

Investigation of the Adsorption of Phosphonic Acid on the Rutile TiO₂(110) Surface for Water Splitting Applications

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Photoelectrochemical (PEC) cells are used to achieve water splitting thanks to a semiconductor photocatalyst. A suitable photocatalyst should be stable and have band-edge potentials suitable for overall water splitting, as in order to have spontaneous water splitting, the band edges of the semiconductor must straddle the potentials for the hydrogen and oxygen evolution reactions¹. Titania has been the pioneer electrode material since the discovery of its UV light-driven photocatalytic water splitting properties in 1972, but it has some intrinsic limitations like the inability to harvest visible light². In this regard, functionalization of TiO₂ surfaces with functional organic molecules is considered a way to tune titania's properties.

In this joint experimental and theoretical work, the (110) surface of rutile TiO₂ has been functionalized with phosphonic acid (H₃PO₃), which has good long-term stability and high affinity towards metal oxide surfaces³. The exact binding of the phosphonic acid to the TiO₂ surface is not easy to assess experimentally and is still much debated^{3,4}. With *ab-initio* simulations carried out with the CP2K code we show that the bidentate mode is the most favorable adsorption mode of phosphonic acid on rutile (110).

Theoretical models and computational studies are fundamental to describe PEC interfacial properties; in this regard the band alignment between photoelectrode band edges and water redox potentials is of crucial interest⁵. An electronic analysis shows that at high H₃PO₃ coverages, the titania bands are shifted upwards, resulting in a higher photo voltage. An analysis of the absorption of benzyl phosphonic acid on titania (110) shows that the cause of the band shift is the dipole moment of the molecule.

The computational results will be compared to the experimental data and possible reasons for disagreements will be discussed.

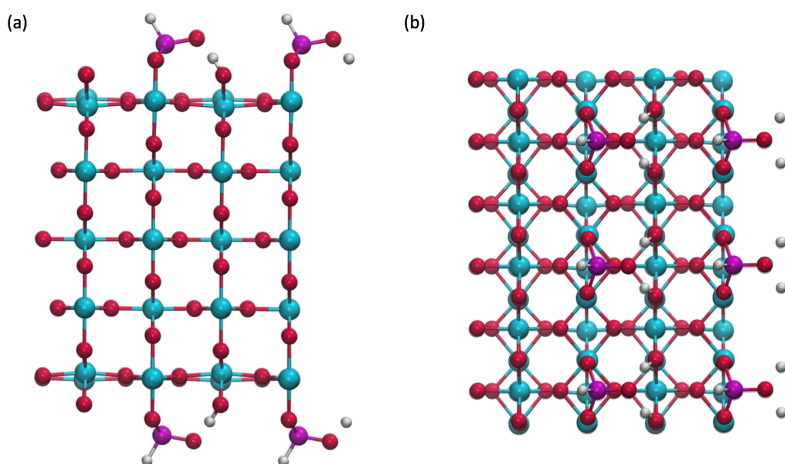


Fig. 1: Optimized side (a) and top (b) view of phosphonic acid (H₃PO₃) adsorbed on rutile (110) titania. The acid is adsorbed in the bidentate configuration, the most stable one.

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