Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPORTING INFORMATION FOR

Influence of an Electrified Interface on the Entropy and Energy of Solvation of Methanol Oxidation Intermediates on Platinum(111) under Explicit Solvation

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S1. Classical Molecular Dynamics Force Field Parameters

Table S1 and Table S2 show the Lennard-Jones and Coulomb parameters and bond and angle parameters of bonded interaction for cMD simulations, respectively.

Table S1 – Lennard-Jones and Coulomb parameters used for cMD simulations.

Group	Atom/Pair	LJ	C	m (g/mol)	q (e)	σ (Å)	ε (kcal/mol)
Pt	Pt	UFF	DDEC	195.084	a	2.7540	0.0800
H_2O	O	TIP3P	TIP3P	15.9994	-0.8340	3.1507	0.1521
	H	TIP3P	TIP3P	1.00794	0.4170	0.4000	0.0460
CH_3OH	C	OPLS-AA	DDEC	12.0107	a	3.5000	0.0660
	O	OPLS-AA	DDEC	15.9994	a	3.1200	0.1700
	H (bound to C)	OPLS-AA	DDEC	1.00794	a	2.5000	0.0300
	H (bound to O)	OPLS-AA	DDEC	1.00794	a	0.0000	0.0000
COH	C	OPLS-AA	DDEC	12.0107	a	3.5500	0.0700
	O	OPLS-AA	DDEC	15.9994	a	3.0700	0.1700
	H	OPLS-AA	DDEC	1.00794	a	0.0000	0.0000
CO	C	OPLS-AA	DDEC	12.0107	a	3.7500	0.1050
	O	OPLS-AA	DDEC	15.9994	a	2.9600	0.2100

[a] Partial charges are given in Table S7,Table S8 and Table S9.

Table S2 – Bond and angle parameters of bonded interactions for cMD simulation.

Molecule	**Bond**	**K_r(kcal/mol-Å^2)**	**r_{eq} (Å)**	**Angle**	**K_θ (kcal/mol-rad^2)**	**θ_{eq} (°)**
H_2O	H-O	450.0	0.9572	H-O-H	55.00	104.52

S2. Multiscale Sampling Method Schematic Figure

Figure S1 illustrated the procedure to calculate energies and entropies of surface species using multiscale sampling method.

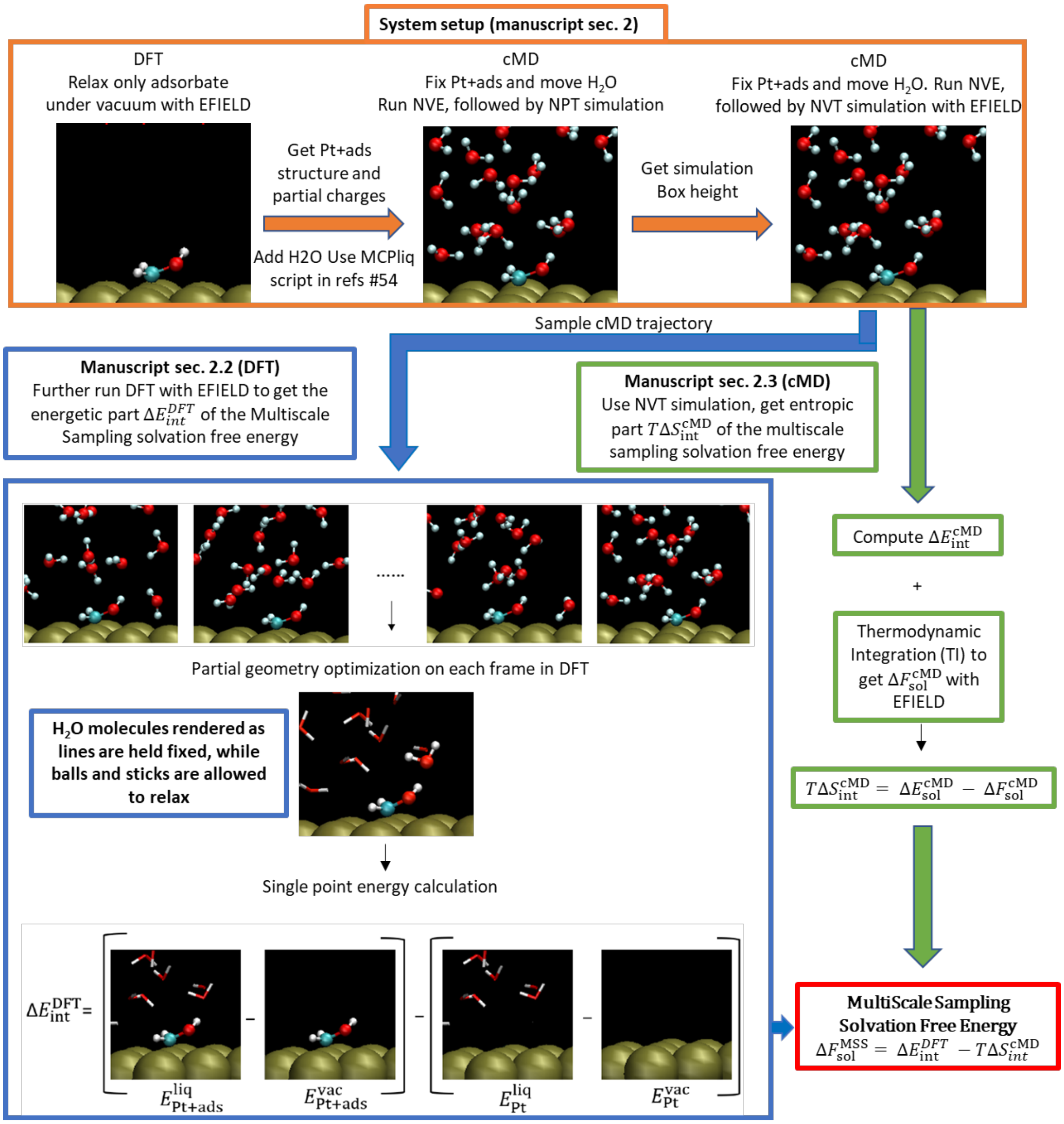


Figure S1- Multiscale sampling method scheme.

