Lessons from a challenging system: accurate adsorption free energies at the amino acid / ZnO interface

SUPPORTING INFORMATION

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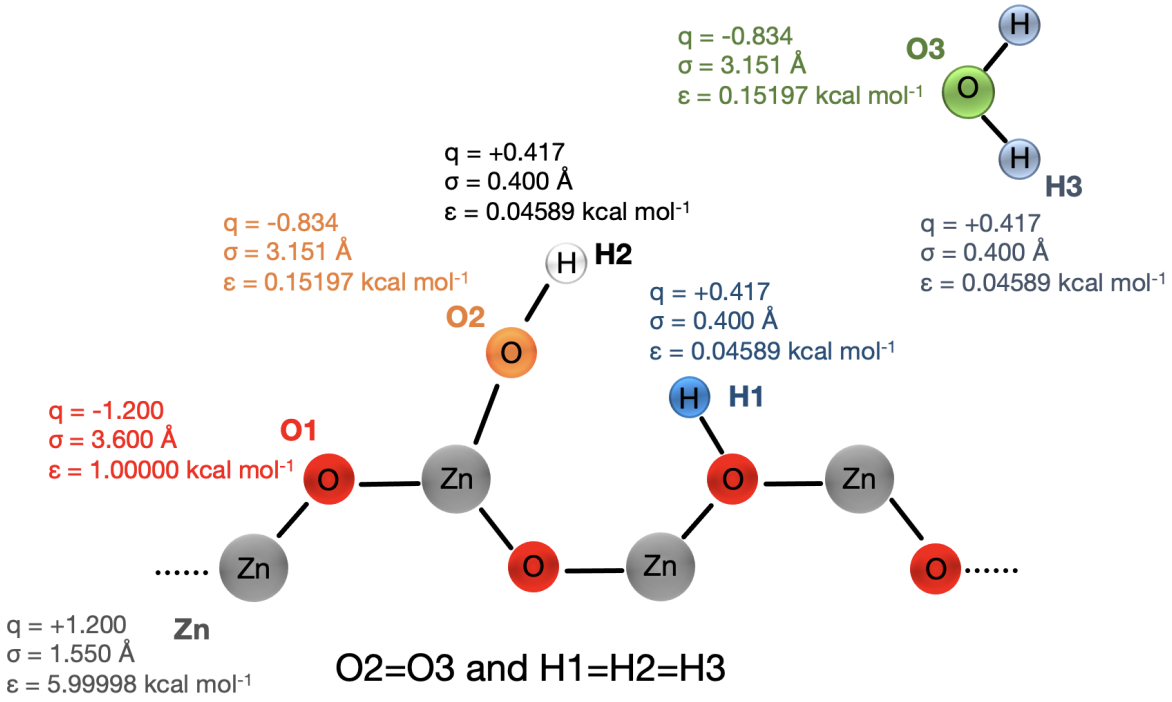
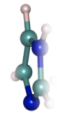


Pair interaction



N

q = -0.7
σ = 3.296 Å
ε = 0.19993 kcal mol-1

σ_{ij} = 2.080 Å
ε_{ij} = 3.22040 kcal mol-1

Zn

q = +1.200
σ = 1.550 Å
ε = 5.99998 kcal mol-1

Figure S1: *Final parameter set for the ZnO force field employed in the present paper.*

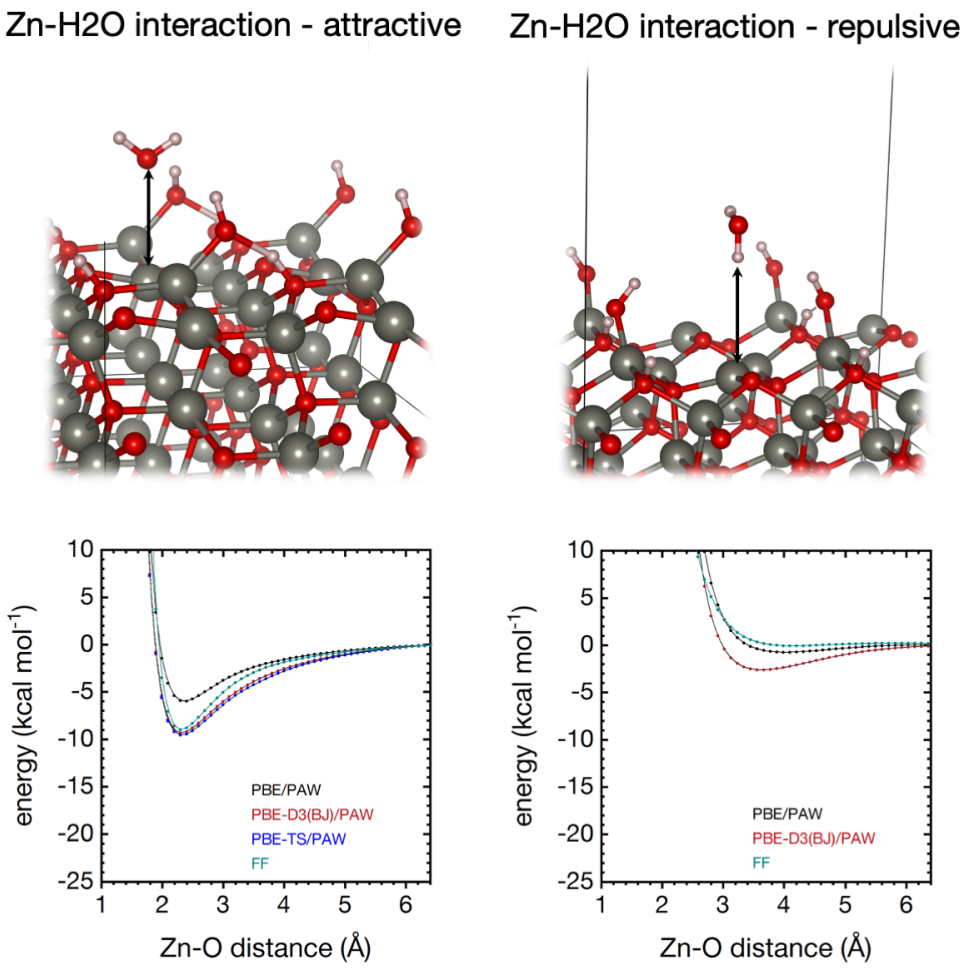


Figure S2: *Distance-energy curves for the water-Zn(O) interactions. Both DFT and classical (FF) curves are provided. Above the curves, a ball and stick representation of the investigated interaction is reported (Color code: O, red; Zn, grey; C, cyan; N, blue; S, yellow; H, white).*

