively. Notably, the broad band for both calculated spectra at 400 K, with and without dispersion corrections, have maxima around 3500 cm^{-1} . At all temperatures, the bulk water spectra include high frequency sub-peaks above 3600 cm^{-1} . The most pronounced high frequency sub-peak is on the 400 K spectra without dispersion correction, centered at 3750 cm^{-1} . Conversely, the 400 K dispersion correction spectra shows a slight shoulder at high frequency and a slight plateau

at the peak of the central band. In contrast, the PVDOS for the H₂O system comprises a single broad band with a maximum around 3450 cm⁻¹, and a slight high frequency shoulder around 3700 cm⁻¹. As for the extended interfacial layer plus bulk-like water, the spectra for water molecules from the first solvation layer at 300 and 350 K comprise broad bands with sub-peaks, whereas the 400 K spectra contain narrower well-defined peaks (Figure S1, upper plot). At 300 K, the broad spectral band crests at 3260 cm⁻¹, whereas the 350 K spectral band and 400 K peaks are blue shifted and centered approximately at 3500 cm⁻¹.

The lower plot in Figure S1 shows the vibration analyses for the hydroxyl groups of the (001) surfaces. There is a marked variation in the PVDOS of the OH groups at the different temperatures. The spectra at 300 and 350 K, and 400 K with dispersion correction comprise a single peak with a high frequency shoulder. In contrast, the spectra for the 400 K system without dispersion correction differs from the other spectra, comprising two sharp peaks with a high frequency peak centered at 3790 cm⁻¹. Nevertheless, the dominant spectral peaks at 400 K (approximately 3590 cm⁻¹) are slightly blue shifted relative to the predominant peak of the 300 and 350 K spectra (about 3530 cm⁻¹).

As noted in the main text, in water the intermediate frequency (3250–3400 cm⁻¹) vibrational signatures arise from thermal fluctuations and dynamic H-bonding.^{10, 11} Accordingly, the general red shift in the spectra from 400, through 350, to 300 K suggests less thermal fluctuation and stronger H-bonding, thus the 400 K spectra is the best representation of liquid water and is in closest agreement with the H₂O system.⁶ Furthermore, the calculated vibrational spectra for the OH groups of the 400 K system without dispersion correction agrees most closely with the results of sum frequency vibration spectroscopy (SFVS).^{12, 13} Specifically, the high frequency peak (3790 cm⁻¹) arises from O–H stretches of surface μ -OH (Al₂OH) groups and from weaker H-bonding, whereas the intermediate frequency peak (3590 cm⁻¹) is attributed to stronger H-bonding. Taken together, these results support elevating the temperature to 400 K for the *NVT* ensemble simulations.