S3. The Effect of Cell Size and Force Field (FF)

To see the effect of cell dimension, we modify the size of the cell and number of atoms as per Table S3.

Table S3 – Cell size and number of molecules.

Cell	Dimension L x W x H, Å*	No. of water molecules	No. of platinum atom
Cell #1	11.2 x 9.7 x H	40	48
Cell #2	11.2 x 9.7 x H	100	48
Cell #3	16.8 x 14.6 x H	240	108

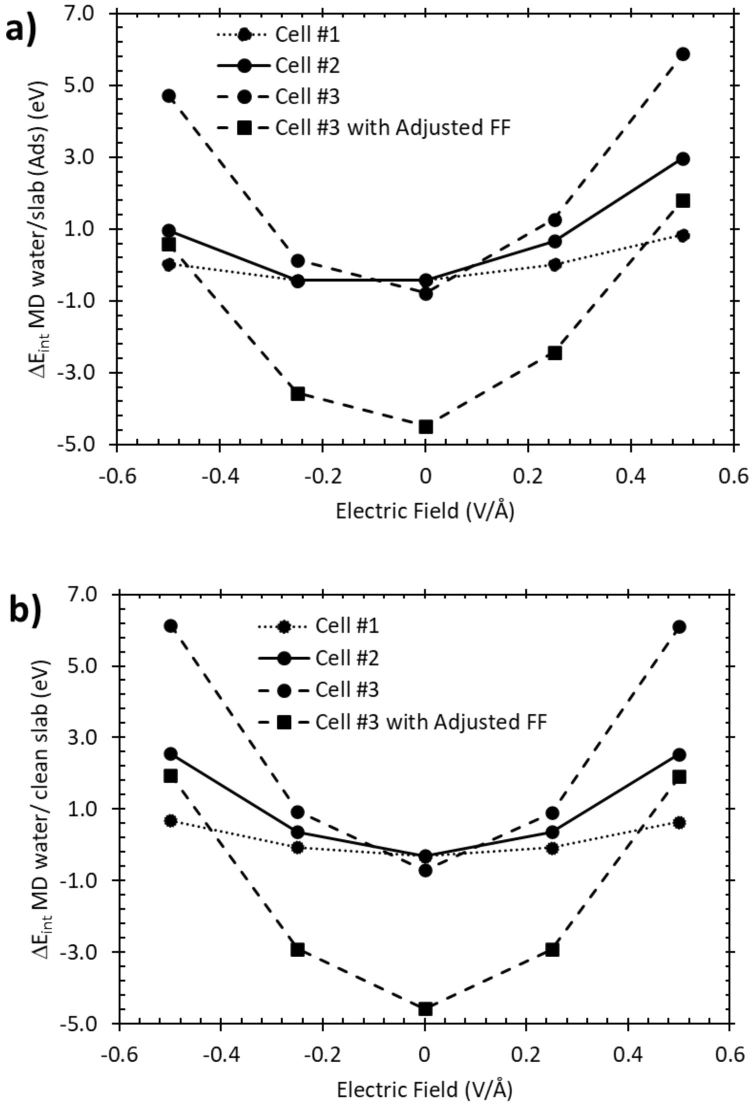
*Heights of the cells are shown in Table S4.

Table S4 – Cell heights for different adsorbate and electric field determined in NPT (see Figure S1).

Adsorbate	Cell	-0.5	-0.25	0	+0.25	+0.5
CH_3OH	Cell #1	19.62	19.73	19.58	19.35	19.22
	Cell #2	35.97	36.18	36.19	35.90	35.64
	Cell #3	37.47	37.64	37.64	37.50	37.30
COH	Cell #1	19.34	19.44	19.43	19.21	19.07
	Cell #2	35.87	36.27	35.95	35.72	35.39
CO	Cell #1	19.05	19.22	19.18	19.24	19.23
	Cell #2	35.31	35.63	35.59	35.69	35.71

Note: Height of the cells were calculated by NPT run

The interaction energy between the water and platinum surface when methanol is present and when there is no methanol (clean surface) for cells #1, #2 and #3 are shown in Figure S2 a and b, respectively. The significant difference between water and slab interaction energy at potentials other than 0.0 V/Å could be attributed to the platinum forcefield and specifically the attractive term, epsilon, in Lennard-Jones potential. Due to the applied electric field, H_2O molecules become strongly attracted to the Pt surface and the Pt-H_2O distance can become infeasibly small. Considering that the epsilon value of the UFF (0.0800 kcal/mol) is relatively small and was designed for neutral or close to neutral (no electric field) Pt atoms, we increase epsilon to 1.1775 kcal/mol value, which gives a density of the first layer of water on a Pt(111) surface that is more in line with QM/MM (quantum mechanics/molecular mechanic) results [1]. The results are depicted in Figure S2. The water-surface interaction at the location of the adsorbate and water-adsorbate interaction are shown in Figure S2 (c) and (d) respectively. Actually, Figure S2 (c) is the result of subtraction of Figure S2 (b) from (a).