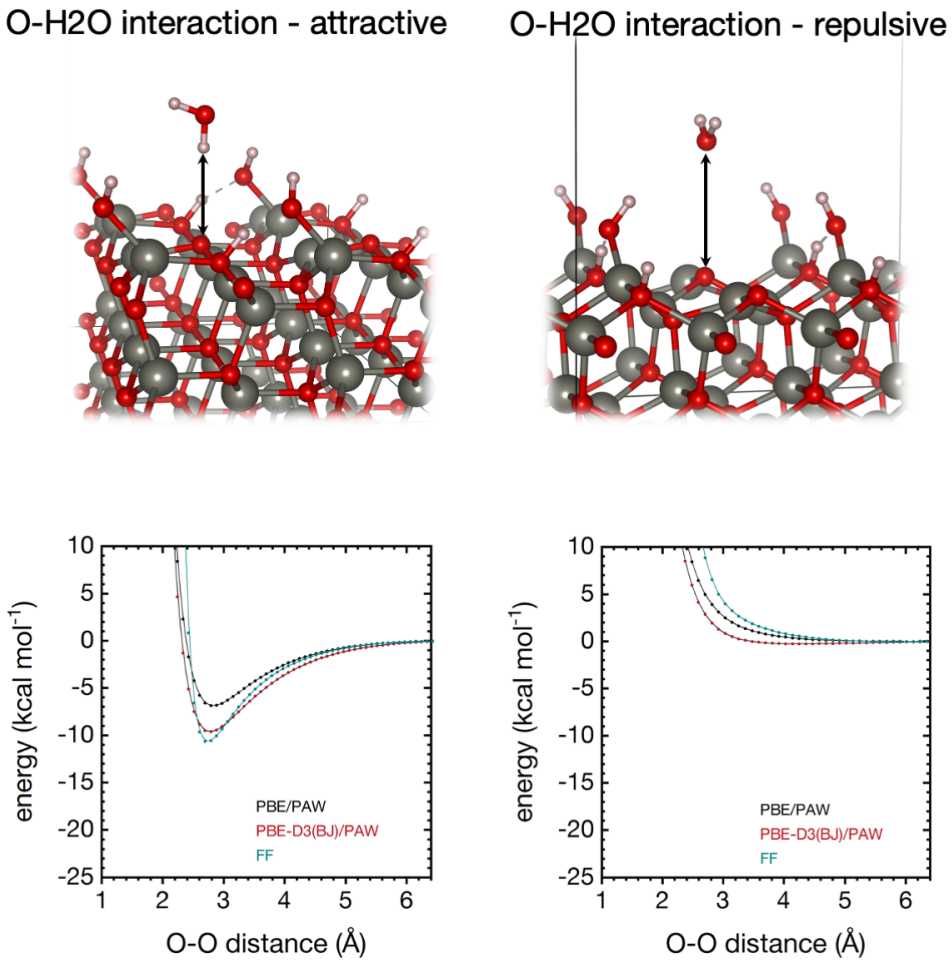


Figure S3: *Distance-energy curves for the water-O(Zn) interactions. Both DFT and classical (FF) curves are provided. Above the curves, a ball and stick representation of the investigated interaction is reported (Color code: O, red; Zn, grey; C, cyan; N, blue; S, yellow; H, white).*

