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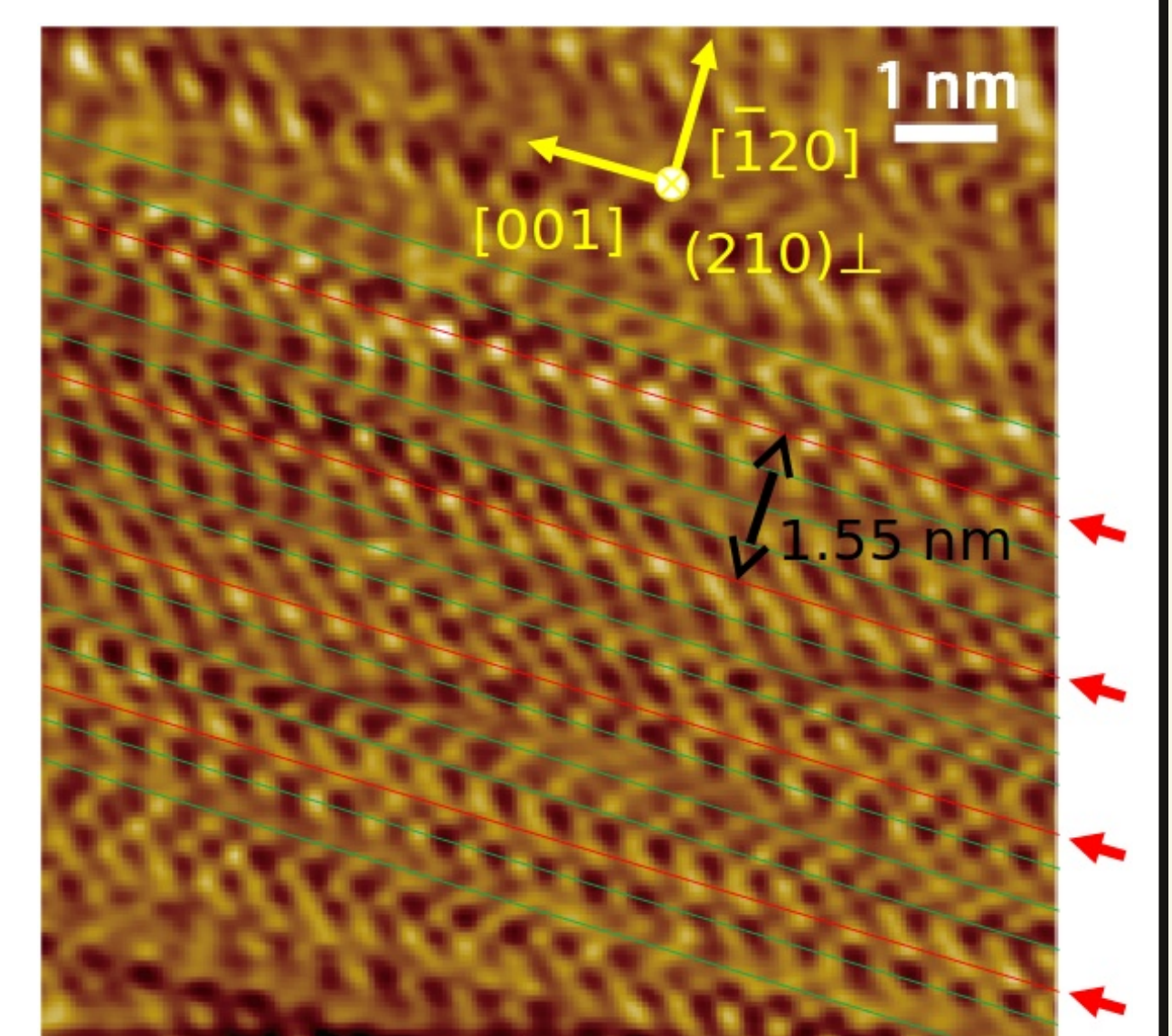
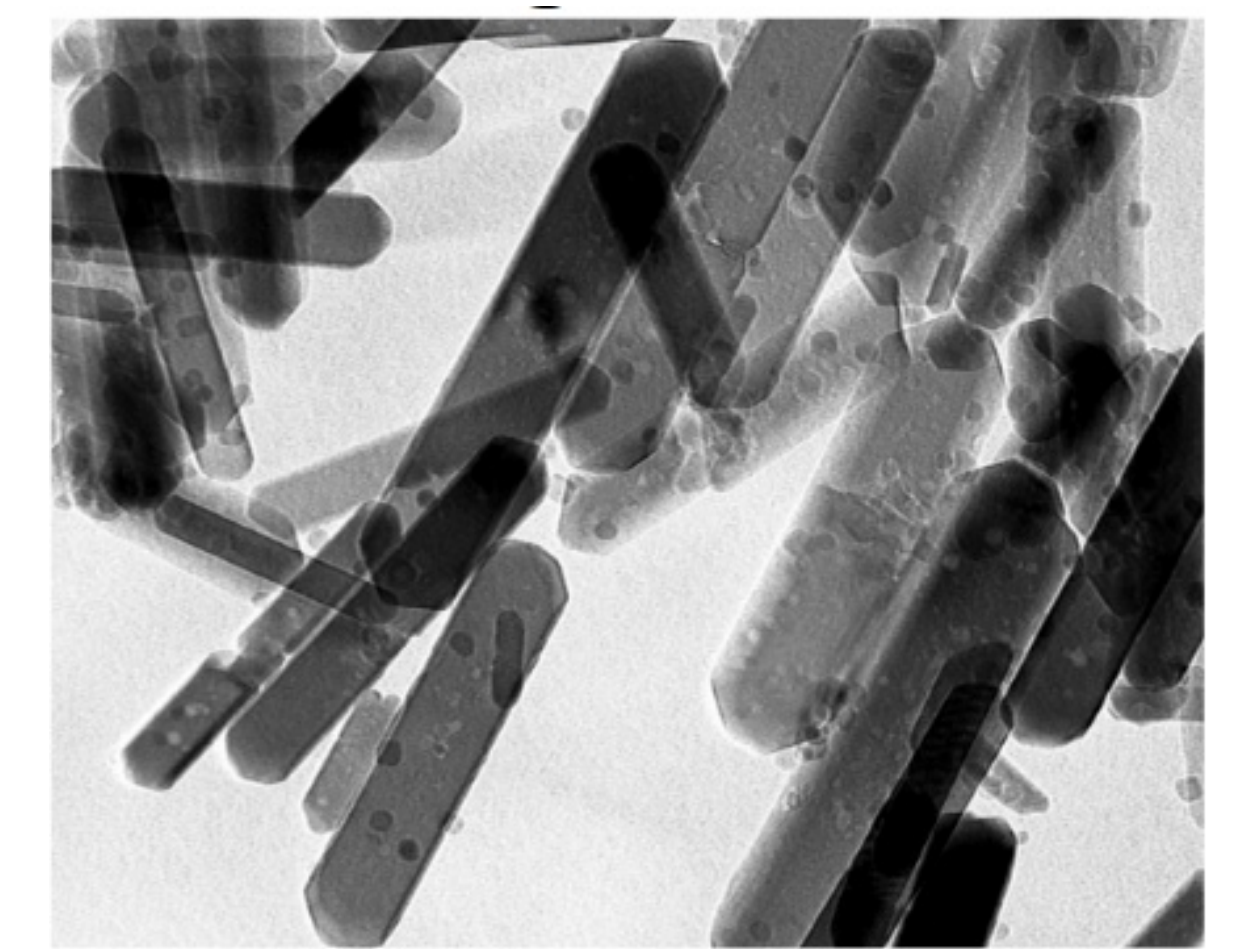
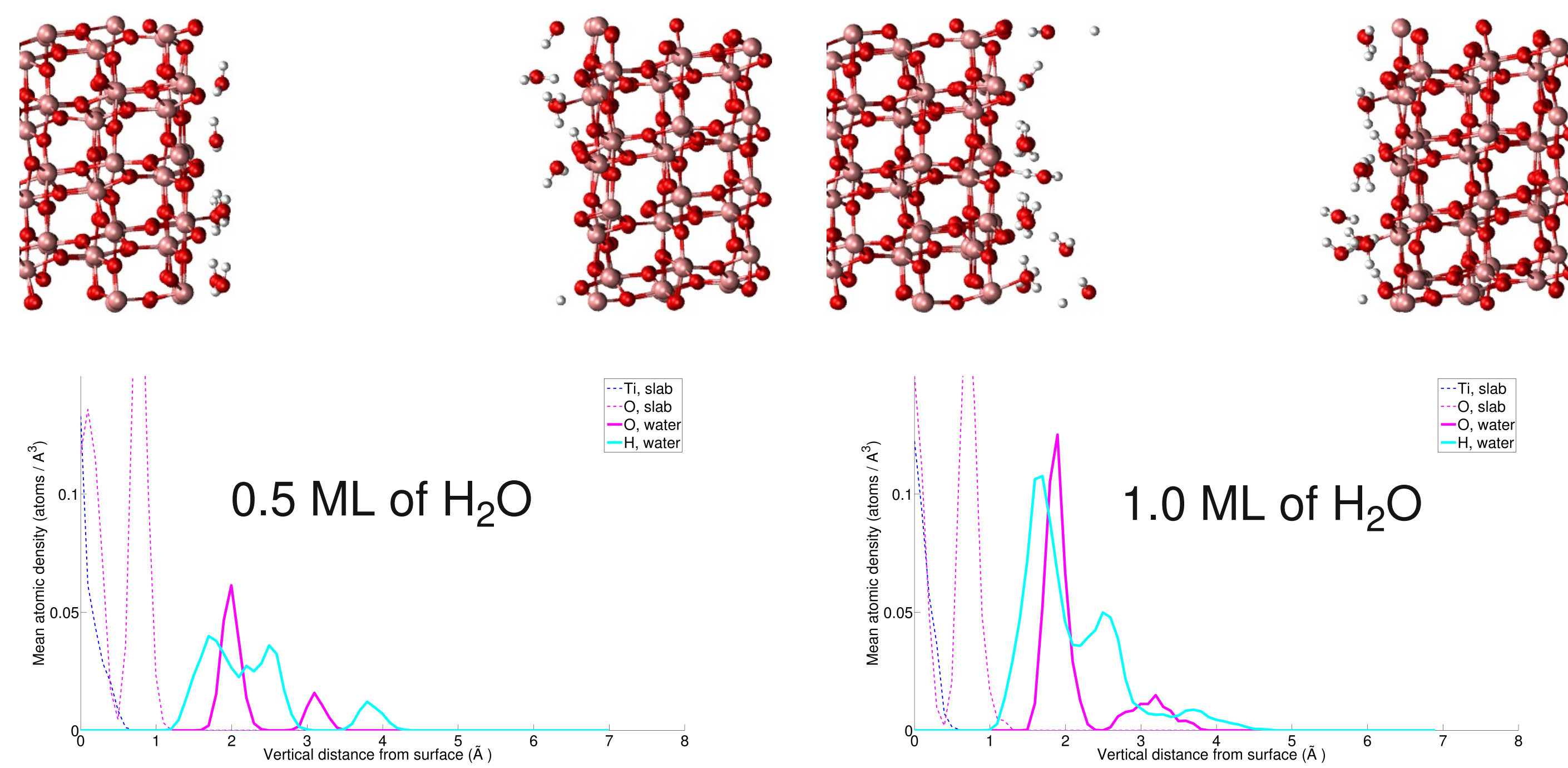