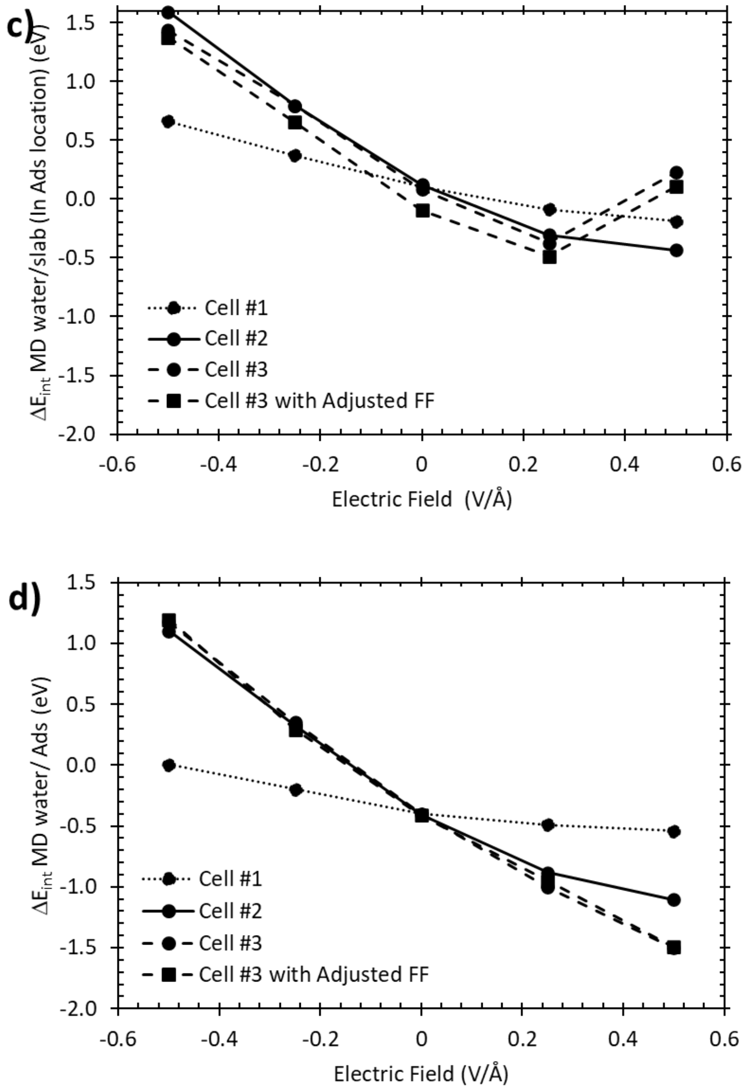


Figure S2 – Effect of cell size and LJ epsilon parameter on the interaction energy calculated by cMD between a) water and slab when there is adsorbate (methanol) on the slab, b) water and clean slab, c) water and slab in place of adsorbate (subtraction of values in b from values in a), and d) water and adsorbate.

There are two relevant energies here: the energy of interaction between H_2O and the adsorbate (Figure S1d) and the energy of interaction between H_2O molecules and the region of the Pt electrode surface that is covered by the adsorbate (Figure S1c). This region is illustrated in Figure S3. These two energies influence the free energy of solvation that is reported in the main text. Cells #2 and #3 both with and without adjusted FF give similar energies of interaction between H_2O and the adsorbate (Figure S1d) and the region of the Pt electrode where the adsorbate resides (Figure S1c), suggesting that the LJ epsilon parameter is not significantly influencing the results reported in the main text. Thus, we decided to use original LJ epsilon parameter of 0.08 kcal/mol. Additionally, cell #1 deviations from #2 and #3 and similarity between two latter in Figure S2d convinced us to select cell #2 as base for cMD calculations since it is much less computationally expensive than cell #3. The largest differences between cells #2 and #3 is at +0.50 V/Å, and we find that this is due to differences in the calculated partial charges (from DFT) for cells #2 and #3 at this field strength. It is worthwhile to note that the number of platinum atoms of cells #1 and #2 are the same, thus, the partial charges of adsorbate and surface are the same for these two cells. Whereas cell #3 has 60 more Pt atoms, so the charge distribution is different for this cell, as shown in (Figure S4). Figure S4 shows the partial charges of methanol on Pt surface for these cell sizes. At +0.5 V/Å the differences are more pronounced than other fields. We note that solvation free energies, particularly at large fields, are dependent on adsorbate partial charges, which themselves will depend on the coverage of adsorbates under electrocatalytic operating conditions. The results presented in the manuscript are accurate given the methods described at the coverages (1/16 ML) that were reported.

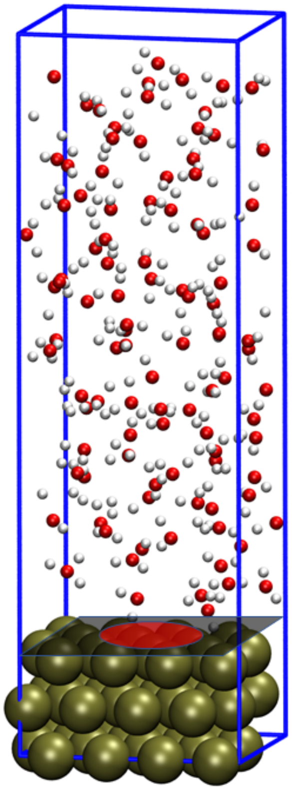


Figure S3 – Interaction region between H_2O molecules and the Pt electrode surface that is covered by the adsorbate (red circle).

