A Classical Potential to Model the Adsorption of Biological Molecules on Oxidized Titanium Surfaces (Supporting Information)

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S1 Structures and Charges

Table S1: The basic structure of the oxidized titanium surface, obtained by symmetrically repeating the DFT model along the surface normal (z-axis). To obtain the DFT supercell the atoms with negative z-coordinates must be omitted. To obtain the full classical surface the structure has to repeated periodically in x- and y-directions. The corresponding cell lengths are L_x = 8.807300 Å and L_y = 10.1698 Å. The charges are the full EEM charges. To calculate the interactions with adsorbate molecules these charges have to be scaled by a factor of 0.77 as explained in section 4.1.

	x[Å]	y[Å]	z[Å]	q[e]
Ti	0.000000	-0.029170	0.000330	0.026013
Ti	2.936210	-0.029650	0.000740	0.026572
Ti	5.871090	-0.029650	0.000740	0.005577
Ti	1.467440	2.512800	0.000740	0.009360
Ti	4.403650	2.513280	0.000330	-0.001339
Ti	7.339860	2.512800	0.000740	0.002197
Ti	0.000000	5.055720	0.000330	0.008593
Ti	2.936210	5.055250	0.000740	0.004459
Ti	5.871090	5.055250	0.000740	-0.002873
Ti	1.467440	7.597700	0.000740	-0.002860
Ti	4.403650	7.598180	0.000330	-0.011622
Ti	7.339860	7.597700	0.000740	-0.010400
Ti	1.481470	0.825090	2.156960	-0.005889
Ti	1.481470	0.825090	-2.338960	0.000234
Ti	4.416970	0.801440	2.145760	0.001950
Ti	4.416970	0.801440	-2.327760	-0.005330
Ti	7.337240	0.889930	2.158640	-0.007111
Ti	7.337240	0.889930	-2.340640	-0.008437
Ti	0.035740	3.390500	2.156520	-0.001105
Ti	0.035740	3.390500	-2.338520	-0.003913
Ti	2.962500	3.395530	2.179080	-0.000741
Ti	2.962500	3.395530	-2.361080	0.006422
Ti	5.914860	3.414540	2.142100	0.008892
Ti	5.914860	3.414540	-2.324100	0.016835
Ti	1.410200	5.927140	2.152780	0.000013
Ti	1.410200	5.927140	-2.334780	-0.009633
Ti	4.396130	5.940850	2.149770	-0.002002
Ti	4.396130	5.940850	-2.331770	0.012831
Ti	7.312690	5.901210	2.233100	-0.014859
Ti	7.312690	5.901210	-2.415100	-0.021281
Ti	-0.056900	8.470950	2.160740	-0.006799
Ti	-0.056900	8.470950	-2.342740	-0.012324
Ti	2.934190	8.475640	2.173110	0.011999
Ti	2.934190	8.475640	-2.355110	0.009698
Ti	5.910020	8.455330	2.167570	-0.001820
Ti	5.910020	8.455330	-2.349570	0.010439
Ti	0.091970	0.077600	4.505460	-0.077870
Ti	0.091970	0.077600	-4.687460	-0.082706
Ti	2.972670	0.169390	4.601070	-0.094081
Ti	2.972670	0.169390	-4.783070	-0.090961
Ti	5.998330	-0.030500	4.541980	-0.063908
Ti	5.998330	-0.030500	-4.723980	-0.064207