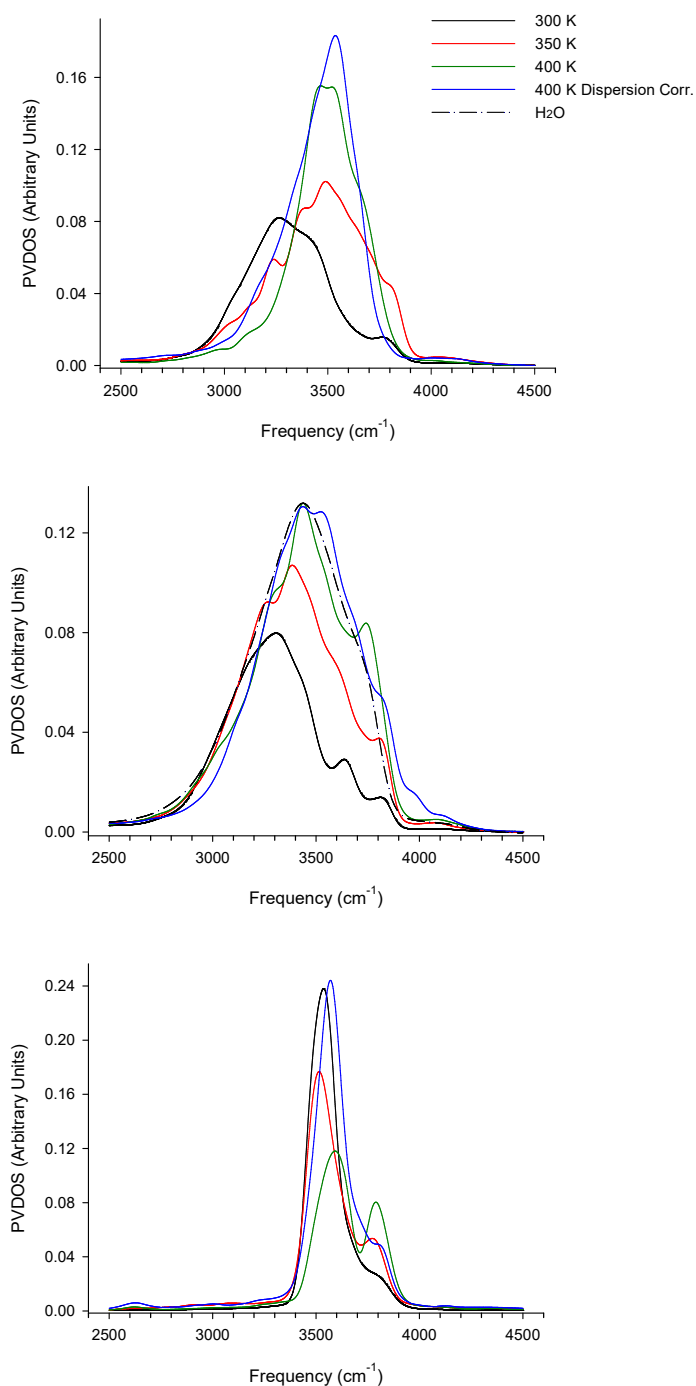


Figure S1. Partial vibrational density of states (PVDOS) of the H atoms of water and surface OH groups at the hydroxylated (001) alumina surface. The plots show PVDOS for water molecules from the first solvation layer of the surfaces (upper plot), the remaining water molecules including extended interfacial layer plus bulk-like water (middle plot), and surface hydroxyl groups (lower plot). The vibrational spectra are for simulations performed at 300, 350, and 400 K, and including dispersion correction (Dispersion Corr.) at 400 K. The middle plot also includes spectra for the H₂O system.

