

Supporting Information for “Interfacial Effects on the Band Edges of Functionalized Si Surfaces in Liquid Water”

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Methods to Compute Semiconductor Band Edges

In this section, we first briefly summarize the approach to compute the valence band maximum (VBM) and conduction band minimum (CBM) positions of a semiconductor in vacuum, widely employed in, e.g., Refs. 1–4. We then propose a scheme to compute these quantities for semiconductors in the presence of liquid water. Results obtained with the former approach may be compared with photoemission measurements in the absence of water, while those obtained with the latter are to be compared to electrochemical measurements.

Calculations of the VBM and CBM positions of a semiconductor with respect to vacuum are relatively straightforward to carry out, following two separate steps as shown in

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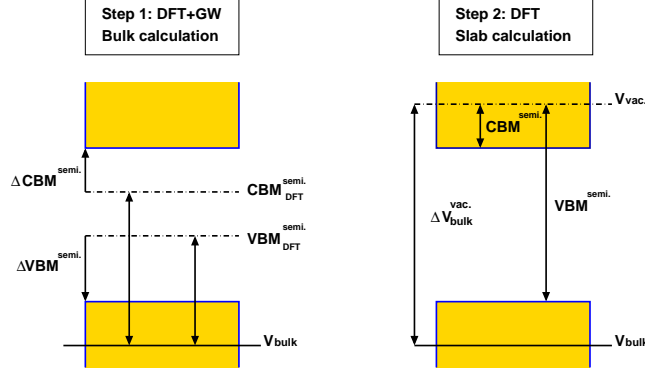


Figure S1: A computational approach to compute band edge positions ($V(C)BM^{\text{semi.}}$) of a semiconductor in vacuum: $V(C)BM_{\text{DFT}}^{\text{semi.}}$ are band edge positions computed at the DFT level of theory with respect to the average electrostatic potential of the bulk semiconductor in a periodic supercell; $\Delta V(C)BM^{\text{semi.}}$ are many-body corrections to the bulk semiconductor band edges, obtained at the G_0W_0 level of theory; and $\Delta V_{\text{bulk}}^{\text{vac.}} = V_{\text{vac.}} - V_{\text{bulk}}$ is the electrostatic potential of the semiconductor relative to vacuum.

Figure S1. In the first step, DFT band edge positions ($V(C)BM_{\text{DFT}}^{\text{semi.}}$) and many-body corrections ($\Delta V(C)BM^{\text{semi.}}$) are computed with respect to the average electrostatic potentials of the corresponding bulk system. The second step involves the evaluation of the average electrostatic potential ($\Delta V_{\text{bulk}}^{\text{vac.}}$) of the bulk semiconductor relative to vacuum by employing a slab model with a specific surface structure in contact with an appropriately thick vacuum region. The band edge positions relative to the vacuum level, i.e., band edge positions on an absolute scale, are then computed as:

$$\begin{aligned} VBM^{\text{semi.}} &= VBM_{\text{DFT}}^{\text{semi.}} + \Delta VBM^{\text{semi.}} + \Delta V_{\text{bulk}}^{\text{vac.}} \\ CBM^{\text{semi.}} &= CBM_{\text{DFT}}^{\text{semi.}} + \Delta CBM^{\text{semi.}} + \Delta V_{\text{bulk}}^{\text{vac.}}, \end{aligned} \quad (1)$$

where the many-body corrections were obtained at the G_0W_0 level of theory, and $\Delta V_{\text{bulk}}^{\text{vac.}}$ was computed within DFT, since in our GW calculations we did not update the wavefunctions self-consistently.

The VBM and CBM obtained from Eq. 1 correspond to the ionization potential (IP) and electron affinity (EA) of the semiconductor measured in photoemission experiments, in the absence of water. In contrast, band edge positions measured in electrochemical

experiments on an absolute scale provide energies relative to a point in the vacuum just outside the solution.⁵⁻⁷ A computational framework to compute these band edge positions is outlined in Figure S2 and it involves two steps: (i) calculation of the band offset between liquid water and the semiconductor with a specific surface structure; and (ii) calculation of band edge positions of liquid water relative to vacuum.

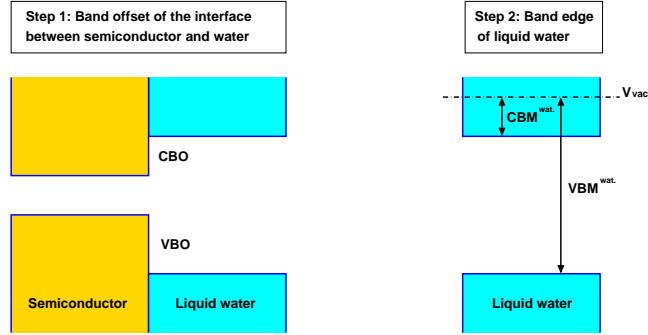


Figure S2: A computational approach to compute band edge positions of a semiconductor in the presence of liquid water: VBO and CBO are valence and conduction band offsets between liquid water and a semiconductor, respectively; $\text{VBM}^{\text{wat.}}$ and $\text{CBM}^{\text{wat.}}$ are band edges of liquid water relative to vacuum.