Ti	1.434260	2.572760	4.434490	-0.031317
Ti	1.434260	2.572760	-4.616490	-0.033436
Ti	4.646730	2.511140	4.454060	-0.096434
Ti	4.646730	2.511140	-4.636060	-0.098384
Ti	7.423560	2.654640	4.629340	-0.061529
Ti	7.423560	2.654640	-4.811340	-0.054106
Ti	-0.002580	5.014260	4.580670	-0.033176
Ti	-0.002580	5.014260	-4.762670	-0.035607
Ti	2.869320	5.334640	4.533670	-0.059059
Ti	2.869320	5.334640	-4.715670	-0.058110
Ti	5.746220	5.074820	4.567680	-0.081354
Ti	5.746220	5.074820	-4.749680	-0.088257
Ti	1.499410	7.742910	4.529760	-0.050687
Ti	1.499410	7.742910	-4.711760	-0.042172
Ti	4.495310	7.717210	4.585500	-0.105547
Ti	4.495310	7.717210	-4.767500	-0.114868
Ti	7.395290	7.429600	4.732550	0.251160
Ti	7.395290	7.429600	-4.914550	0.244894
Ti	1.586990	1.160830	6.997000	0.500968
Ti	1.586990	1.160830	-7.179000	0.502437
Ti	4.614890	1.002580	6.770330	0.434005
Ti	4.614890	1.002580	-6.952330	0.436982
Ti	7.464500	1.011390	6.849320	0.324571
Ti	7.464500	1.011390	-7.031320	0.325572
Ti	0.068960	3.684760	7.096600	0.646841
Ti	0.068960	3.684760	-7.278600	0.646815
Ti	3.200900	3.577540	6.463250	0.553813
Ti	3.200900	3.577540	-6.645250	0.553696
Ti	5.969580	3.575320	6.930000	0.651690
Ti	5.969580	3.575320	-7.112000	0.647933
Ti	1.354640	6.220520	6.870720	0.276107
Ti	1.354640	6.220520	-7.052720	0.278564
Ti	4.369560	6.108650	6.870050	0.518596
Ti	4.369560	6.108650	-7.052050	0.519974
Ti	7.158150	6.125810	7.954030	1.091909
Ti	7.158150	6.125810	-8.136030	1.094249
Ti	0.177200	8.833230	6.763990	0.553085
Ti	0.177200	8.833230	-6.945990	0.543543
Ti	3.030170	8.668440	6.846950	0.663208
Ti	3.030170	8.668440	-7.028950	0.659958
Ti	5.886000	8.575210	6.920130	0.669773
Ti	5.886000	8.575210	-7.102130	0.675610
Ti	6.137190	9.749430	9.373840	1.042665
Ti	6.137190	9.749430	-9.555840	1.054651
Ti	0.158450	0.050020	9.201690	1.291550
Ti	0.158450	0.050020	-9.383690	1.297049
Ti	3.044400	0.221820	9.318770	1.134250
Ti	3.044400	0.221820	-9.500770	1.138111
Ti	1.458360	2.634970	9.591220	1.672788
Ti	1.458360	2.634970	-9.773220	1.686022
Ti	4.718210	1.510950	11.220460	1.518946
Ti	4.718210	1.510950	-11.402460	1.519518
Ti	7.059280	2.508400	9.651550	1.748747
Ti	7.059280	2.508400	-9.833550	1.747915