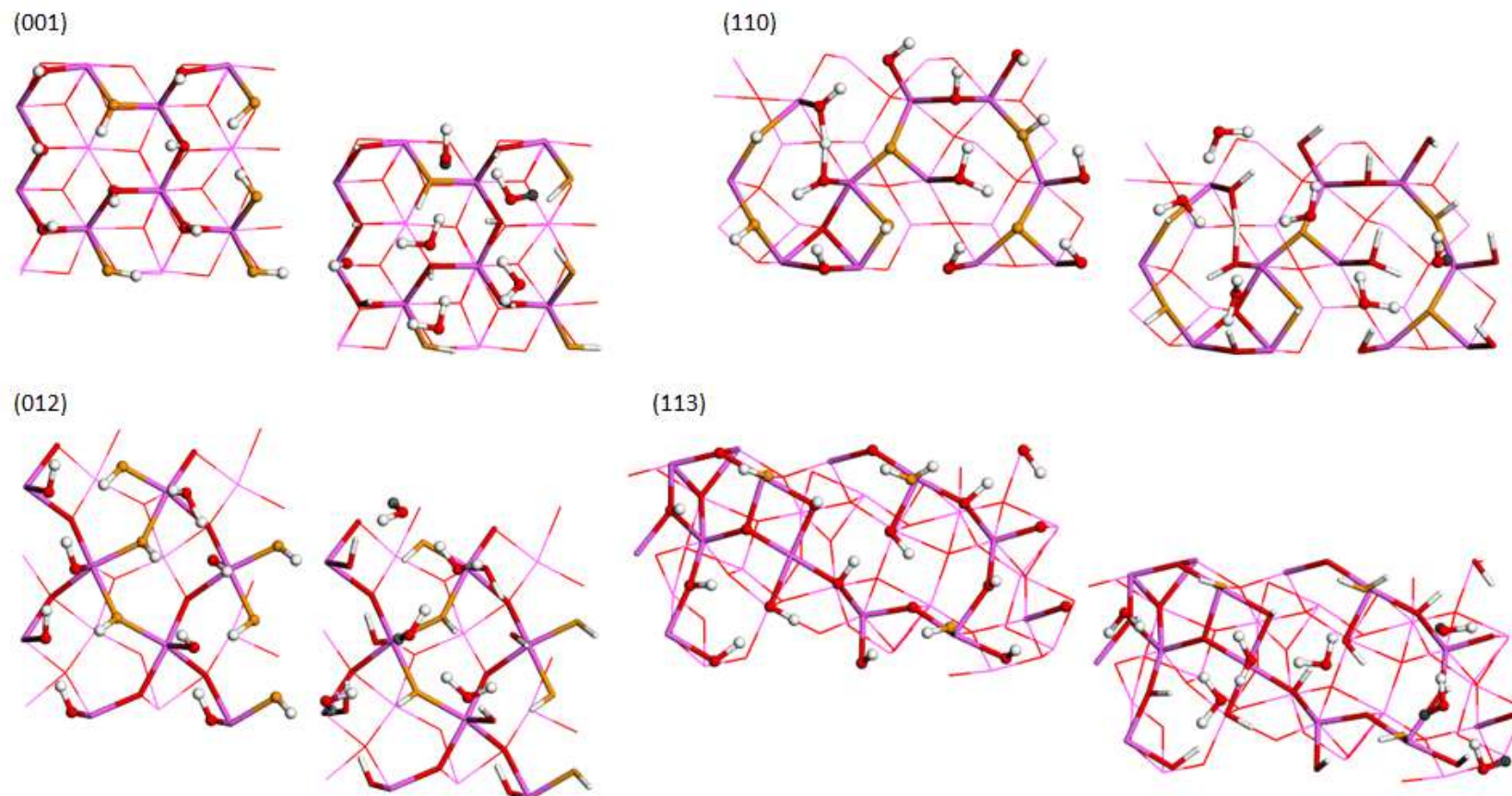


Figure S2. Snapshots of the top-view of each Al_2O_3 surface–water system following *NVE* FPMD simulations. Two top-views are shown for each surface, the upper-left snapshot shows the surface with all water molecules removed, and the lower-right includes the interfacial water molecules (i.e., water molecules in the first solvation layer to a thickness of about 4–5 Å). In the upper-left views, H atoms are in white, and O atoms are in red or orange. Oxygen atoms in orange are from hydroxyl groups lying mostly in-the-plane (OH_{\parallel}) of the (001) surface; $-\text{OH}$ groups positioned along the valleys of the (012) and (110) surfaces; and singly coordinated surface groups, positioned above the doubly and triply coordinate hydroxyls groups, on the (113) surface. The lower-right views use the same color scheme, although for clarity, top layer surface atoms are shown with bars. For the interfacial water molecules, O atoms are in red, H atoms orientated towards the surface are gray, and all remaining H atoms are white. In all figures, top layer aluminum atoms are shown with pink bars. For clarity, lower atomic layers are shown as lines, with pink and red lines representing the bonds between aluminum and oxygen atoms, respectively.

