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Hole localization, water dissociation mechanisms, and band alignment at aqueous-titania interfaces¹

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Photocatalytic water splitting is a promising method for generating clean energy, but materials that can efficiently act as photocatalysts are scarce. This is in part due to the fact that exposure to water can strongly alter semiconductor surfaces and therefore photocatalyst performance. Many materials are not stable in aqueous environments; in other cases, local changes in structure may occur, affecting energy-level alignment. Even in the simplest case, dynamic fluctuations modify the organization of interface water. Accounting for such effects requires knowledge of the dominant local structural motifs and also accurate semiconductor band-edge positions, making quantitative prediction of energy-level alignments computationally challenging. Here we employ a combined theoretical approach to study the structure, energy alignment, and hole localization at aqueous-titania interfaces. We calculate the explicit aqueous-semiconductor interface using ab initio molecular dynamics, which provides the fluctuating atomic structure, the extent of water dissociation, and the resulting electrostatic potential. For both anatase and rutile TiO_2 we observe spontaneous water dissociation and re-association events that occur via distinct mechanisms. We also find a higher-density water layer occurring on anatase. In both cases, we find that the second monolayer of water plays a crucial role in controlling the extent of water dissociation. Using hybrid functional calculations, we then investigate the propensity for dissociated waters to stabilize photo-excited carriers, and compare the results of rutile and anatase aqueous interfaces. Finally, we use the GW approach from many-body perturbation theory to obtain the position of semiconductor band edges relative to the occupied $1b_1$ level and thus the redox levels of water, and examine how local structural modifications affect these offsets.

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