Ti	0.116900	5.072920	9.857700	1.451333
Ti	0.116900	5.072920	-10.039700	1.456442
Ti	2.511870	6.685490	9.943810	1.745328
Ti	2.511870	6.685490	-10.125810	1.743287
Ti	4.012440	4.124870	9.832960	1.905345
Ti	4.012440	4.124870	-10.014960	1.903382
Ti	-0.329910	7.965780	11.646710	1.949987
Ti	-0.329910	7.965780	-11.828710	1.932047
Ti	2.334000	9.825810	11.820890	1.700738
Ti	2.334000	9.825810	-12.002890	1.698619
Ti	5.854710	7.026740	10.568390	1.749241
Ti	5.854710	7.026740	-10.750390	1.747408
O	2.813280	8.521620	10.509020	-1.072487
O	2.813280	8.521620	-10.691020	-1.064128
O	5.964860	1.815170	8.064560	-0.979758
O	5.964860	1.815170	-8.246560	-0.975104
O	7.372070	4.163530	8.307220	-1.081535
O	7.372070	4.163530	-8.489220	-1.088113
O	1.602330	9.500230	8.044940	-1.118806
O	1.602330	9.500230	-8.226940	-1.114893
O	1.869070	3.053760	7.709590	-1.061359
O	1.869070	3.053760	-7.891590	-1.063361
O	2.117170	4.549840	9.994330	-1.171586
O	2.117170	4.549840	-10.176330	-1.175564
O	-0.180940	3.254350	10.551220	-0.965809
O	-0.180940	3.254350	-10.733220	-0.970112
O	5.554060	3.333490	10.653070	-0.999999
O	5.554060	3.333490	-10.835070	-0.999310
O	1.396050	10.971190	10.597610	-1.115244
O	1.396050	10.971190	-10.779610	-1.125397
O	4.458900	9.616630	8.086790	-1.026519
O	4.458900	9.616630	-8.268790	-1.038063
O	6.421300	0.915240	10.772730	-1.047891
O	6.421300	0.915240	-10.954730	-1.049165
O	4.347980	4.359170	8.016820	-1.047072
O	4.347980	4.359170	-8.198820	-1.047475
O	-1.206330	7.545970	6.690110	-1.149655
O	-1.206330	7.545970	-6.872110	-1.139723
O	8.701980	1.827720	8.320000	-1.149083
O	8.701980	1.827720	-8.502000	-1.150383
O	2.851000	6.891870	8.044080	-0.972179
O	2.851000	6.891870	-8.226080	-0.974792
O	-1.577240	5.954010	9.985540	-1.037972
O	-1.577240	5.954010	-10.167540	-1.034098
O	0.805140	6.613260	10.945850	-1.110889
O	0.805140	6.613260	-11.127850	-1.103687
O	0.791100	9.021590	12.598490	-0.922155
O	0.791100	9.021590	-12.780490	-0.919568
O	4.257140	5.984230	10.583800	-1.080495
O	4.257140	5.984230	-10.765800	-1.081509
O	3.426140	2.175220	9.863840	-1.210625
O	3.426140	2.175220	-10.045840	-1.215201
O	-0.877230	-1.228150	10.151350	-1.117233
O	-0.877230	-1.228150	-10.333350	-1.117844

O	3.689120	0.689680	12.529630	-0.945529
O	3.689120	0.689680	-12.711630	-0.939510
O	5.895220	7.630020	8.694990	-0.980642
O	5.895220	7.630020	-8.876990	-0.986557
O	6.767040	7.514120	12.139420	-0.938691
O	6.767040	7.514120	-12.321420	-0.938548

Table S2: The basic structure of the 4-Layer TiO_2 rutile 110 slab as used to compute the classical PES of water and ammonium. The corresponding cell lengths are L_x = 8.945378 Å and L_y = 6.563488 Å. The charges are the full EEM charges. To calculate the interactions with adsorbate molecules these charges have to be scaled by a factor of 0.77 as explained in section 4.1.