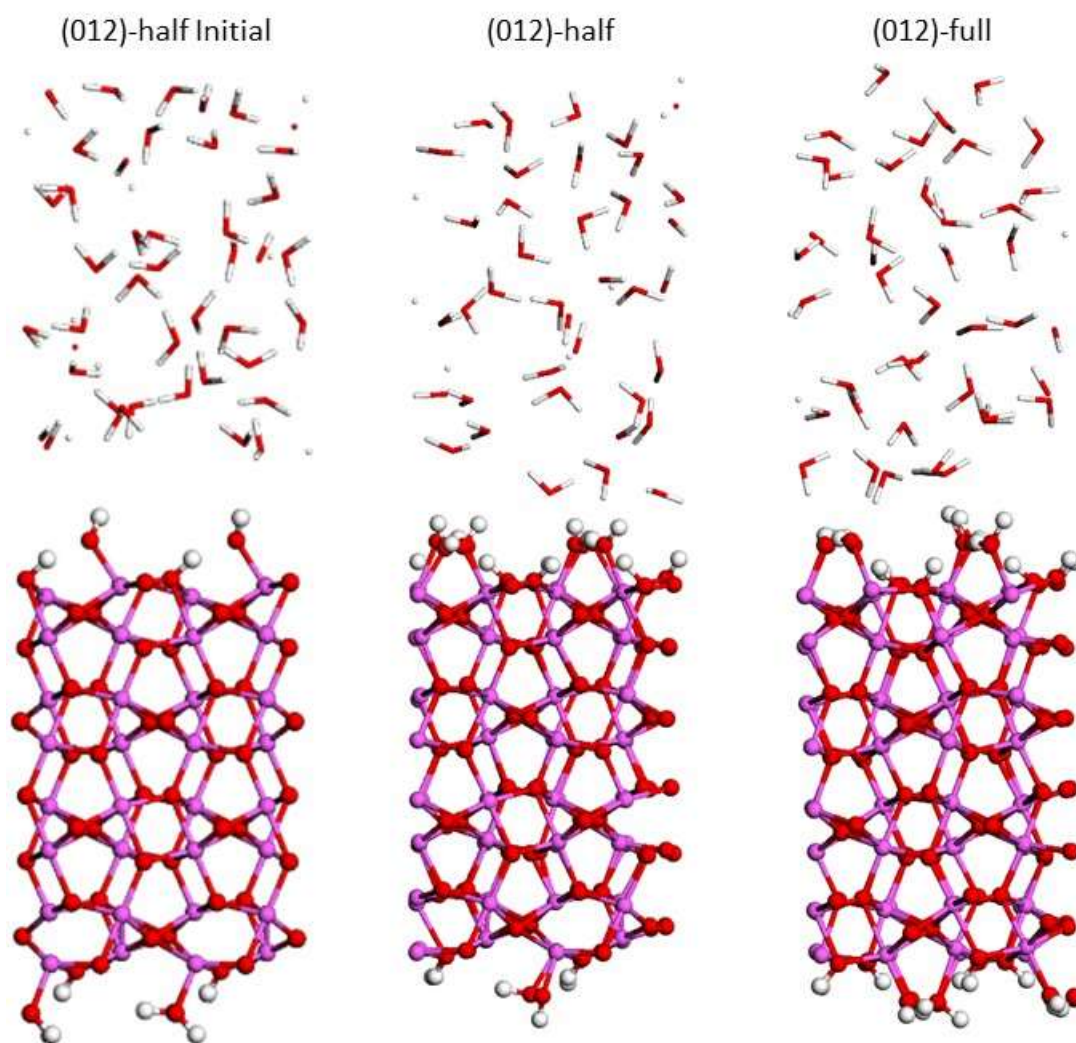


Figure S3. The two Al₂O₃ (012) surface–water systems considered in the study are shown. The figure on the left shows the initial structure of the (012)-half system used in the DFT calculations, with only half of the surface atoms hydroxylated. The center and right figures are snapshots following *NVE* FPMD simulations for the (012)-half (center figure) and (012) fully (right figure) hydroxylated surfaces. As noted in the main text, following equilibration the two surfaces are comparable. The surfaces are aligned along the topmost plane of Al atoms. The Al atoms are pink, O atom are red, and H atoms are white.