The latter (step 2 of Figure S2) were computed in Ref. 8 using many-body perturbation theory within the G_0W_0 approximation. Thus, we are left with the task of carrying out band offset calculations at the semiconductor-liquid interface (step 1 of Figure S2), which we performed using a bulk-plus-line up procedure⁹ that contains two terms, i.e., the bulk band positions, $\text{V(C)BM}_{\text{bulk}}^{\text{semi.}(\text{wat.})}$, and the line up term ΔV :

$$\begin{aligned} \text{VBO} &= \text{VBM}_{\text{bulk}}^{\text{semi.}} - \text{VBM}_{\text{bulk}}^{\text{wat.}} - \Delta V, \\ \text{CBO} &= \text{CBM}_{\text{bulk}}^{\text{semi.}} - \text{CBM}_{\text{bulk}}^{\text{wat.}} - \Delta V. \end{aligned} \quad (2)$$

Here $\text{V(C)BM}_{\text{bulk}}^{\text{semi.}(\text{wat.})}$ are band edge positions of semiconductor and liquid water with respect to the average electrostatic potentials of the corresponding bulk systems, while ΔV is the discontinuity of the average electrostatic potential across the semiconductor-liquid interfaces. The line up term ΔV is computed within DFT for the whole interface containing

the semiconductor and water; to correct the DFT errors on band offsets, we included G_0W_0 corrections obtained from bulk calculations on VBM and CBM eigenvalues, following the scheme described in Ref. 10.

Details of GW Calculations

All the GW results presented in this work were calculated at the G_0W_0 level of theory,¹¹ i.e., the quasiparticle energies (E_n^{qp}) were computed as a first-order correction to the Kohn-Sham energies:

$$E_n^{qp} = \epsilon_n + \langle \psi_n | \Sigma_{G_0W_0}(E_n^{qp}) | \psi_n \rangle - \langle \psi_n | V_{xc} | \psi_n \rangle, \quad (3)$$

where V_{xc} is the exchange-correlation potential entering the chosen Kohn-Sham Hamiltonian, and $\Sigma_{G_0W_0}$ is the self-energy operator, computed from the one-particle Green's function (G_0) and the screened Coulomb interaction (W_0).

The G_0W_0 calculations were carried out with the method recently developed in Refs. 12,13, which was implemented as a post-processing module in the Quantum-ESPRESSO code.¹⁴ In particular, our G_0W_0 approach does not require the explicit calculation of empty electronic orbitals nor the use of a plasmon-pole model;¹¹ in addition, the convergence of the calculations was controlled by only one parameter, i.e., the number of eigenpotentials employed in the spectral decomposition of the dielectric matrix. These advantages allowed us to carry out G_0W_0 calculations for systems with several hundreds electrons, and to converge quasiparticle energies in a systematic way.^{12,13} Our approach was previously employed to study electronic properties of a variety of systems, including aqueous solutions^{8,15,16} and semiconductors,^{13,17} yielding good agreement with experiments.

Details of Band Edge Calculations

Calculations of the absolute band edge positions of Si(111) surfaces in liquid water require (see Eq. S2): (i) the evaluation of band edge positions of the semiconductor and the liquid with respect to the average electrostatic potentials of the corresponding bulk systems, with many-body corrections; and (ii) the line up term ΔV , i.e., the discontinuity of the average electrostatic potentials accross the solid-liquid interface.

Many-body corrections to the band edge positions of bulk liquid water and Si were carried out using the G_0W_0 approach described in the previous section. For liquid water, we used 1000 dielectric eigenpotentials to represent the dielectric matrix, and we averaged our results over 10 configurations chosen to be equally spaced in time over a trajectory of 20 ps generated by *ab initio* simulations (additional details of the simulations are given in Ref. 8). Calculated positions of the VBM and CBM of liquid water are 8.8 eV and 0.7 eV below the vacuum level, in qualitative agreement with the experimental values of 9.3–9.9 eV and 0.74–1.2 eV,¹⁸ respectively. For bulk Si, we used 800 dielectric eigenpotentials to represent the dielectric matrix, and we obtained a band gap of 1.3 eV, in good agreement with the experimental value of 1.17 eV.¹⁹

The line up term ΔV was computed with DFT-PBE using snapshots extracted every ≈ 0.5 ps from the NVT simulations, and we averaged our results over 30 snapshots. When compared to the value obtained with 20 snapshots, we found a difference less than 0.1 eV, as shown in Fig. S3.