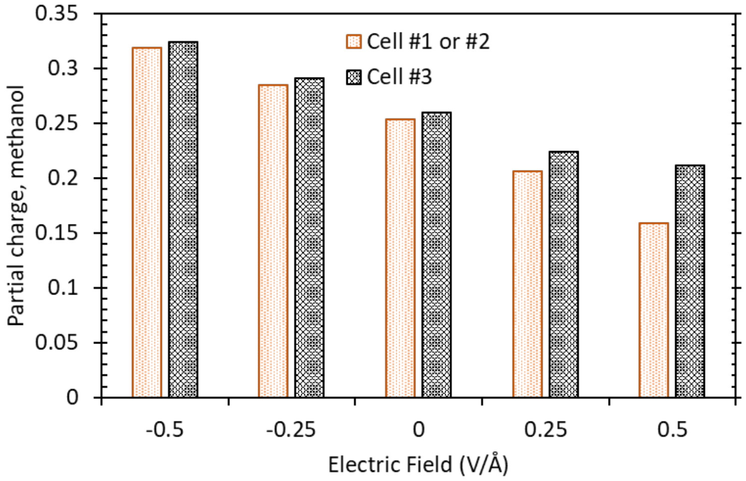


Figure S4 – DFT-calculated partial charge of methanol on Pt surface for cell #1 (or #2) and comparison to cell #3. The difference at +0.50 V/Å is most significant.

Another important parameter to evaluate the cell size is water density. Figure S5 a, b and c show water density versus cell height for these 3 cells at -0.50, 0.0, and +0.50 V/Å. In these figures, interfacial water is where the trend is oscillating with respect to cell height, and bulk water is where the trends have leveled out at 1 g/cm^3. There is no bulk water in the cell #1, however cells #2 and #3 both exhibit bulk water along the height which is another reason to pick cell #2 for cMD calculations. Cell #1 does a reasonable job at capturing the first solvation shell of the adsorbate when compared with cell #2, making it a reasonable cell for performing the DFT calculations. From the density plots, the first solvation shell is at 7.5 Å. Additionally, at -0.5 and +0.5 V/Å the water layer at the surface of the catalyst is noticeable with density of approximately 3.5.

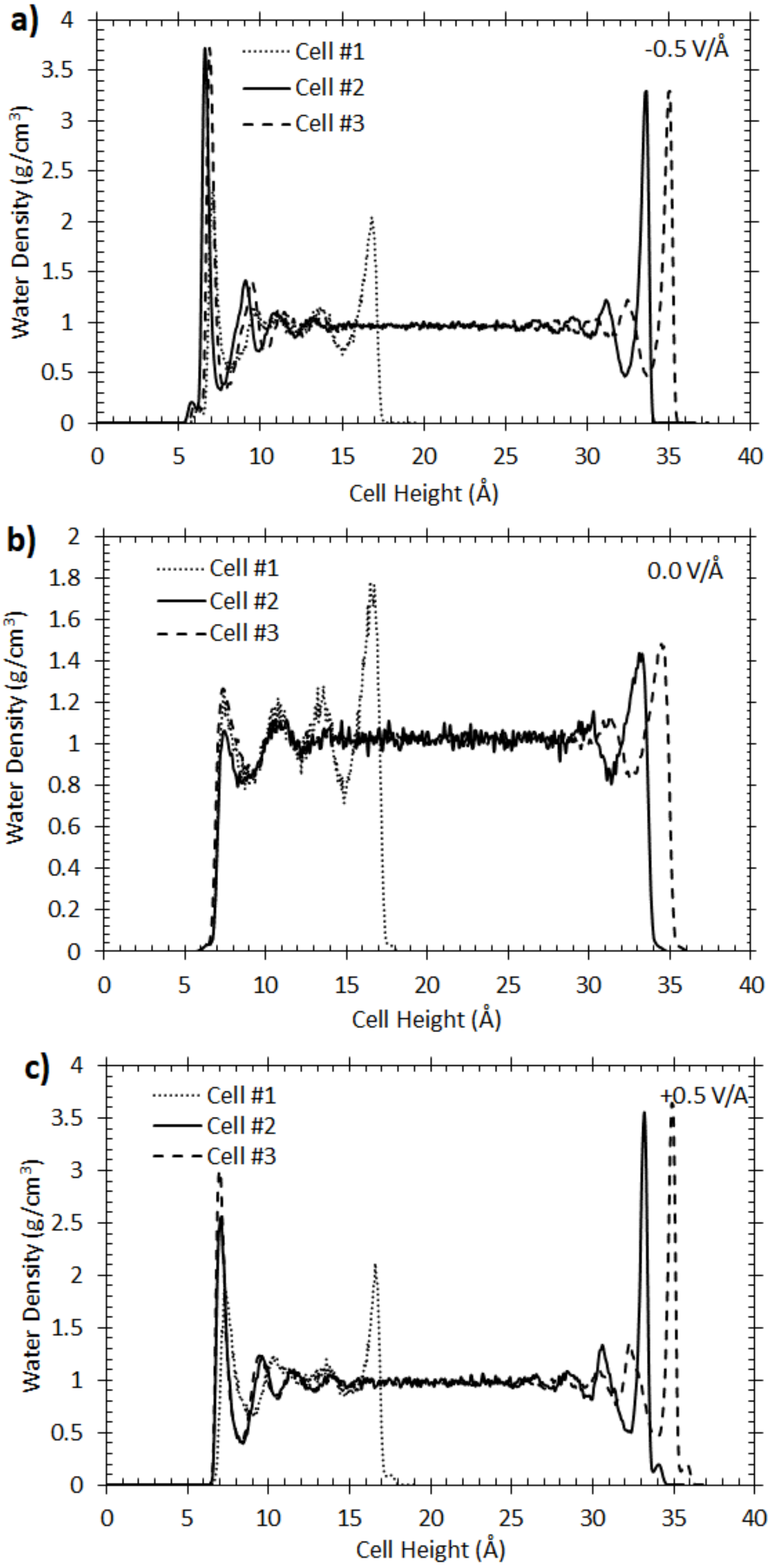


Figure S5 – Water density calculated by cMD vs the cell height at -0.50, 0.0 and +0.5 V/Å with CH_3OH as adsorbate.