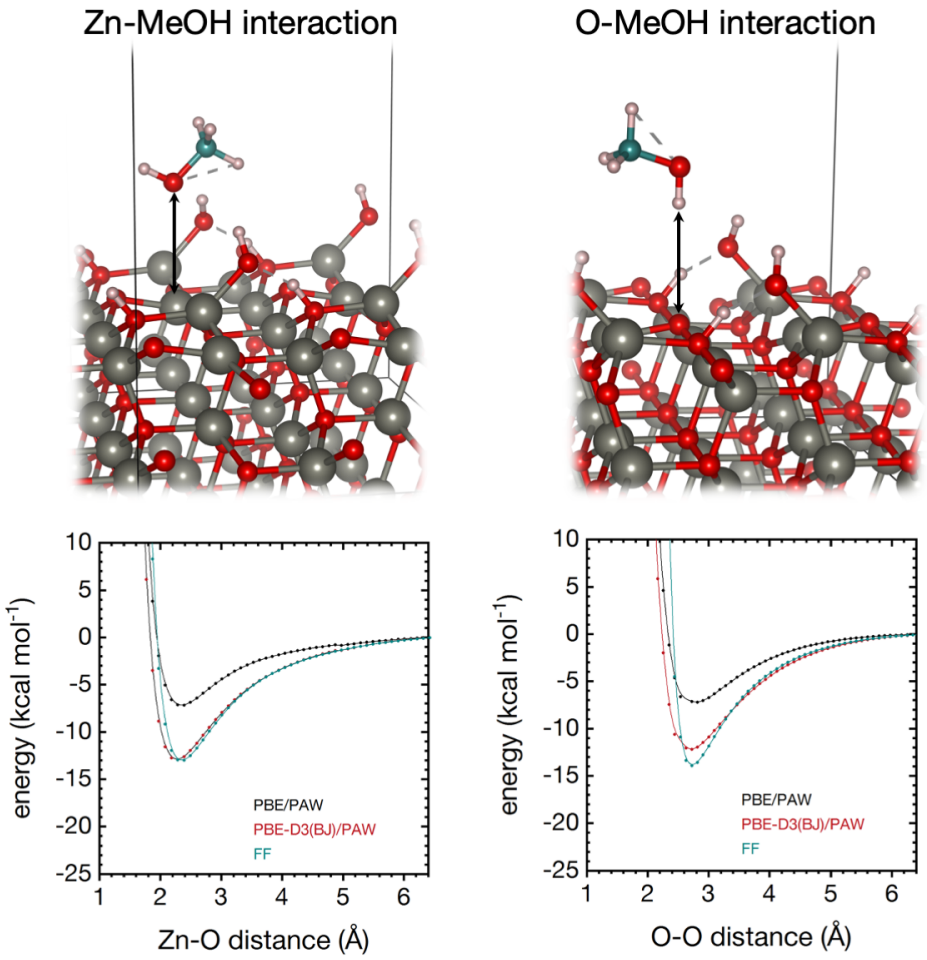


Figure S4: *Distance-energy curves for the methanol-ZnO interactions. Both DFT and classical (FF) curves are provided. Above the curves, a ball and stick representation of the investigated interaction is reported (Color code: O, red; Zn, grey; C, cyan; N, blue; S, yellow; H, white).*

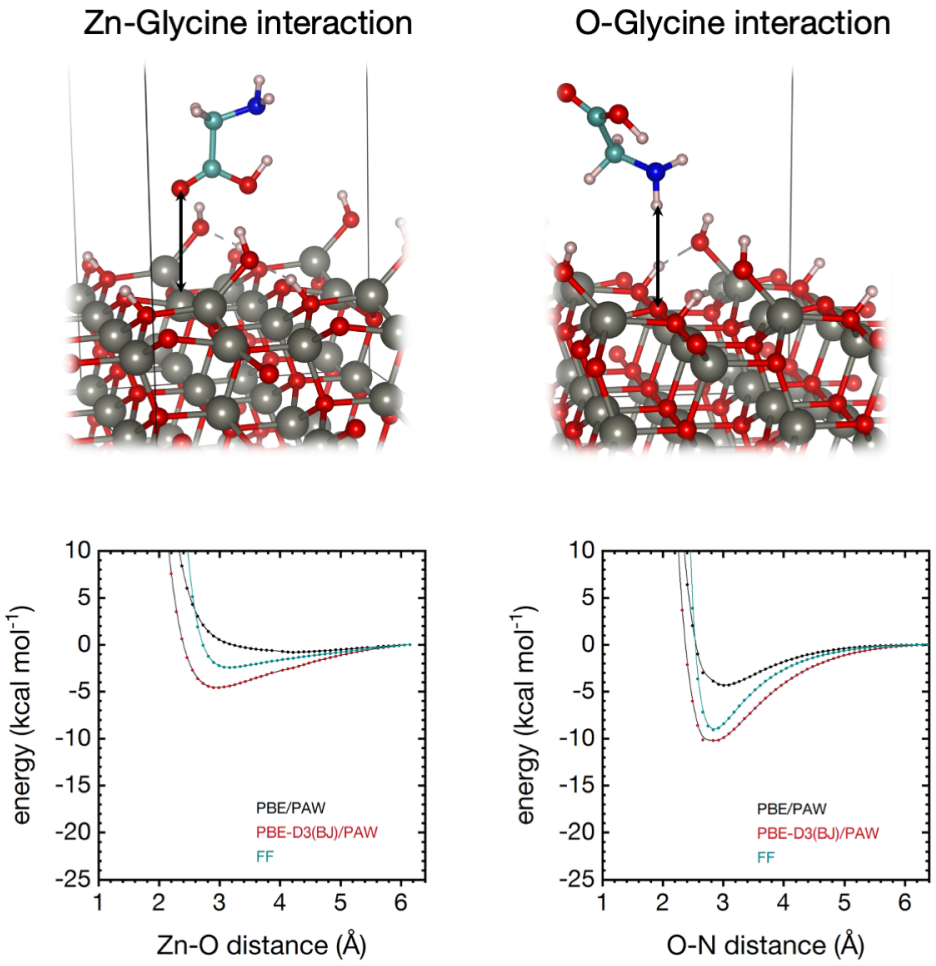


Figure S5: *Distance-energy curves for the glycine-ZnO interactions. Both DFT and classical (FF) curves are provided. Above the curves, a ball and stick representation of the investigated interaction is reported (Color code: O, red; Zn, grey; C, cyan; N, blue; S, yellow; H, white).*