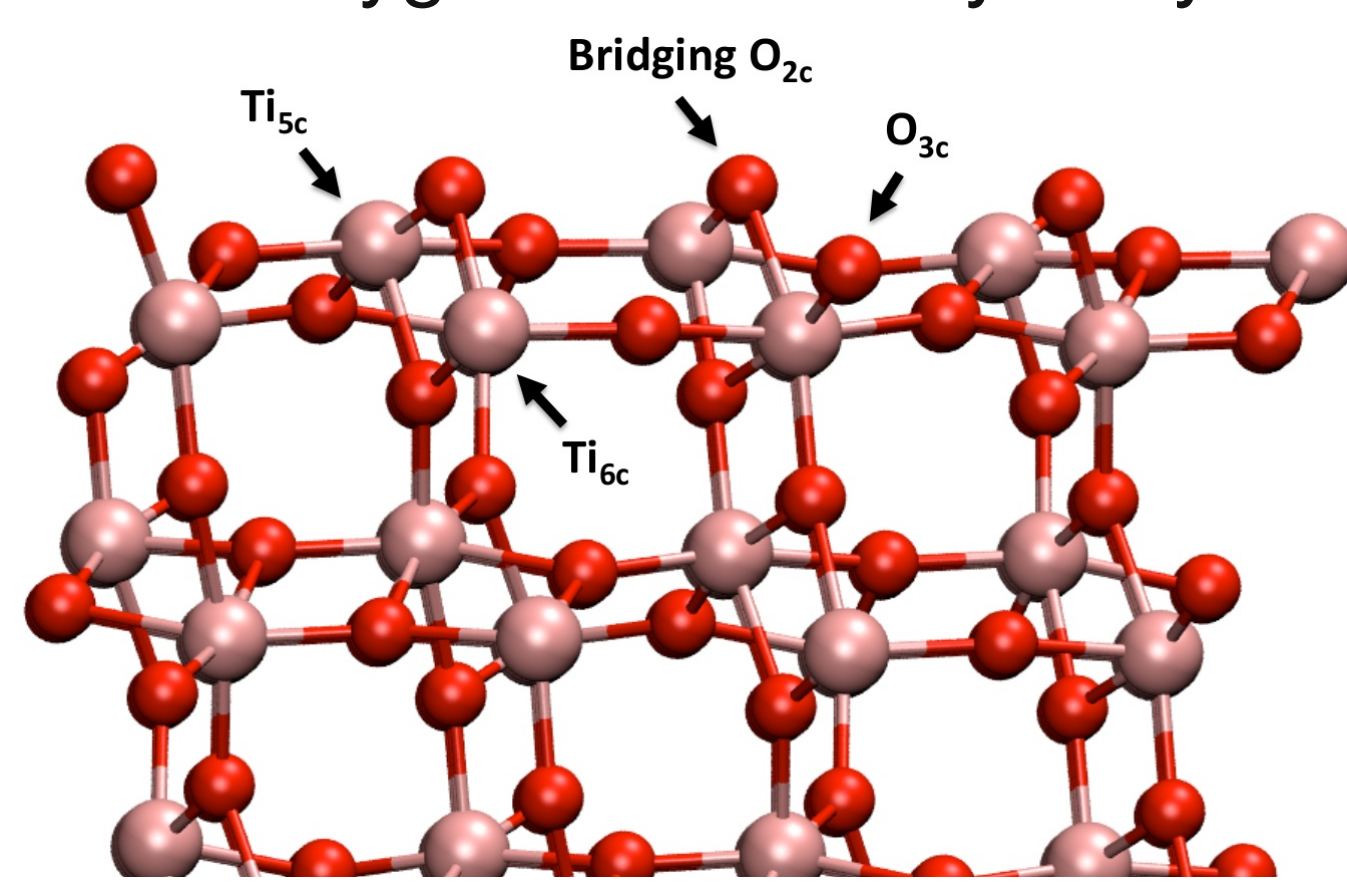
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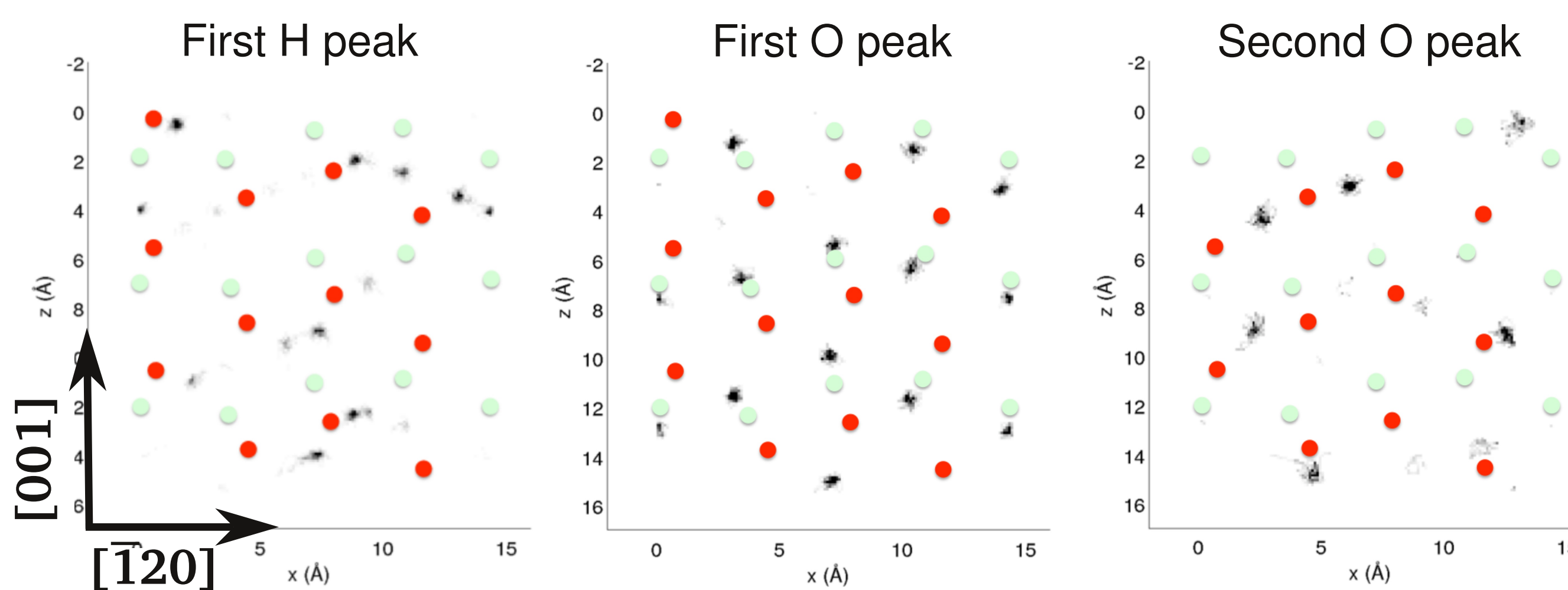
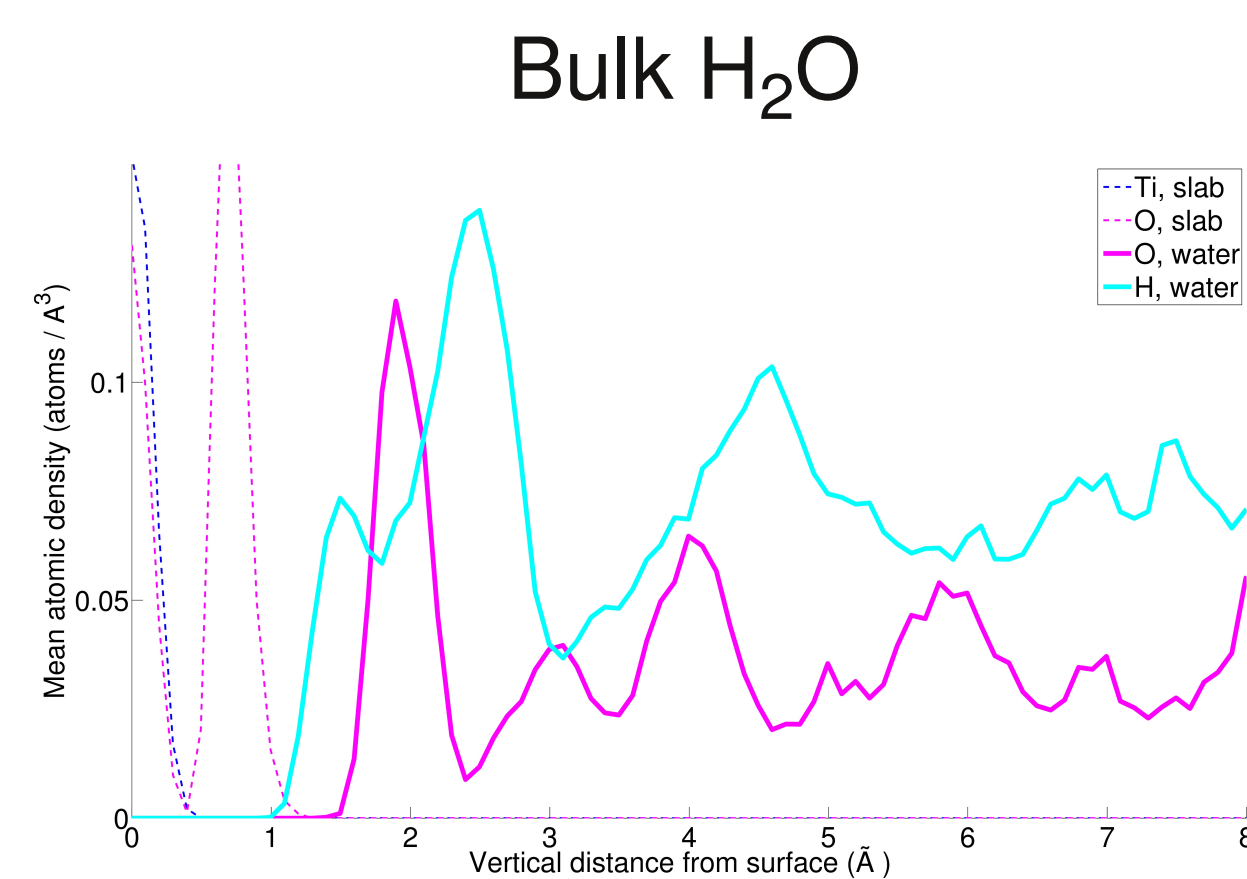
