Aqueous Semiconductor Interface Structure and Electrochemical Energy Level Alignment.[1]

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Understanding structure-function relationships at aqueous semiconductor interfaces must start from the discovery of the key interface structure motifs themselves. Important examples include the alignment of electrochemical redox levels with the semiconductor band edges and the identification of catalytic active sites. We simulate interface structure using ab initio molecular dynamics (AIMD) [1]. The degree to which interface water molecules are dissociated depends on the specific semiconductor. The proximal hydration layer structure affects the kinetic processes that control the interface equilibration. To connect the interface structure to the electrochemical redox levels, the calculated, average interface dipole is combined with the GW approach from many-body perturbation theory to calculate the energy level alignment between the semiconductor band edges and the centroid of the occupied $1b_1$ energy level of water and thus, the electrochemical levels [2]. The degree of interface water dissociation and the dynamical flexibility of the hydration layer both affect the level alignment. Finally, the presence of protons and hydroxyl groups at the interface affect hole localization. Results will be discussed for GaN, ZnO, and both rutile and anatase forms of TiO_2. [1] N. Kharche, et al., *Phys. Chem. Chem. Phys.* 16, 12057 (2014). [2] N. Kharche, et al., *Phys. Rev. Lett.* 113, 176802 (2014).