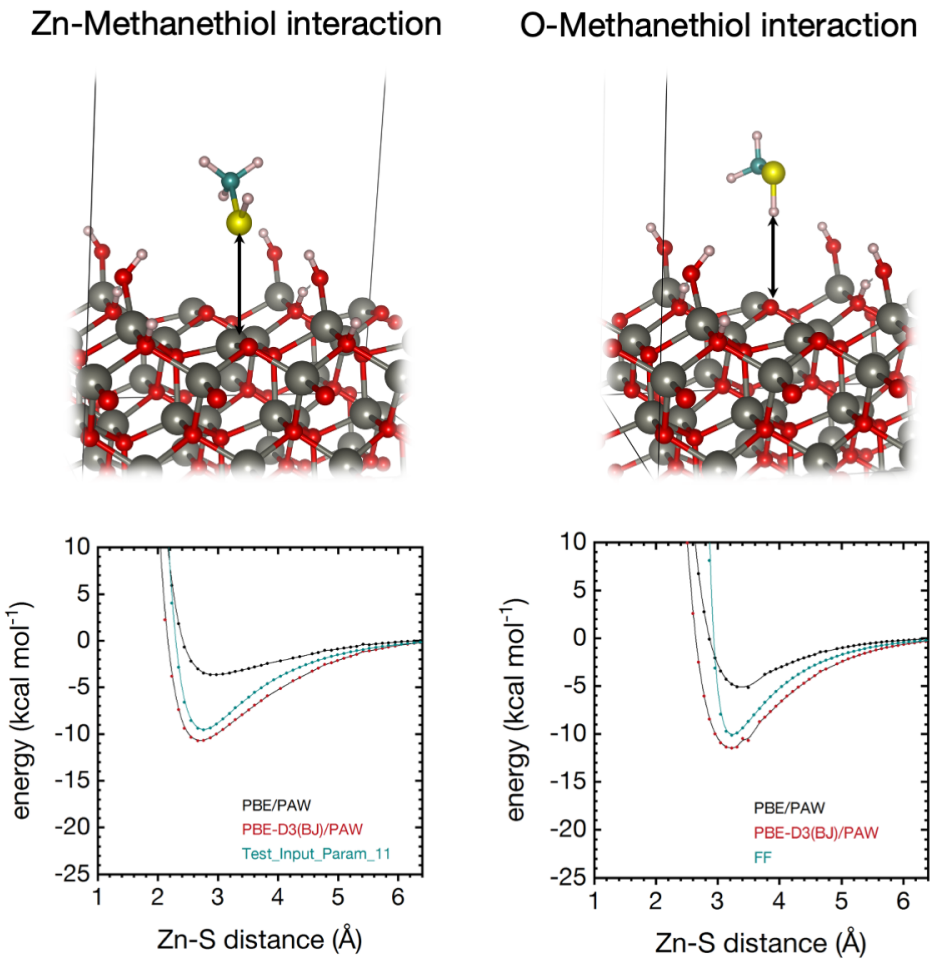


Figure S6: *Distance-energy curves for the methanethiol-ZnO interactions. Both DFT and classical (FF) curves are provided. Above the curves, a ball and stick representation of the investigated interaction is reported (Color code: O, red; Zn, grey; C, cyan; N, blue; S, yellow; H, white).*

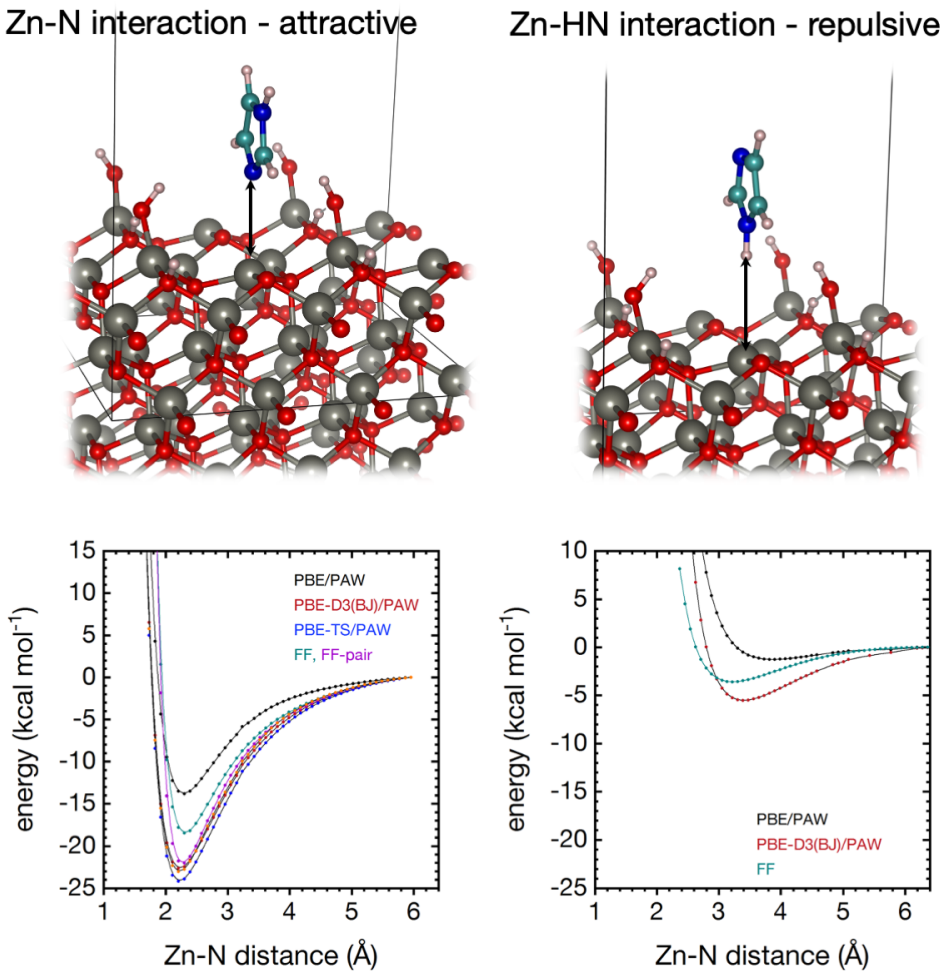


Figure S7: *Distance-energy curves for the imidazole-ZnO interactions. Both DFT and classical (FF) curves are provided. Above the curves, a ball and stick representation of the investigated interaction is reported (Color code: O, red; Zn, grey; C, cyan; N, blue; S, yellow; H, white).*