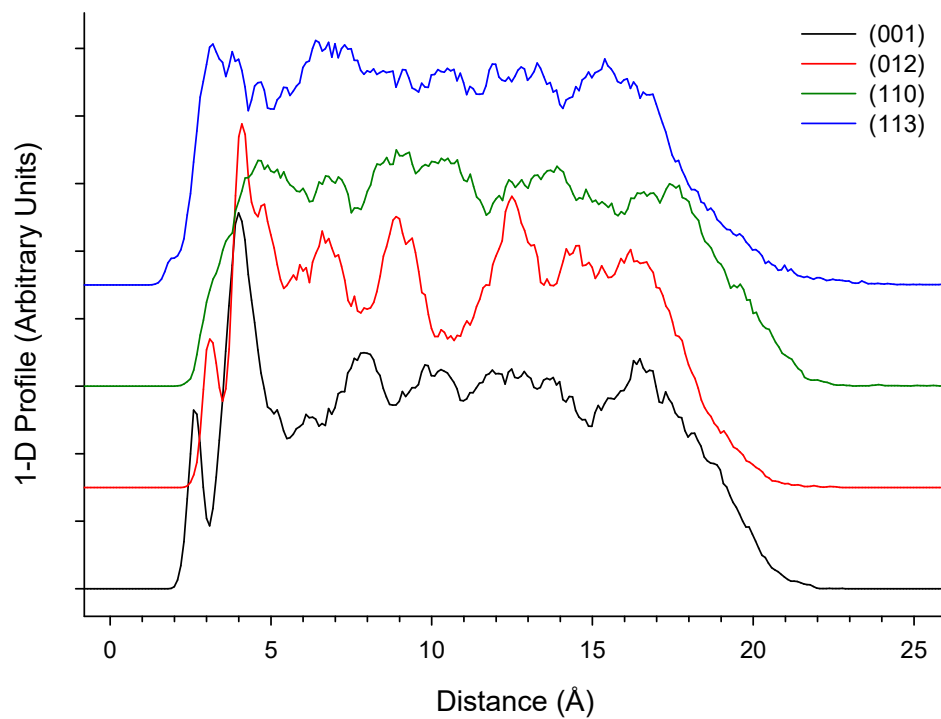


Figure S4. Atomic density 1-D profiles of water above the Al_2O_3 surfaces. All profiles are referenced to the topmost plane of Al atoms (Distance = 0.0 \AA). The profiles are offset to aid visualization.

Comparison of Atomic 1-D Profiles and Electron Density Profiles from Specular X-ray Reflectivity Measurements

The ordering of water near the (001),¹⁴ (012),¹⁵ and (110)¹⁶ surfaces of corundum has been studied using in situ specular X-ray reflectivity (XR) measurements. Although XR techniques provide information on the arrangement and ordering of water near mineral surfaces, it is not possible to measure H atoms directly. Consequently, the orientation of interfacial water molecules with respect to the surface cannot be determined. Despite this limitation, the atomic density 1-D profiles presented in Figure 2 of the main text and the electron density profiles from XR measurements¹⁴⁻¹⁶ deserves comparison.

As electron density profiles from XR measurements result from the density of O and Al atoms, Figure S5 shows just the atomic density 1-D profiles of O atoms from the Al₂O₃ slab and from the water molecules. As in the main text, the atomic density profiles are referenced to the topmost plane of Al atoms (distance = 0.0 Å). To align both profiles, the electron density peak of the uppermost layer of Al and/or O atoms from the Al₂O₃ surfaces was centered over the corresponding peak of the atomic density profile.

An important consideration when comparing the different profiles is the effect that sample cleaning protocols have on the results of experimental studies. In particular, annealing temperature determines surface roughness.^{13, 17, 18} Furthermore, high-temperature annealing (>1000 °C) may stabilize surfaces and limit protonation when later doused with water.¹⁹ In this context, sample preparation of the (001),¹⁴ (012),¹⁵ and (110)¹⁶ corundum surface was varied. The (001) surface was annealed for 24 hours at 1100 °C, whereas the (012) surface was heated for 4 hours at 350 °C. For the (110) surface, two crystals were annealed under different conditions. One crystal was annealed for 18 hours at 1100 °C, and a second for 12 hours at 450 °C. Notably, there was surface reconstruction of the (110) crystal heated at 1100 °C, and AFM measurements revealed atomically flat terraces.¹⁶

Considering the (001) surface (Figure S5, upper plot), there is good agreement between the O atom peak at 3.6 Å of the atomic density profile and the broad peak of the electron density profile, with the peak corresponding to the first hydration layer. A depleted region in the electron density profile is present between the first and second hydration layers, approximately between 5–5.5 Å. Although not as pronounced, there is a somewhat depleted region around 6 Å in the atomic

density profile. As noted in the main text, similar ordering of water molecules above the (001) surface were reported by Argyris et al.²⁰ and Ma et al.¹⁰ Although Catalano¹⁴ suggests that the broad peak centered at ~ 3.6 Å indicates a first layer of water molecules at a single height with weak ordering, the XR measurements cannot provide information on the orientation of water molecules. Significantly, both the H atom profiles in Figure 2 (main text) and the results of Argyris et al.²⁰ and Ma et al.¹⁰ show preferential orientation of water molecules in the first hydration layer of the (001) surface. Explicitly, water molecules are orientated either with the H atoms pointing towards or away from the surface. Additionally, when interpreting the (001) electron density profiles, potential effects of the high annealing temperature used in the sample preparation should not be overlooked,²¹ see below.