Band Edge Positions of Si(111) Surfaces

Table S1 presents our results obtained at the DFT and G_0W_0 levels of theory for IPs and EAs of different Si(111) surfaces in vacuum, and their comparison with available photoemission experiments. Table S2 presents the calculated band edge positions of the Si(111) surfaces in liquid water obtained at the DFT and G_0W_0 levels of theory. We also summarized our

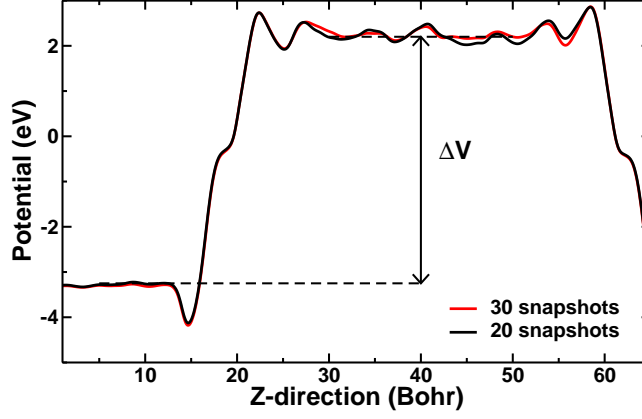


Figure S3: The line-up term ΔV (see text) computed at the COOH–Si(111)/water interface, using 30 snapshots (red) and 20 snapshots (black) extracted from *ab initio* MD simulations performed at constant T (NVT).

results in Table S1 and Table S2 in Figure S4.

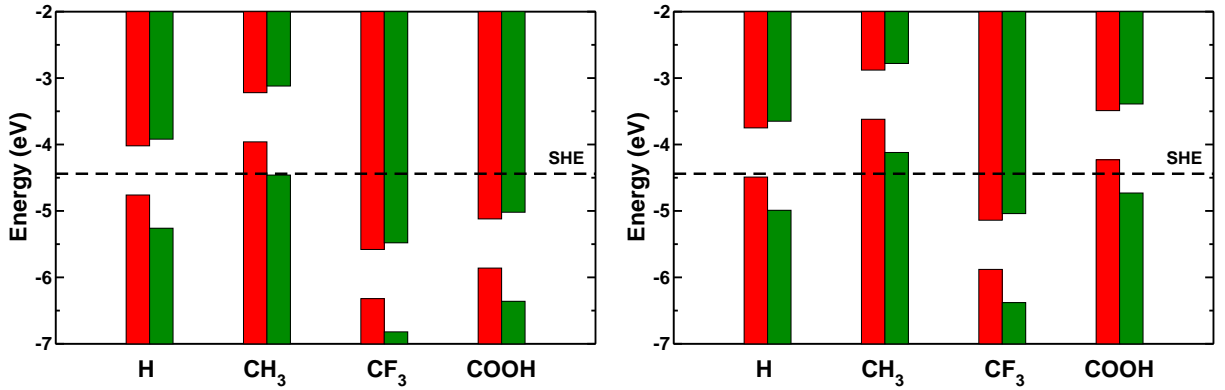


Figure S4: Left panel: Band edge positions of the functionalized Si(111) surfaces in the absence of liquid water, as computed at the DFT/PBE (red) and G_0W_0 (green) levels of theory. Right panel: same quantities computed for functionalized Si(111) surfaces in the presence of liquid water.

Table S1: Ionization potential (IP) and electron affinity (EA) of H–, CH₃–, CF₃– and COOH–terminated Si(111) surfaces in the absence of liquid water, as computed using Density Functional Theory (DFT) with the PBE functional and the G₀W₀ approximation. Results from photoelectron spectroscopy (Expt.) are also included when available.^{20,21} Theoretical results obtained with the LDA approximation are given in parentheses.²¹

	DFT	G ₀ W ₀	Expt. ^{20,21}
H–			
IP	4.76 (4.83)	5.26 (5.46)	5.29-5.31
EA	4.02 (4.10)	3.92 (3.93)	
CH ₃ –			
IP	3.96 (4.06)	4.46 (4.71)	4.76-4.80
EA	3.22 (3.36)	3.12 (3.21)	
CF ₃ –			
IP	6.32	6.82	
EA	5.58	5.48	
COOH–			
IP	5.86	6.36	
EA	5.12	5.02	

Table S2: Band edge positions of H–, CH₃–, CF₃– and COOH–terminated Si(111) surfaces in the presence of liquid water, as computed at the DFT/PBE and G₀W₀ levels of theory. Results from electrochemical measurements are also included when available.²²

	DFT	G ₀ W ₀	Expt. ²²
H–			
VBM	4.49	4.99	5.10
CBM	3.75	3.65	3.98
CH ₃ –			
VBM	3.62	4.12	
CBM	2.88	2.78	
CF ₃ –			
VBM	5.88	6.38	
CBM	5.14	5.04	
COOH–			
VBM	4.23	4.73	
CBM	3.49	3.39	

Geometrical Coordinates

We provided geometrical coordinates (xyz files) for all functionalized Si(111) surfaces optimized in vacuum using DFT with the PBE functional, and for 20 snapshots of Si-water interfaces extracted equally from each molecular dynamics trajectory. For surfaces optimized in vacuum, we used an orthorhombic supercell and lattice parameters $a = 11.625 \text{ \AA}$, $b = 13.424 \text{ \AA}$ and $c = 37.0 \text{ \AA}$. We used orthorhombic supercells with lattice parameters (\AA) of (11.625, 13.424, 33.435), (11.625, 13.424, 35.735), (11.625, 13.424, 37.035) and (11.625, 13.424, 35.735) for H-, CH₃-, CF₃- and COOH-terminated Si(111) surfaces interfaced with liquid water, respectively.

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