S4. The Effect of Platinum Layer on DFT Calculations

To see the effect of platinum layer, we add additional layers to the slab and compare the ΔE_{int}^{DFT} at -0.25, 0 and +0.25 V/Å. Figure S6 shows the results. Data reported in the main text use 3 layer slabs; this choice makes a maximum 0.09 eV difference in the calculated interaction energy when compared with 4 and 5 layer models. Since this difference is small, we used the 3 layer slabs since they are more computationally efficient.

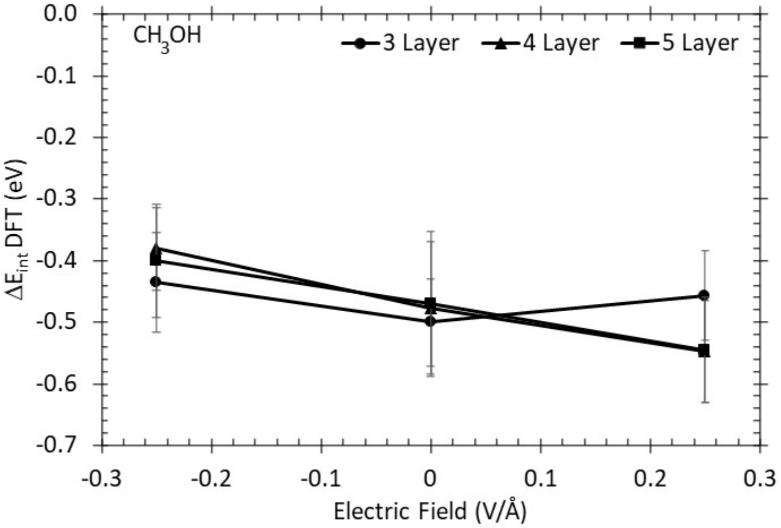


Figure S6 – Interaction energy calculated by DFT for CH_3OH, at -0.25, 0 and +0.25 V/Å with 95% confidence interval for 3 layer (circle), 4 layer (triangle) and 5 layer (square) of platinum atom in a 4 x 4 arrangement.

S5. The Effect of Cell Size and Number of Water Molecules on DFT Calculations

To see the effect of platinum layers, cell size (in Z direction) and the number of water molecules in the supercell on DFT calculations, we compare the results for ΔE_{int}^{DFT} at +0.25 V/Å for CH_3OH and show them in Figure S7. Comparing 3 layer Pt slabs, we find that the number of

H_2O molecules has a 0.03 eV influence on the DFT calculated interaction energy. We hence use the 40 H_2O molecule models since they are significantly more computationally efficient.

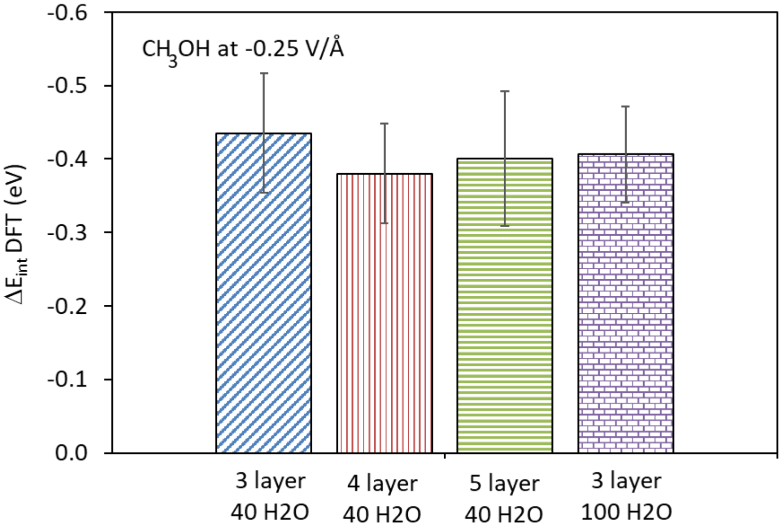


Figure S7– Interaction energy calculated by DFT for CH_3OH, at -0.25 V/Å with 95% confidence interval for 3 layer platinum and 40 water molecule (inclined blue stripes), 4 layer platinum and 40 water molecule (vertical red stripes), 5 layer platinum and 40 water molecule (horizontal green stripes) and 3 layer platinum and 100 water molecule (brick type violet).

S6. Effect of Relaxation Method on DFT Calculations

To investigate the effect of relaxation method on DFT calculation, identical to our prior work [2], we compare the following two methods: 1) water molecules that hydrogen bond with the adsorbate are allowed to relax, while the adsorbate is held fixed, and 2) adsorbate and water molecules that are hydrogen bonded to it are allowed to relax. Due to the need to relax fewer degrees of freedom in these complicated systems, method 1 is significantly less computationally demanding than method 2. In prior work, performed under thermal-catalytic conditions, we found that methods 1 and 2 give nearly identical results, except when the adsorbate forms an exceptionally strong hydrogen bond with a H_2O molecule [2]. In such cases, the second method gives an interaction energy ~ 0.4 eV stronger than method 1. The influence of the relaxation method on the DFT interaction energy for the electrocatalytic systems investigated in this work is shown in Figure S8. Similar to prior work [2], we observe a maximum difference of 0.26 eV between these two methods. The conclusions from both methods, i.e., that the interaction energy in general decreases with field strength, are the same for both methods. Since the conclusions from both methods are the same, and since the "shift" in the DFT calculated interaction energy seems to be consistent (~ 0.3-0.4 eV), we used method 1 in this work, since it is significantly less computationally demanding.