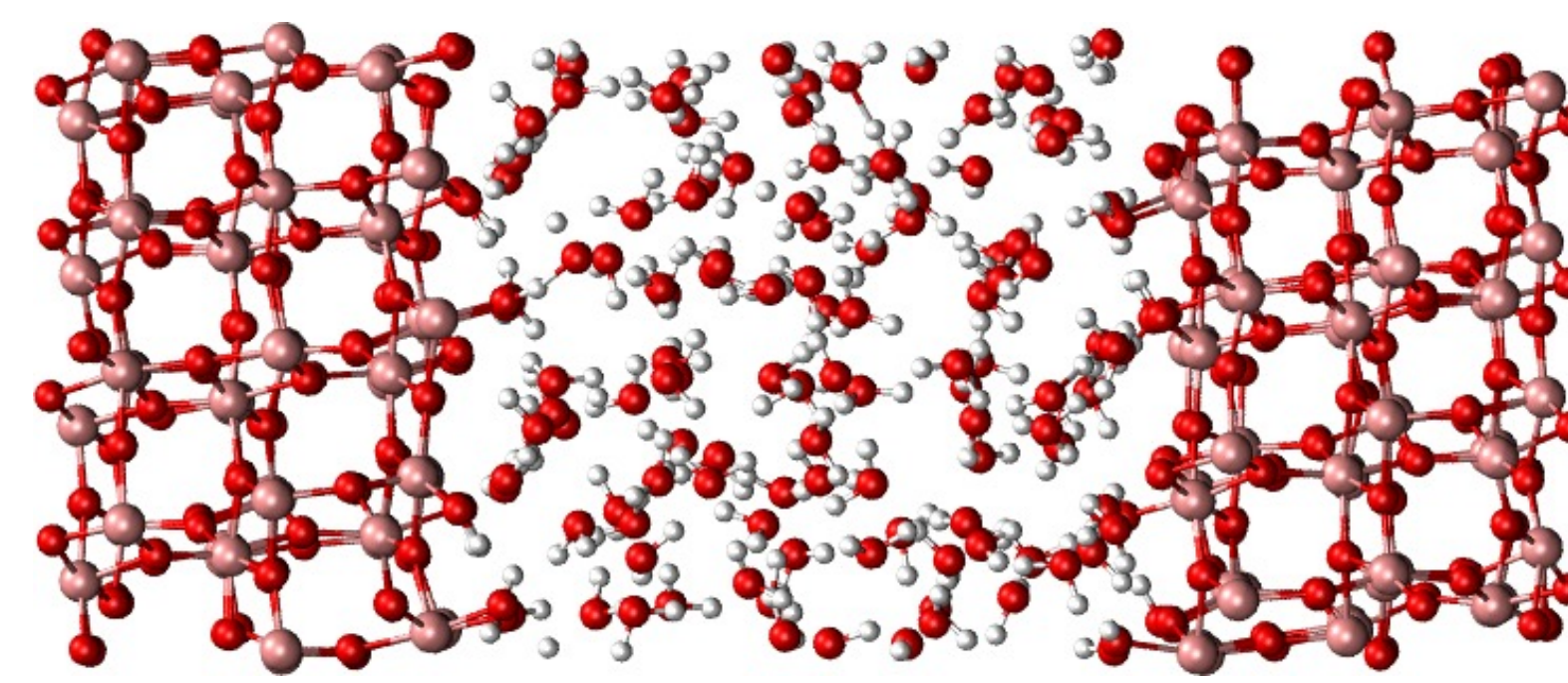


A promising application of TiO_2 is the photocatalytic reduction of atmospheric CO_2 into hydrocarbons. Of