	x[Å]	y[Å]	z[Å]	q[e]
Ti	0.147994	0.069507	-0.026877	2.018039
Ti	3.399185	0.080626	1.487451	2.195726
Ti	3.086717	3.351048	-0.000374	2.179538
Ti	-0.204978	3.374427	1.501096	2.102133
Ti	6.777799	-0.065648	0.000755	2.176768
Ti	10.070727	-0.093503	1.484957	2.102074
Ti	9.714967	3.213504	0.026956	2.014853
Ti	6.464767	3.202799	1.494257	2.193981
Ti	0.148223	0.066580	2.955795	2.018799
Ti	3.398778	0.079878	4.471475	2.190933
Ti	3.086540	3.347943	2.981176	2.177127
Ti	-0.206704	3.372629	4.482331	2.101601
Ti	6.779630	-0.065707	2.982062	2.178071
Ti	10.072677	-0.091377	4.466224	2.101575
Ti	9.715774	3.216122	3.008224	2.020272
Ti	6.464176	3.202792	4.473529	2.194460
Ti	0.148282	0.067007	5.936820	2.017110
Ti	3.398561	0.080298	7.454666	2.193991
Ti	3.086881	3.348002	5.963238	2.177789
Ti	-0.203094	3.375654	7.463408	2.103659
Ti	6.779979	-0.065865	5.964524	2.178073
Ti	10.070504	-0.093083	7.447236	2.102929
Ti	9.714383	3.214961	5.990673	2.020188
Ti	6.463953	3.202418	7.453228	2.195134
O	1.981497	-0.033192	-0.000282	-1.097890
O	4.550742	0.018575	-0.001135	-1.080695
O	3.237473	1.998943	1.489459	-1.097441
O	3.294477	4.558218	1.491953	-1.083389
O	1.245383	3.386287	0.001195	-1.092553
O	0.037136	1.298324	1.496292	-1.072093
O	-0.205450	-1.225791	1.495340	-1.095327
O	-1.313111	3.178874	0.006091	-0.874234
O	8.621273	-0.101964	-0.002232	-1.091618
O	11.177660	0.102082	-0.004214	-0.875976
O	9.827394	1.984143	1.485751	-1.071602
O	10.069763	4.507476	1.499449	-1.096321
O	7.887423	3.316308	0.001844	-1.095470
O	6.626734	1.284908	1.490371	-1.097352
O	6.569769	-1.274741	1.493148	-1.082836
O	5.316222	3.261634	0.001260	-1.079395
O	1.978944	-0.033369	2.979548	-1.096533
O	4.547401	0.026858	2.977303	-1.078360
O	3.239856	1.998451	4.473175	-1.096906
O	3.296210	4.559196	4.472394	-1.082739
O	1.242646	3.378444	2.983486	-1.092121
O	0.035482	1.298947	4.478702	-1.073056
O	-0.208200	-1.227143	4.475059	-1.095093

O	-1.314148	3.180706	2.987405	-0.875295
O	8.620505	-0.096431	2.979495	-1.092445
O	11.180593	0.100612	2.976339	-0.874410
O	9.831916	1.983270	4.467930	-1.072895
O	10.070340	4.510180	4.471134	-1.095104
O	7.881759	3.316839	2.983696	-1.098292
O	6.625021	1.284508	4.472518	-1.097339
O	6.571352	-1.275837	4.473057	-1.083217
O	5.314443	3.258904	2.982797	-1.080824
O	1.979850	-0.033671	5.963047	-1.096589
O	4.548688	0.027416	5.965121	-1.077657
O	3.236994	1.998891	7.455959	-1.097113
O	3.293525	4.558159	7.453576	-1.083849
O	1.243184	3.379140	5.966919	-1.092485
O	0.040438	1.299814	7.464177	-1.071979
O	-0.205214	-1.225003	7.453662	-1.096224
O	-1.313485	3.179656	5.972157	-0.875282
O	8.621831	-0.096838	5.964432	-1.092766
O	11.180653	0.100776	5.958873	-0.874437
O	9.828062	1.983361	7.448391	-1.071750
O	10.070025	4.507548	7.447209	-1.096040
O	7.881804	3.316990	5.966080	-1.098695
O	6.626945	1.285453	7.454706	-1.097429
O	6.570242	-1.274866	7.452159	-1.082440
O	5.314509	3.259225	5.965732	-1.081270

Table S3: The ESP charges used as partial charges in the classical models for methanol, formic acid and methylamine.

Methanol		Formic Acid		Methylamine	
H	0.000983	H	0.0579	H	-0.070
H	0.000983	C	0.5324	H	-0.070
H	0.000983	O	-0.4837	H	-0.070
C	0.21783	O	-0.5056	C	0.479
O	-0.58329	H	0.3990	N	-0.869
H	0.36251			H	0.300
				H	0.300

S2 Force Field for the dry Ti/TiO_x interface

The classical force field potential, which we have recently developed for the oxidized titanium surface,[S1] is described in the following. The model consists of a Finnis-Sinclair-type manybody-potential for the metal region (E^{met}), coupled to electrostatic Coulomb interactions and a short-ranged repulsive potential for the oxide region:

$$E = E^{met} + \sum_{i<j} \frac{q_i q_j}{r} + \sum_{i<j} A_{ij} \exp\left[-r_{ij}/\rho_{ij}\right] \ . \tag{S1}$$