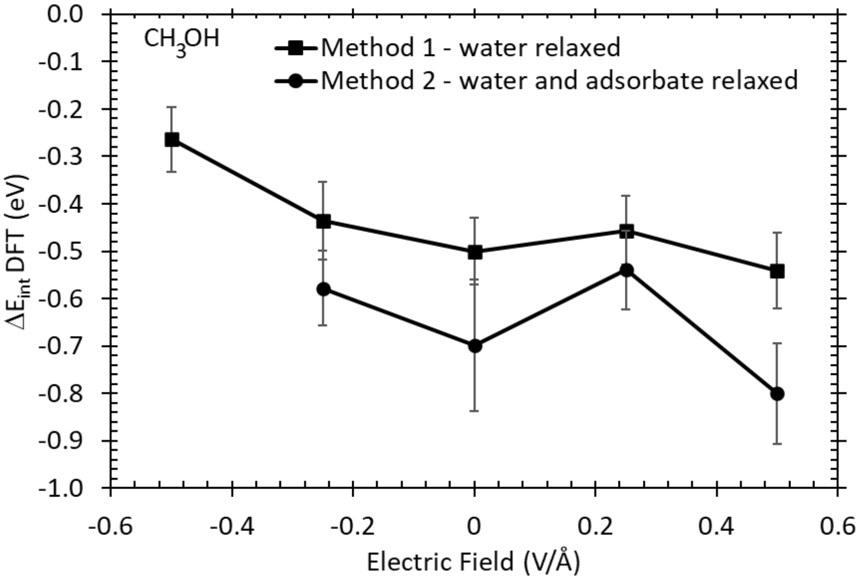


Figure S8 – Effect of relaxation method on DFT calculation. Squares shows the method 1: only those water molecules with hydrogen bond to the adsorbate are relaxed, Circles shows method 2: both adsorbate and those water molecules with hydrogen bond to the adsorbate are relaxed.

S7. Effect of Vacuum Height on DFT Calculations

To investigate the effect of vacuum on DFT calculation, we compare two different height, 14 Å and 28 Å, of vacuum at -0.25 V/Å for CH3OH as shown in Figure S9. We find that the vacuum height influences the results by 0.05 eV. Due to this small difference, we used the cells with 14 Å vacuum height, since they are significantly less computationally demanding.

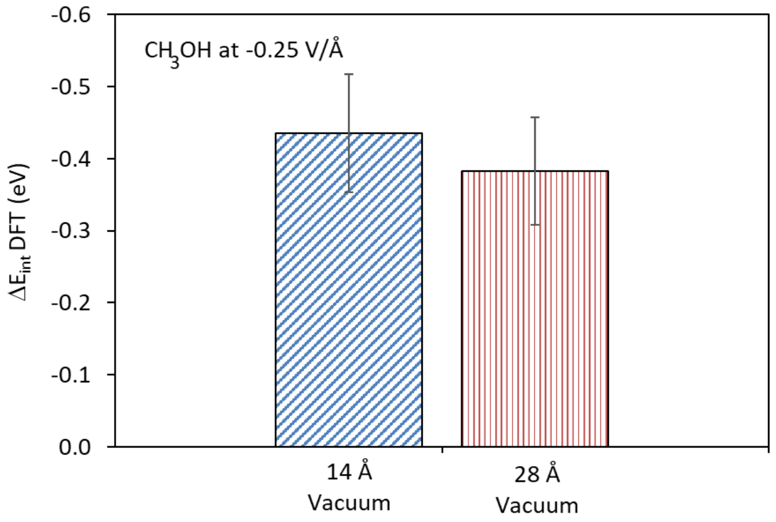


Figure S9 – Effect of vacuum height on the interaction energy calculated with DFT with 95% confidence interval for CH_3OH at -0.25 V/Å. 14Å vacuum is shown with inclined blue stripes and 28 Å vacuum with vertical red stripes.

S8. Effect of Spin Polarization on DFT Calculations

To investigate the effect of spin polarization on DFT calculation, we compare the results at -0.5 and +0.5 V/Å for COH as shown in Figure S10. We find inclusion of spin polarization influences the results by a maximum of 0.04 eV. Due to this small difference, we did not include spin polarization in our DFT results, since including spin polarization increases the computational expense significantly.