The density profiles for the water slab above the (012) surface (Figure S5, middle plot) show remarkable agreement for peaks centered at 4 and 6 Å. From the atomic density profile, also considering the H atom profiles (Figure 2), the peak at 4 Å was consistent with preferentially orientated water molecules, including H atoms pointing towards or away from the surface. In particular, the height of the O atoms suggest H-bond acceptor interactions with the terminal hydroxyl groups along the ridges of the (012) surface. Equally, the 4 Å peak in the electron density profile was interpreted as water molecules positioned above singly coordinated oxygen sites.¹⁵ Although there is good agreement between the density profiles for the peaks at 4 and 6 Å, the electron density profile has an additional peak at ~ 2.6 Å, which Catalano et al.¹⁵ assign to water molecules positioned above the triply coordinated O atoms (along valleys). While no such peak was observed in the O atomic density profile, in the profile of H atoms bound to the Al₂O₃ slab there is a peak at 2.4 Å representing hydroxyl groups orientated normal to the surface (see discussion in the main text and Figure 2).

Unlike the (001) and (012) surfaces, the (110) surface atomic density profile of O atoms does not show any significant peaks that would indicate ordering within the water slab (Figures S4 and S5, lower plot). In contrast, the electron density profiles for the (110) surfaces have defined peaks. However, the profiles of the two (110) samples are quite different. The electron density profile for the (110) sample annealed at 1100 °C (Figure S3, lower plot, dot-dashed green line) is remarkably similar to the profile of the (001) surface that was annealed at the same temperature. Although at different distances from the surface, both profiles comprise a broad-shallow peak representing O atoms (i.e. water molecules) near the surface, a low point in the profile suggesting

a depleted region, followed by a rise in the profile towards a second hydration layer or bulk water. Equally, the profile of the (110) surface heated at 450 °C is comparable to the (012) profile; both profiles comprise three peaks indicating the position of water molecules. Moreover, the distance from the surfaces of three peaks is comparable. As for the (012) surface, the two peaks closest to the (110) surface were inferred to lie above the valleys and ridges.¹⁶