the ambient polymorphs of TiO_2 , we target the hydration structure of brookite for increasing our understanding of the reduction process on this relatively unexplored surface. Using density functional theory molecular dynamics simulations and high-resolution atomic force microscopy, we unravel the structural, electronic, and vibrational properties of the interface of TiO_2 brookite (210) and water.

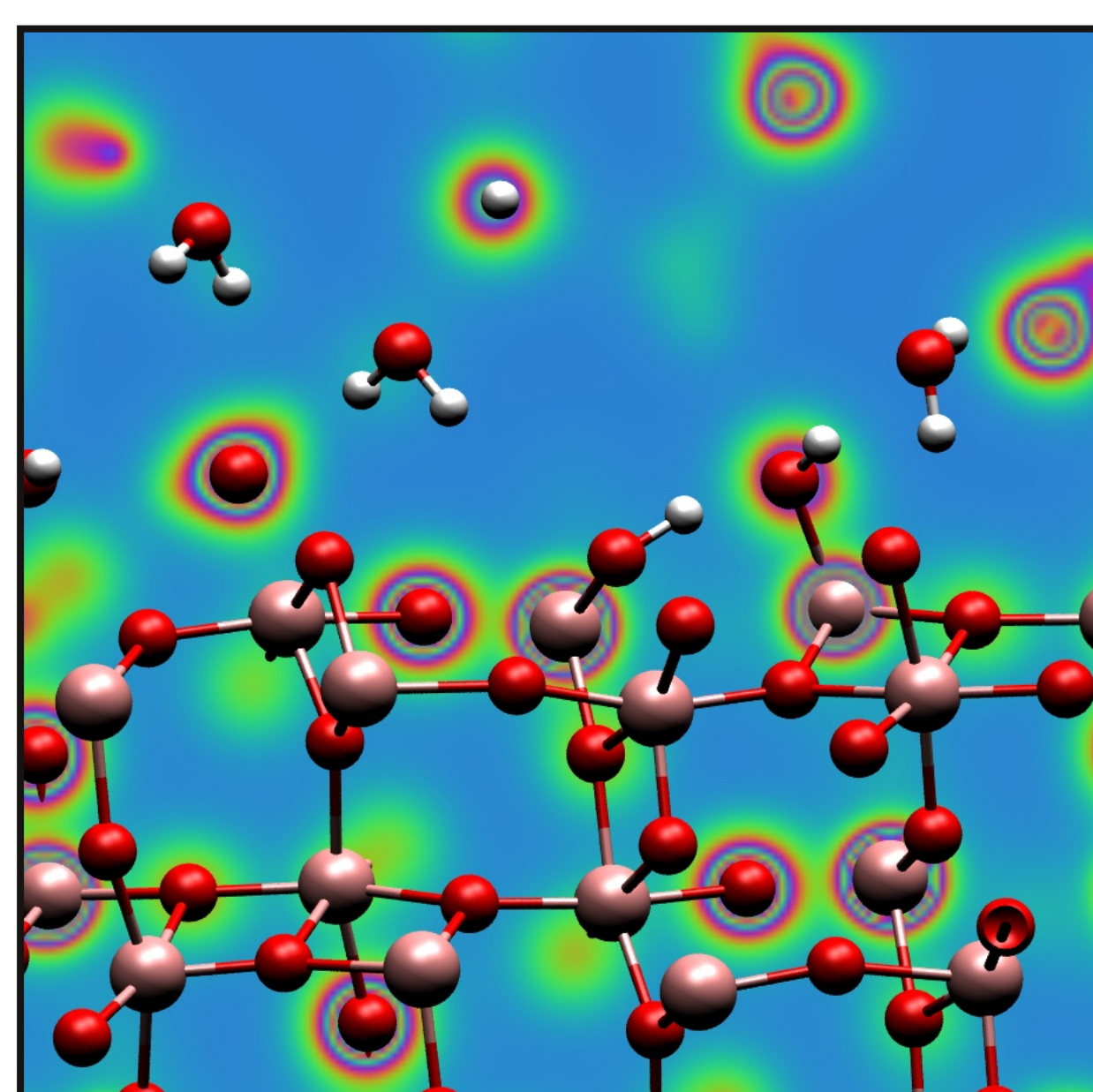
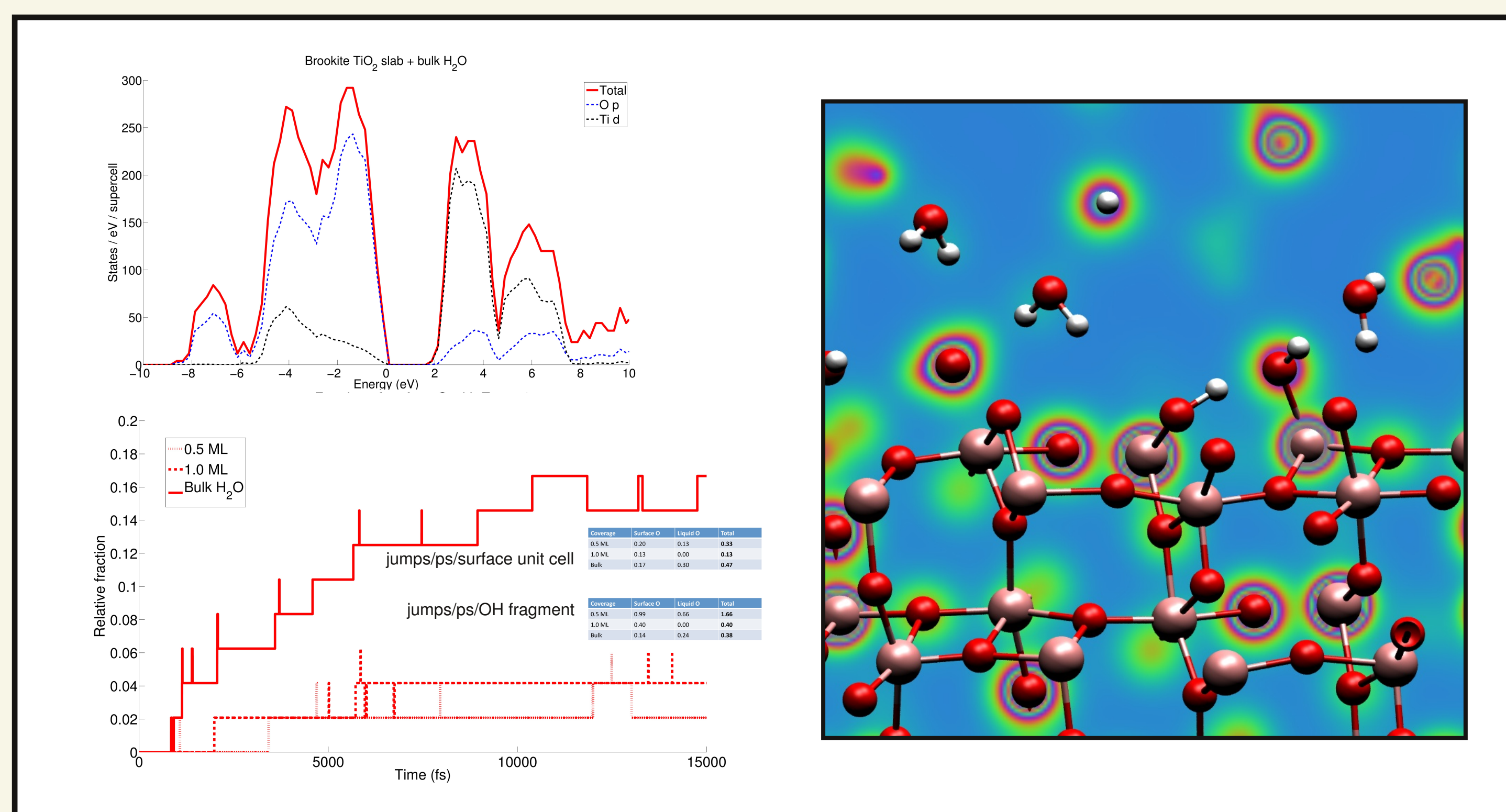
Below: The brookite (210) surface. **Right:** At low coverages, water mainly adsorbs through covalent Ti-O bonds and hydrogen bonding. Only 3-4% of surface oxygens are hydroxylated.