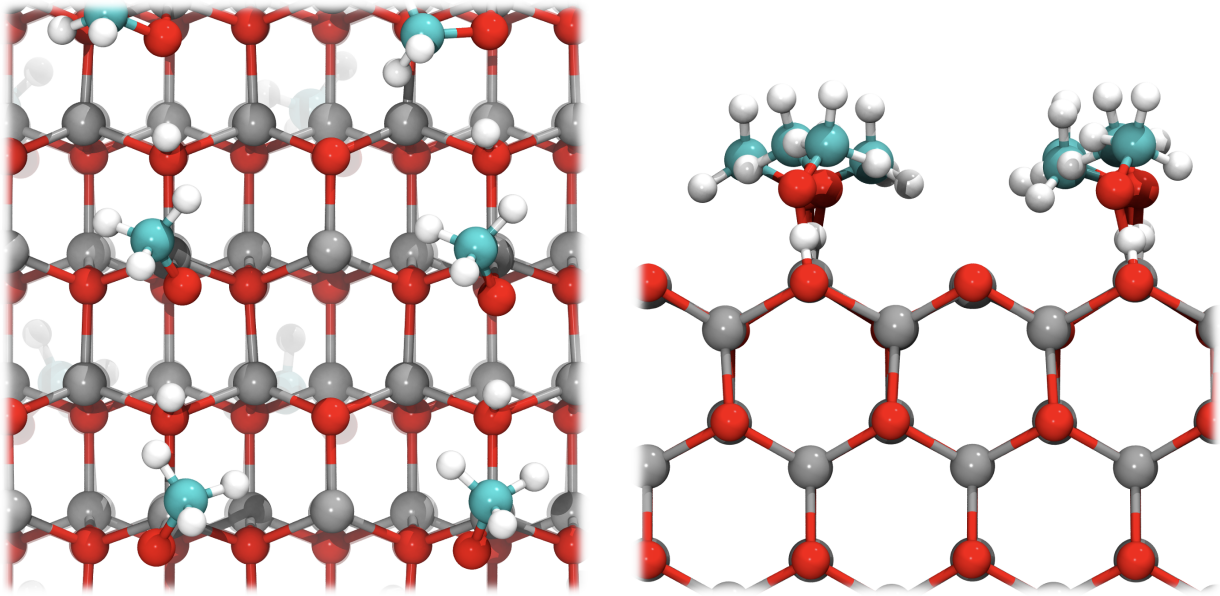


Figure S8: *Top (left) and side (right) view of a ZnO ($10\bar{1}0$) surface after a 50% dissociation of an adsorbed methanol monolayer, resulting in OH and methoxy functionalities (Color code: O, red; Zn, grey; C, cyan; H, white).*

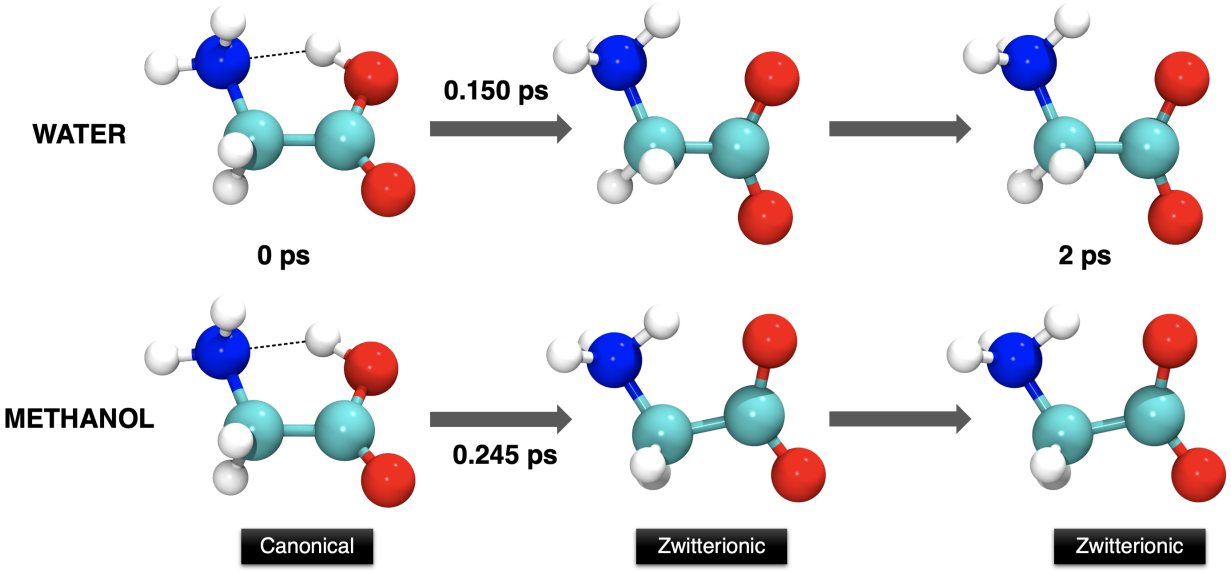


Figure S9: *Visualization of glycine at different times of DFT molecular dynamics simulations in water and methanol, both starting with the amino acid in its canonical form.*