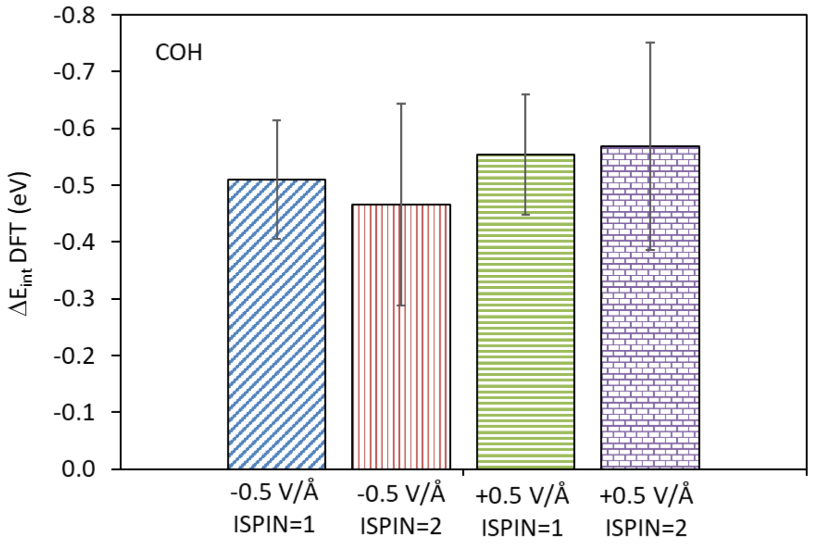


Figure S10 – Spin polarization effects for the water-adsorbate interaction energy for COH calculated by DFT with 95% confidence interval at -0.5 V/Å and ISPIN=1 (inclined blue stripes), -0.5 V/Å and ISPIN=2 (vertical red stripes), +0.5 V/Å and ISPIN=1 (horizontal green stripes) and +0.5 V/Å and ISPIN=2 (brick type violet). ISPIN equals to 1 and 2 calculations averaged over 10 and 5 snapshots, respectively.

S9. Interaction Energy

Table S5 listed all calculated interaction energy ΔE_{int}, interaction entropy $T\Delta S_{int}$, free energy ΔF_{sol} for all adsorbates using different simulation methods, as a complementary table of the manuscript. For example, to get the values presented in the manuscript: $T\Delta S_{int}^{cMD}$ for CH_3OH* at –0.5 V/Å = +1.10 eV + 0.96 eV – 2.56 eV – (+0.01 eV – 0.57 eV) = +0.07 eV. ΔF_{sol}^{MSS} for CH_3OH* at –0.5 V/Å = –0.26 eV – 0.07 eV = –0.33 eV.

Table S5 – Interaction energy ΔEint, interaction entropy TΔSint, and free energy ΔFsol for CH_3OH, COH and CO on Pt(111) at T = 300 K, calculated with cMD, DFT with explicit solvation (DFT) and multiscale sampling (MSS). All values are in units of eV.

Thermodynamics Parameter	**System**	**-0.5**	**-0.25**	**0**	**+0.25**	**+0.5**
(ΔE_{int}^{DFT})	CH_3OH	-0.26	-0.44	-0.50	-0.46	-0.54
	COH	-0.51	-0.65	-0.63	-0.53	-0.55
	CO	+0.07	-0.08	-0.08	-0.13	-0.10
$(T\Delta S_{int}^{cMD})$	CH_3OH	+0.07	-0.06	-0.31	-0.55	-0.84
	COH	+0.25	+0.20	-0.03	-0.32	-0.62
	CO	-0.07	0.00	-0.10	-0.28	-0.33
(ΔE_{int}^{cMD})	CH_3OH	+1.10	+0.32	-0.41	-0.88	-1.10
	COH	+0.46	-0.06	-0.48	-0.70	-0.72
	CO	+0.17	-0.02	-0.09	-0.02	+0.30
	Pt	+2.56	+0.36	-0.30	+0.36	+2.53
	Pt (CH_3OH)*	+0.96	-0.44	-0.42	+0.66	+2.97
	Pt (COH)*	+1.70	-0.02	-0.38	+0.40	+2.46
	Pt (CO)*	+2.39	+0.37	-0.32	+0.20	+2.09
(ΔF_{int}^{cMD})	Pt + CH_3OH	+0.01	-0.48	-0.36	-0.09	+0.73
	Pt + COH	-0.08	-0.71	-0.68	-0.41	+0.38
	Pt + CO	+0.65	-0.07	-0.16	+0.04	+0.74
	Pt	+0.57	-0.06	-0.15	-0.06	+0.56
(ΔF_{sol}^{MSS})	CH_3OH	-0.33	-0.38	-0.19	+0.09	+0.30
	COH	-0.76	-0.85	-0.60	-0.22	+0.07
	CO	+0.13	-0.08	+0.02	+0.15	+0.23

*(ΔE_{int}^{cMD}) is calculated between water and Pt electrode surface but when adsorbate (e.g., CH_3OH) is present

S10. Entropy and Free energy

In our previous group publication [2] , we used equation (S1) to calculate entropy of interaction:

$$T\Delta S_{int}^{cMD} = \Delta E_{int}^{cMD} - (\Delta F_{pt+ads}^{with\ ads} - \Delta F_{pt}^{clean}) \tag{S1}$$

In this equation, (ΔE_{int}^{cMD}) was calculated by simply evaluating the LJ + C potential between the water molecules and the adsorbate at various configurations of water molecules over the course of a NVT MD trajectory, $\left(\Delta F_{pt+ads}^{with\ ads}\right)$ yielded the free energy of solvation for the "Pt + adsorbate" system where Lennard -Jones and coulombic (LJ + C) is scaled for the adsorbate and just C for the surface, capturing the adsorbate to water interaction and the charge redistribution in the surface due to the adsorbate addition, and $\left(\Delta F_{pt}^{clean}\right)$ calculated the free energy for the clean Pt surface by scaling C interaction. The subtraction of these two calculations, $(\Delta F_{pt+ads}^{with\ ads} - \Delta F_{pt}^{clean})$, gave solvation free energy of adsorbate. Alternatively, ΔF_{int}^{cMD} can be calculated by scaling just the LJ and C interactions of the adsorbate, i.e., without scaling the surface at all. In this case, the influence of the Pt electrode interface is not considered. The entropy is given by equation (S2):

$$T\Delta S_{int}^{cMD} = \Delta E_{int}^{cMD} - \Delta F_{int}^{cMD} \tag{S2}$$

If we subtract equation (S1) from (S2), the result is:

$$\Delta F_{int}^{cMD} - \left(\Delta F_{pt+ads}^{with\ ads} - \Delta F_{pt}^{clean}\right) = E_{Coulomb} \tag{S3}$$