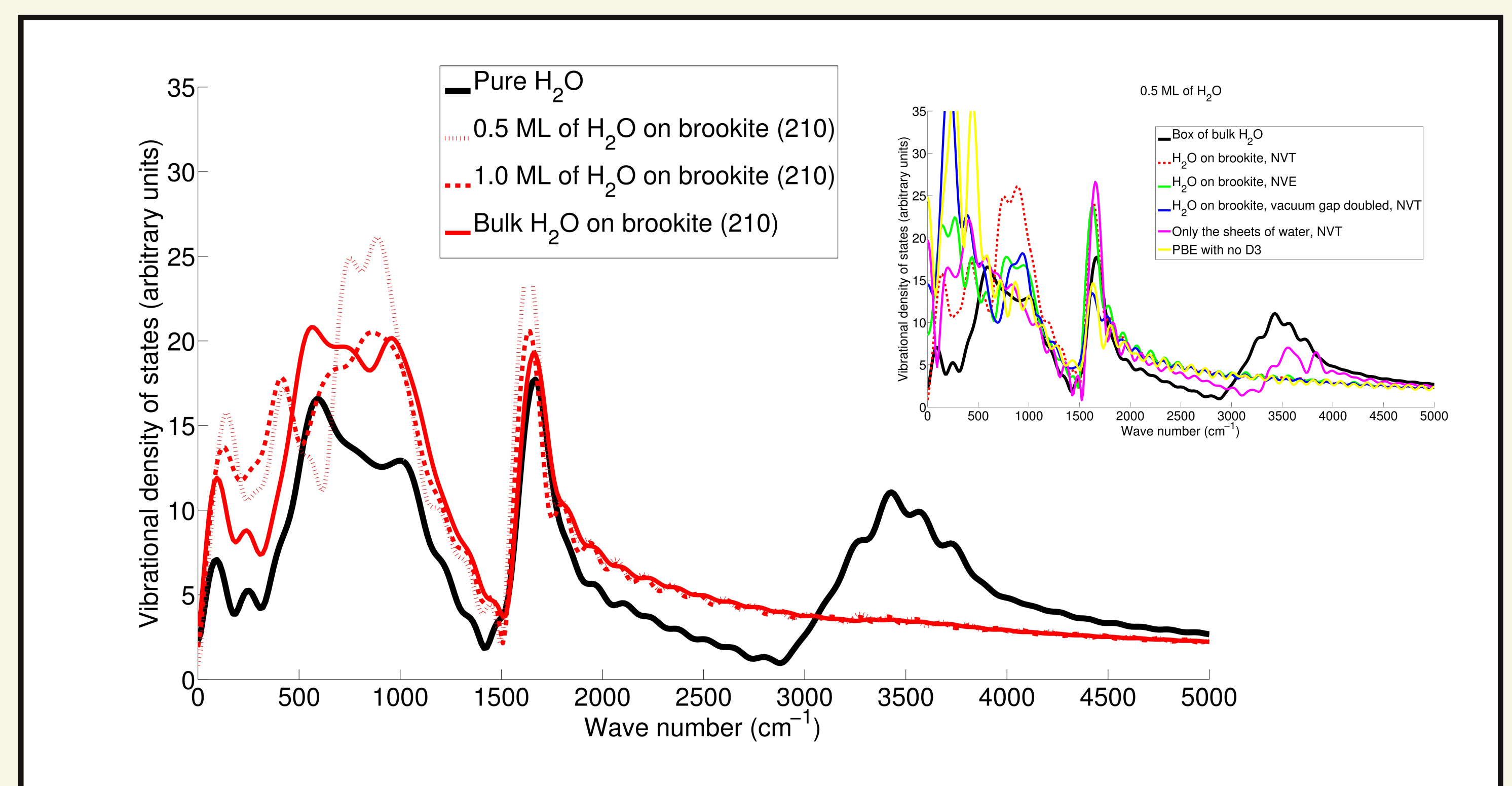
Top: SEM image of brookite nanorods. **Bottom:** FM-AFM on the brookite (210) surface on these at 100 mM KCl aq. These initial AFM results highlight the non-trivial hydration structure of this solid-liquid interface.



Above: Histogram of lateral ionic positions. Red dots signify bridging O_{2c} , light green dots signify Ti_{5c} . At bulk H_2O coverage, about 15% of surface oxygens are hydroxylated. The rows of Ti_{5c} are covered by H_2O molecules, adsorbed through weak covalent Ti-O bonds and through hydrogen bonds to nearby O_{2c} pairs, as well as OH fragments (see panel below).



Top left: The electronic density of states is featureless near the band gap. **Bottom left:** Hydroxylation leads to proton transfer at the interface. **Right:** electronic density in a plane through an OH fragment.



The OH stretching band of H_2O is drastically red-shifted at the solid-liquid interface. We are currently planning experimental measurements to test this theoretical prediction for the vibrational spectrum.