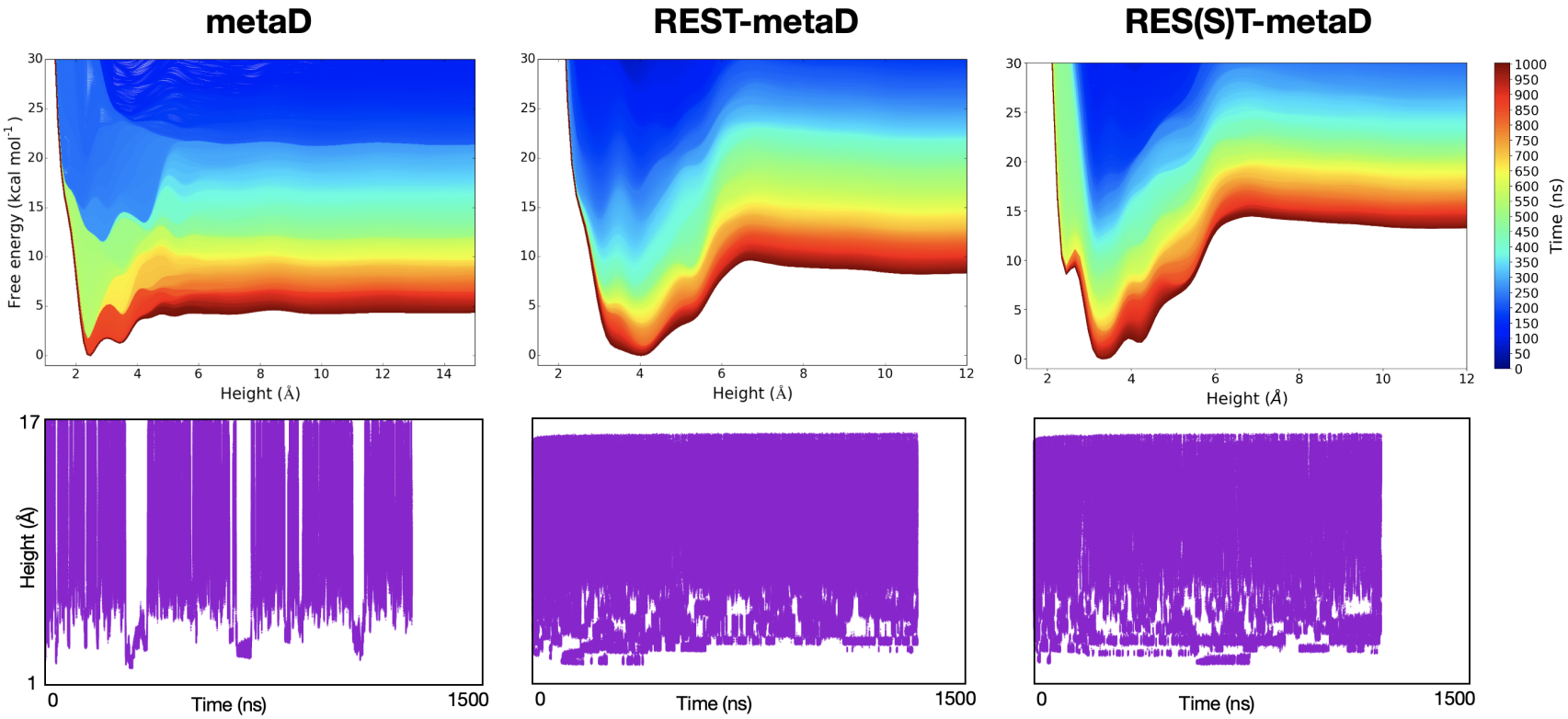


Figure S10: *Comparison in performance between different enhanced sampling methods for the zwitterionic Hid adsorption on the ZnO $(10\bar{1}0)$ surface sporting a 25% degree of surface hydroxylation. metaD: standard metadynamics with CV set as the height h of the amino acid's center of mass with respect to the surface. REST-metaD: metadynamics augmented with Replica Exchange with Solute Tempering (solute = amino acid). RES(S)T-metaD: metadynamics augmented with Replica Exchange with Solute and Surface Tempering. Top: evolution of the free energy profiles profiles during the simulations, according to the color scale on the right. The zero of the free energies is set at the minimum value. Bottom: value of the CV along the simulations.*

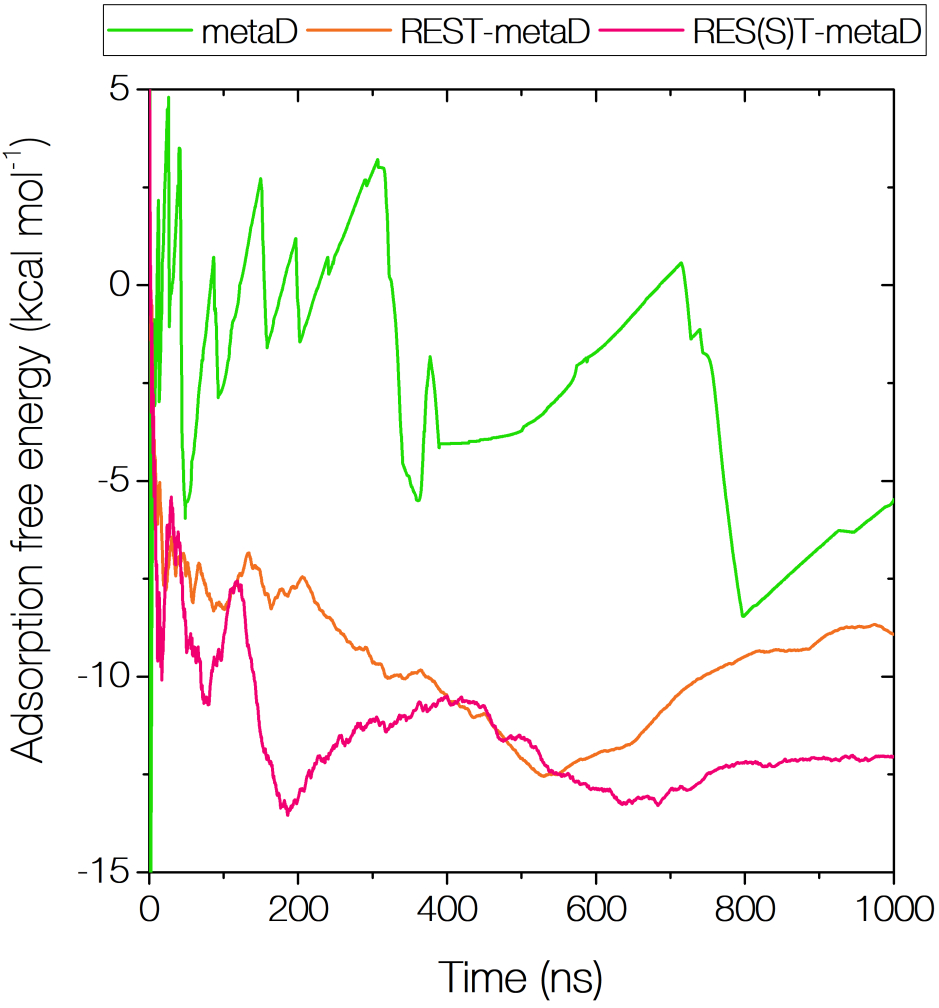


Figure S11: *Variation of the adsorption free energy of zwitterionic Hid on the ZnO (10$\bar{1}$0) surface, along the three tested enhanced sampling simulations. metaD: standard metadynamics with CV set as the height h of the amino acid's center of mass with respect to the surface. REST-metaD: metadynamics augmented with Replica Exchange with Solute Tempering (solute = amino acid). RES(S)T-metaD: metadynamics augmented with Replica Exchange with Solute and Surface Tempering.*