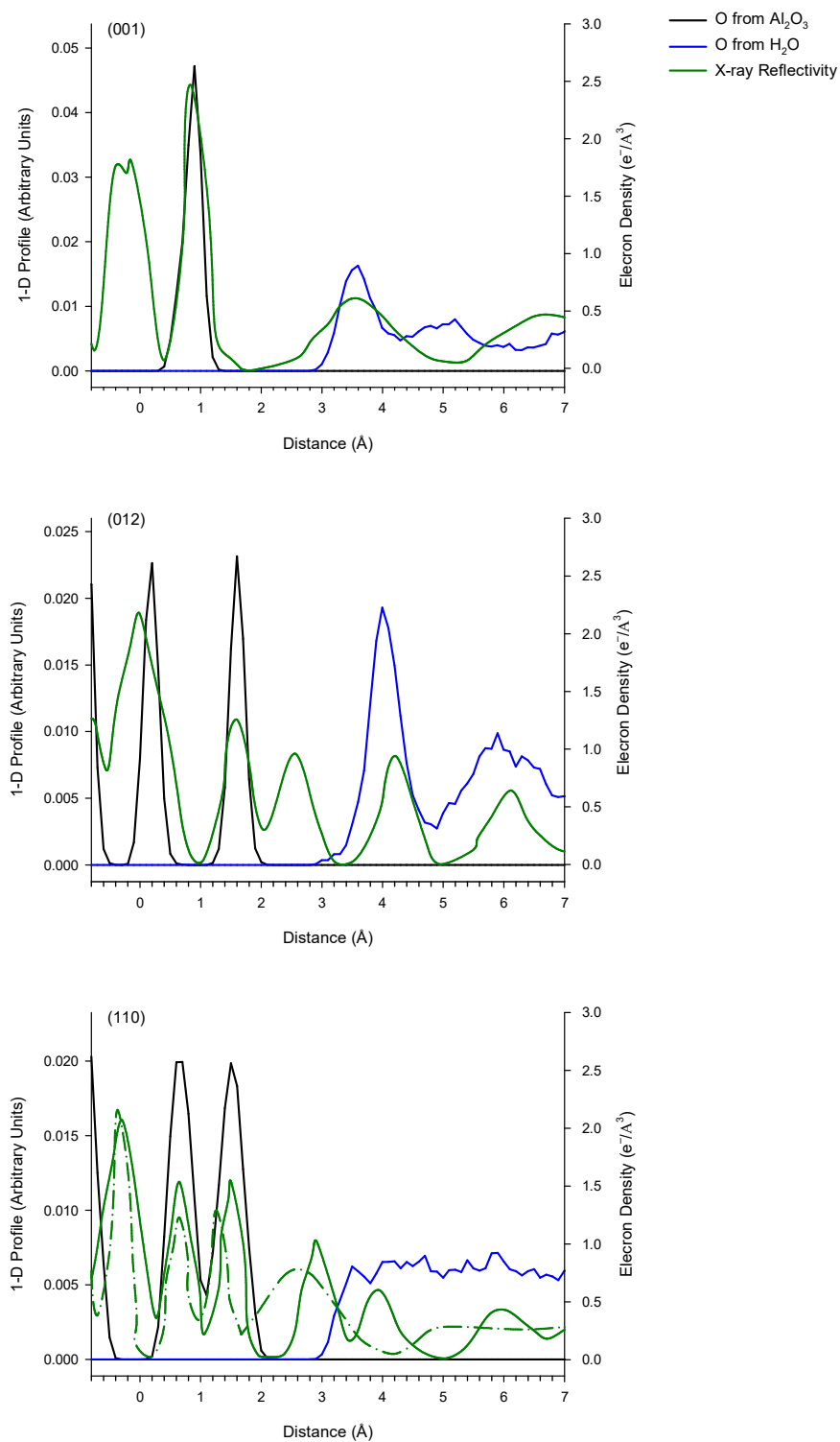


Figure S5. Atomic density 1-D profiles of oxygen from the Al_2O_3 surfaces and from water. Electron density profiles from specular X-ray reflectivity measurements are also shown for the (001),¹⁴ (012)¹⁵ and (110)¹⁶ surfaces. For the (110) surface, the two XR curves reflect sample preparation of 18 h annealing at 1100 °C (dot-dashed green line) and 12 h heating at 450 °C (solid green line).

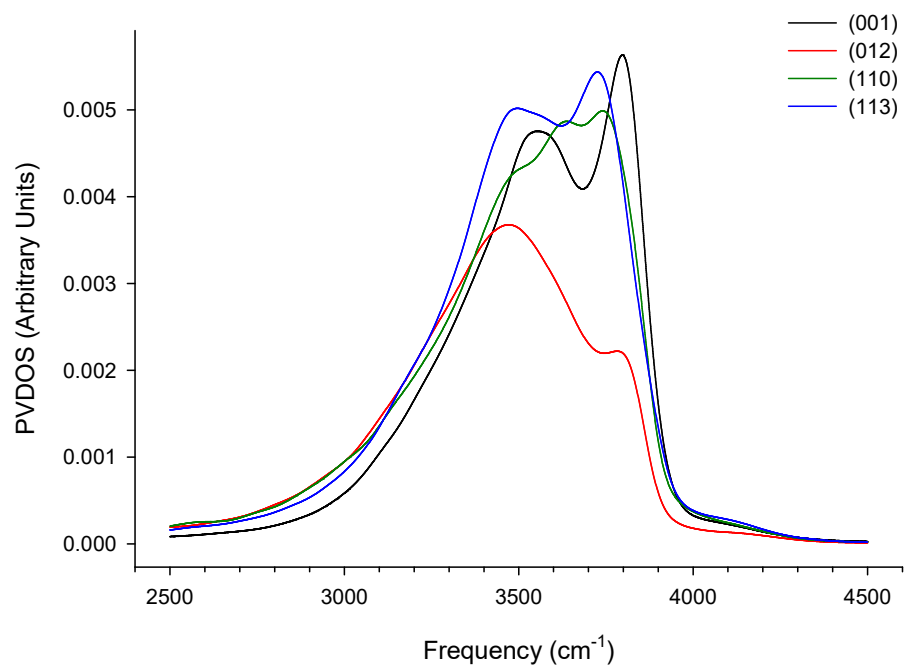


Figure S6. Total vibrational density of states for the four Al₂O₃ slab–water layer systems.

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