As described in more details in Ref.[S1] , E^{met} is taken from Ref.[S2] and yields for each titanium atom an energy contribution of

$$E_i^{met} = \frac{1}{2}\sum_j V^{met}(r)\, f_c^{met}(q_i)\, f_c^{met}(q_j) - \sqrt{\tilde{\rho}_i} \tag{S2}$$

where the sum runs over all atom indexes and

$$\tilde{\rho}_i = \sum_j \rho(r)\, f_c^{met}(q_i)\, f_c^{met}(q_j) \ . \tag{S3}$$

The pair potential $V^{met}(r)$ and the density $\rho(r)$ are parametrized using cubic splines:

$$V^{met}(r) = \sum_k a_k (r_k - r)^3 \Theta(r_k - r) \ ; \tag{S4}$$

$$\rho(r) = \sum_k A_k (R_k - r)^3 \Theta(R_k - r) \ , \tag{S5}$$

where $\Theta(x)$ is the step function. In Eqs. (Eq.(S2) and Eq.(S3)) we have introduced cut-off functions

$$f_c^{met}(q) = \begin{cases} 1, & q < Q_{met} - \Delta \\ 1 - (q - Q_{met} + \Delta)/2\Delta, & Q_{met} - \Delta < q < Q_{met} + \Delta \\ 0, & q > Q_{met} + \Delta \end{cases} \tag{S6}$$

that depend linearly on the atomic charges q. These ensure that the Ti-Ti FS interaction continuously decreases and is eventually switched off when entering in the oxide region. We have increased the the charge Q_{met} for the metal cutoff compared to the original value in ref.,[S1] as the oxide network appeared to be more stable this way when put in contact with water.

The changes in the structure of the dry surface due to this increase are found to be negligible. Moreover, in long simulations of the surface/water interface, we observed events of bond breaking between the TiB and OB atoms. These were not observed in DFT MD simulations, which were however much shorter. Whether the bond-breaking event results from an artefact of our classical potential or is indeed representative of the real physical situation remains thus unclearand will require further investigations, which go beyond the scope of the present work. Here, to ensure consistency with the DFT structure, we have chosen to add a corrective harmonic potential term to the TiB-OB interactions, thus preventing bond breaking:

$$V_{OB}(r_{TiB-OB}) = \frac{k_{OB}}{2}\left(r_{TiB-OB} - r^0_{TiB-OB}\right)^2 \ . \tag{S7}$$

The parameters k_{OB} and r^0_{TiB-OB} have been determined by a fit to the DFT potential energy surface of stretching the TiB-OB bond by vertical displacement of one OB atom.

Table S4: Potential parameters for the dry oxidized titanium surface as developed in Ref.[S1] . The parameters for the FS Ti potential are taken from Ref.[S2] . The lattice parameter for titanium was set to $a = 2.94$ Å.

	Buckingham Potential			
	A_{IJ} [eV]		ρ_{IJ} [Å]	
Ti-Ti	0.000		0.000	
O-O	85.164		0.489	
Ti-O	7211646.2		0.115	
TiB-OB	19875.288		0.184	
	Charge dependencies			
Q_{met} [e]	1.885			
Δ [e]	0.325			
	EEM parameters			
	Ti		O	
χ_I [V]	0.0		8.729	
J_I [V/e]	12.864		17.197	
	Finnis-Sinclair Ti Potential			
k	$A_k\,[eVa^{-3}2^{-3/2}]$	$R_k\,[a2^{1/2}]$	$a_k\,[eVa^{-3}2^{-3/2}]$	$r_k\,[a2^{1/2}]$
1	39.795927	1.22	-57.099097	1.22
2	-40.061305	1.05	80.735598	1.20
3			-21.761468	1.12
4			-10.396479	0.95
5			74.515028	0.80
6			35.921024	0.707107
	Harmonic TiB-OB correction			
r_{TiB-OB} [Å]	0.369			
k_{OB} [eV/Å^2]	0.60943			