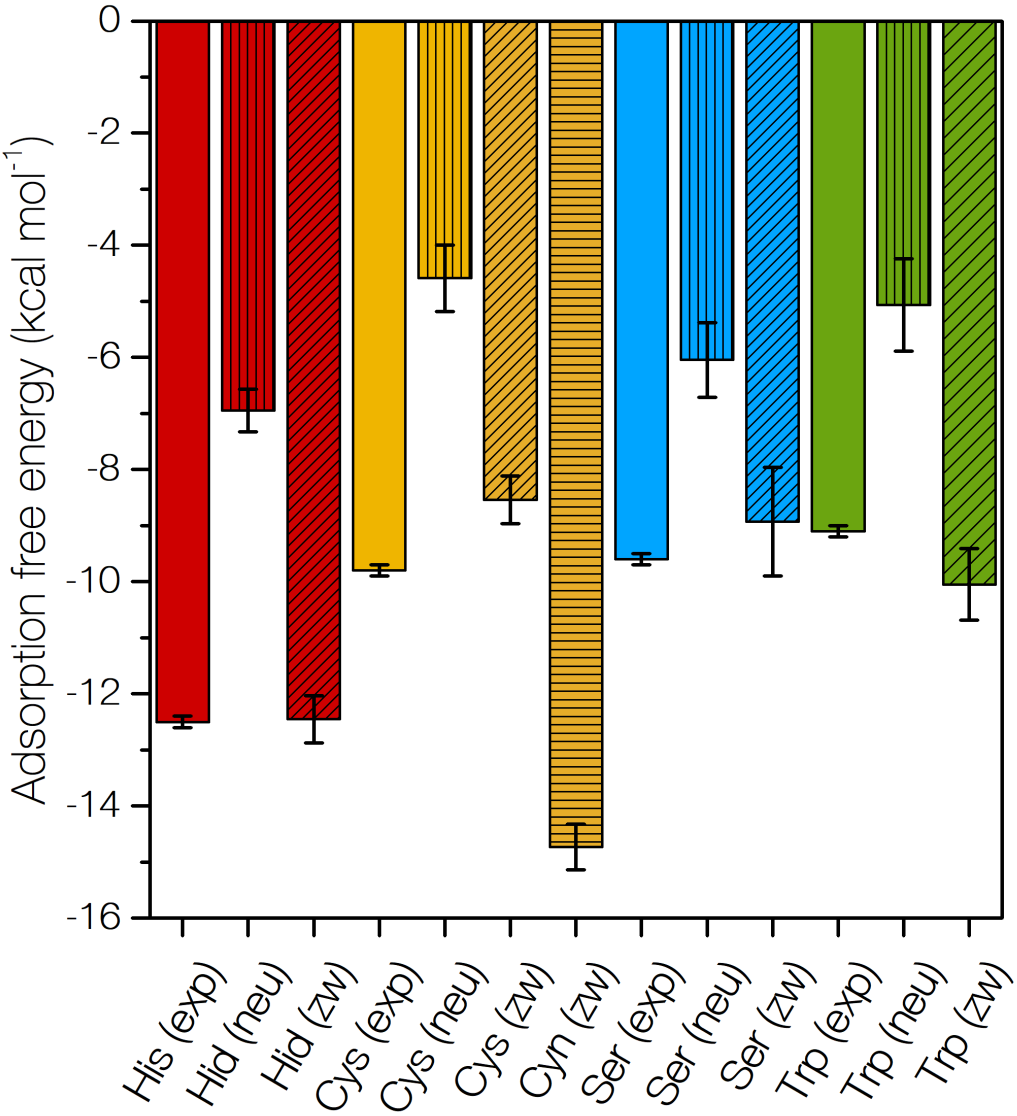


Figure S12: *Adsorption free energy for the selected amino acids in methanol, in comparison with the experimental O-IDA values. exp: experiment; neu: neutral form of the amino acid; zw: zwitterionic form of the amino acid.*

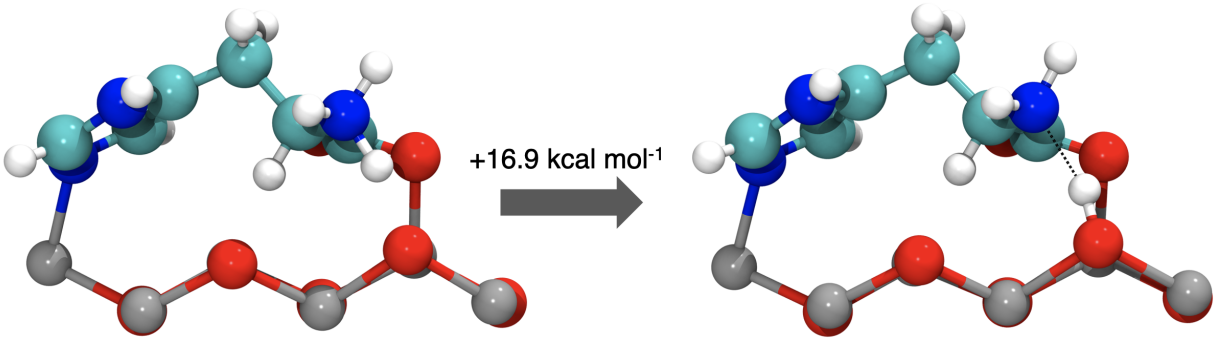


Figure S13: *Full DFT (PBE-D3) geometry optimization of two situations, extracted from the closest adsorption configuration of histidine on the surface: one with zwitterionic histidine (left) and one in which a proton from NH3+ has moved to the surface (right). Only a cutout of the interested atoms is shown, out of the full 844 atoms model.*