S3 Equilbration

The equilibration of the system is an important issue, in particular when dealing with molecules of large size. Before collecting the final results in the production run, one has to make sure that the system has reached equilibrium. As stated in section 2.2, the preparation procedure for our systems comprised several hundreds of picoseconds, completed by a final equilibration run of at least 200 ps, with the final settings of the simulation applied. In Figure S1 we provide running averages of the potential respectively the total energies for two representative cases, i.e. the rutile 110 surface in contact with water and the oxidized titanium surface with an adsorbed and solvated RGD-peptide. In the first case, the potential energies itself are the quantities of interest for calculating the heat of immersion. The figure shows on the one hand the energy during the 200 ps production run of the crystal surface with bulk water and on the other hand of the dry surface with only 144 molecules adsorbed. In both cases no energy drift can be observed, which is a strong indication the the system is in equilibrium. The same holds for other properties like the pressure, the temperature, etc. In the case of RGD the time evolution of the total energies are shown during umbrella simulation runs for 3 different umbrella windows (close to the surface, adsorbed and free). Obviously the energy decreases during the first 200 ps, which are discarded from the evaluation (cf. section 6). During the actual production run the energy reveals some fluctuations, while no further drift of the average value is found.

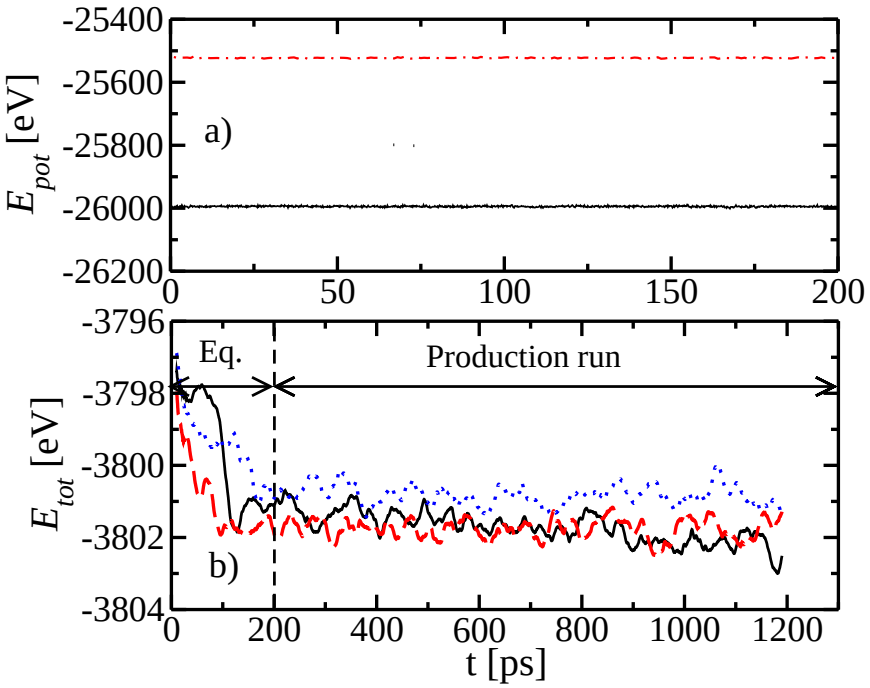

Figure S1: Running averages of the energies: Potential energy of the TiO_2 rutile 110 surface in contact with bulk water (*solid line*) and 144 adsorbed molecules (*dot-dashed line*) during production run for heat of immersion simulations (*a*).
Total energy for the solvated RGD peptide on the oxidized Ti surface during umbrella simulation runs at z_0=16.0 Å (*solid line*), 20.0 Å (*dashed line*) and 26.0 Å (*dotted line*) (*b*).

References

[S1] Schneider, J.; Colombi Ciacchi, L. *Surf. Sci.* **2010**, *604*, 1105–1115.

[S2] Ackland, G. J. *Phil. Mag. A* **1992**, *66*, 917–932.