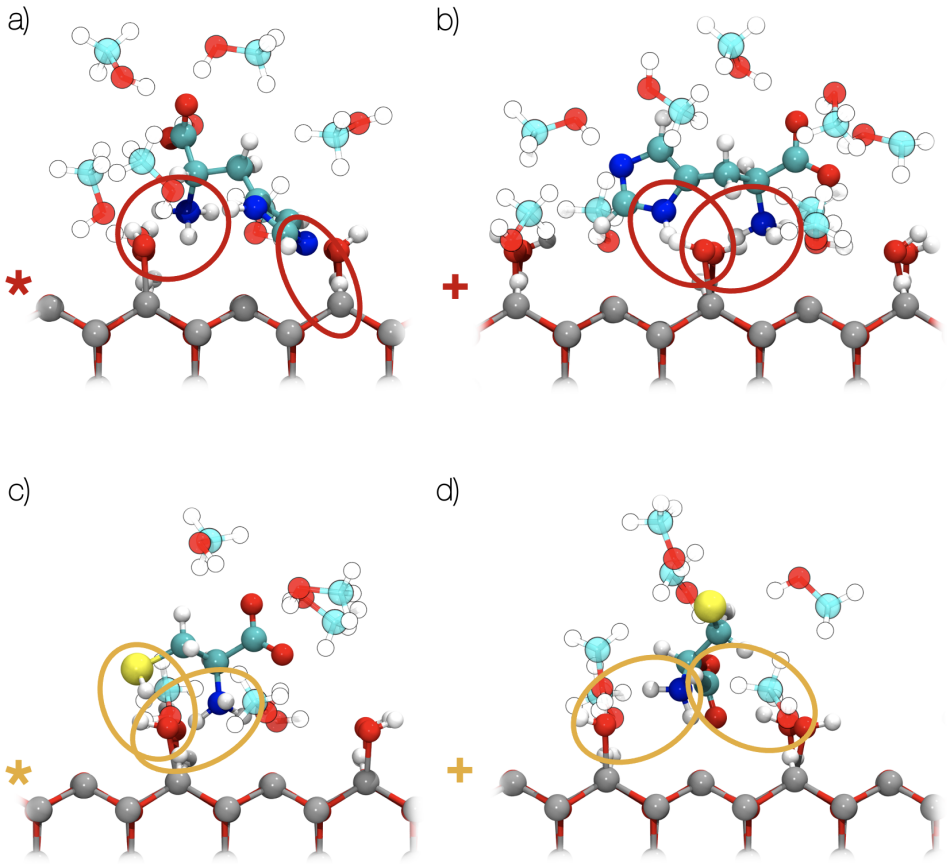


Figure S14: *Exemplary snapshots of the most stable adsorption configurations for the zwitterionic forms of Hid (a-b), Cys (c), Cyn (d) on the ZnO (10$\bar{1}$0) surface in methanol, extracted from the free energy minima identified in the profiles of Fig.6. Color code as in Fig.2 and 3. Only the methanol molecules in close proximity to the amino acids are shown. Circles highlights the main interactions.*

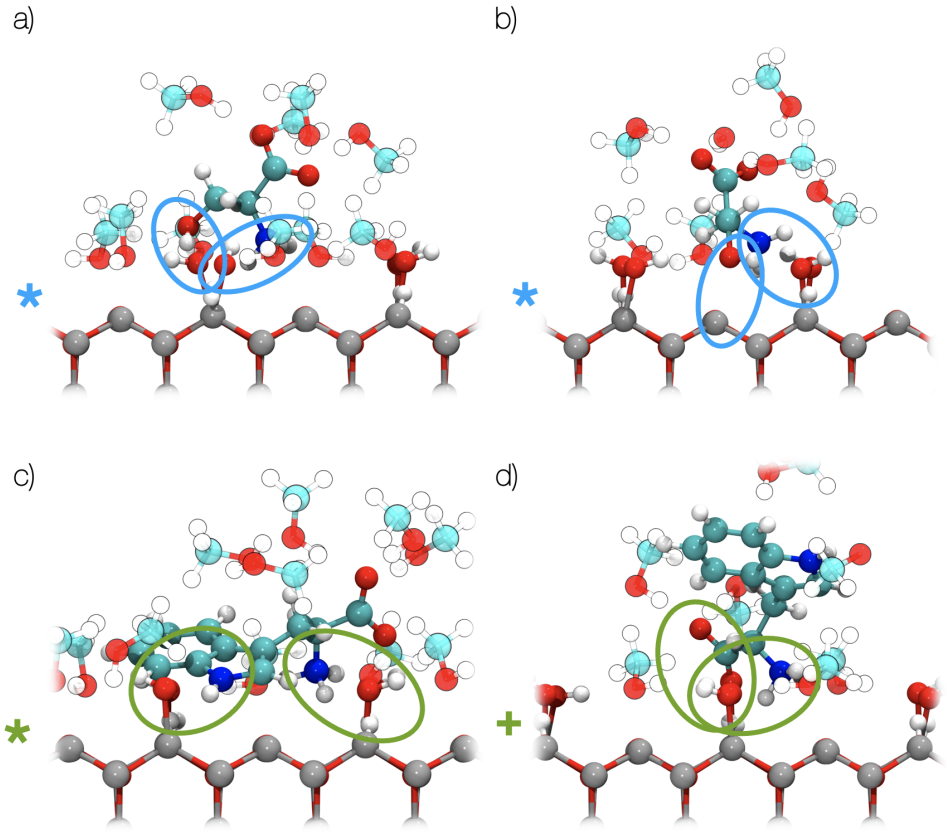


Figure S15: *Exemplary snapshots of the most stable adsorption configurations for the zwitterionic forms of Ser (a-b) and Trp (c-d) on the ZnO (10$\bar{1}$0) surface in methanol, extracted from the free energy minima identified in the profiles of Fig.6. Color code as in Fig.2 and 3. Only the methanol molecules in close proximity to the amino acids are shown. Circles highlights the main interactions.*