Where $E_{Coulomb}$ is the Coulombic part of free energy interaction between water and surface in the areas where the adsorbate resides. $E_{Coulomb}$ is equal to 0 at the potential of zero charge, but it is finite at all other potentials. $E_{Coulomb}$ is plotted as a function of electric field in Figure S11 for CH_3OH, COH and CO. Given that we seek to isolate the solvation thermodynamics of the adsorbates (and eliminate contributions from the Pt electrode surface), and also that $E_{Coulomb}$ is large for some adsorbates at some potentials, equation (S1) is insufficient for computing $T\Delta S_{int}^{cMD}$, since it includes the interaction between H_2O and the area of the Pt electrode surface where the adsorbate resides in addition to the contribution due to the adsorbate. However, the method of scaling just the adsorbate is also not fully correct, since it does not properly account for the charge transfer that occurs due to adsorption (this quantity contributes to $E_{Coulomb}$ but is not the only contribution to $E_{Coulomb}$). When only the adsorbate is scaled, the clean Pt electrode surface retains the same charge distribution as when the adsorbate is present. Charge redistribution is hence not accounted for. So, if this charge redistribution influences the solvation free energy, then this simple method of scaling just the adsorbate will not be fully accurate.

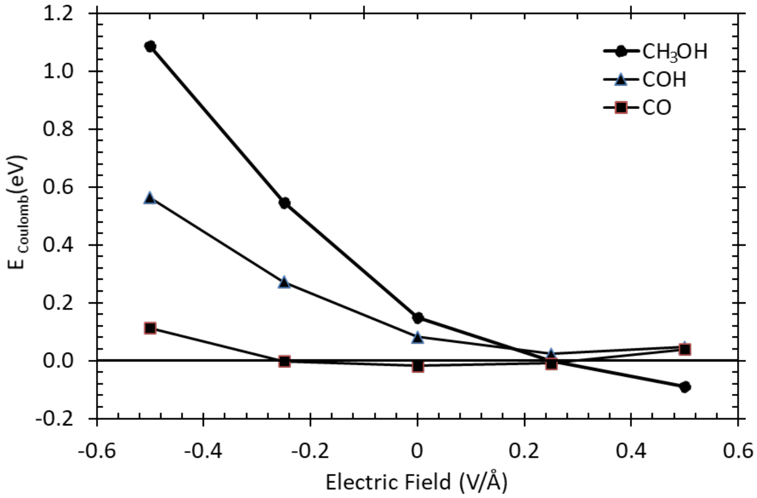


Figure S11 – Coulombic interaction of free energy calculated by cMD for CH_3OH, COH and CO.

To account for the charge redistribution that occurs due to adsorption, we calculate entropy of solvation by using:

$$T\Delta S_{int}^{cMD} = \left(\Delta E_{pt+ads}^{with\ ads} - \Delta E_{pt}^{clean}\right) - \left(\Delta F_{pt+ads}^{with\ ads} - \Delta F_{pt}^{clean}\right) \quad \text{(S4)}$$

which is the equation used in the main text. Here, $\left(\Delta E_{pt+ads}^{with\ ads}\right)$ calculates the interaction energy between water and the Pt electrode surface and the adsorbate, and $\left(\Delta E_{pt}^{clean}\right)$ calculates the interaction energy between water and the Pt electrode surface when there is no adsorbate on the surface. Entropies of CH_3OH calculated by equations (S1), (S2) and (S4) are shown in Figure S12a. The fact that equations S2 and S4 give similar results suggests that contributions related to H_2O-Pt electrode surface interactions have been successfully accounted for by using Equation (S4). The differences between $T\Delta S_{int}^{cMD}$ calculated using equation (S*2*) versus equation (S*4*) are due to charge redistribution that occurs upon adsorption. This is captured when the adsorbate and Pt electrode surface are scaled (as in equation (S*4*)) but not when the adsorbate only is scaled (as in equation (S*2*)). Hence, we scale the adsorbate and Pt electrode surface and calculate $T\Delta S_{int}^{cMD}$ according to equation (S*4*) in this manuscript.

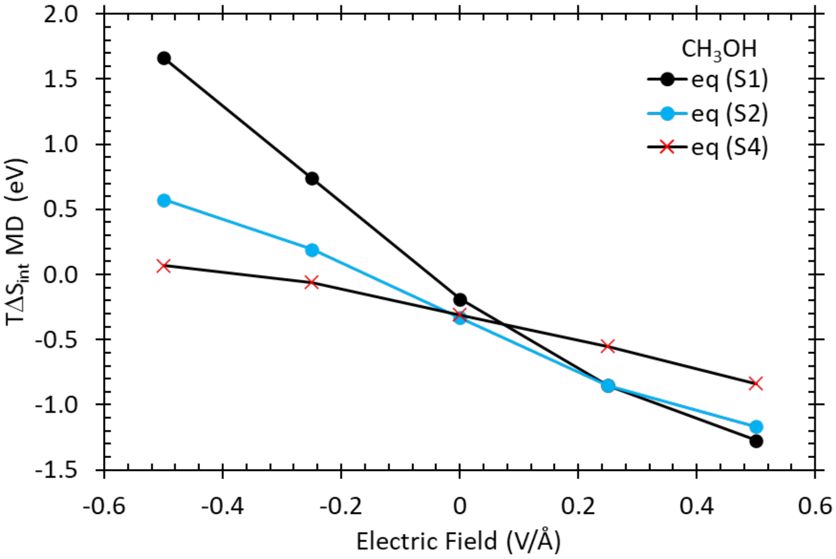


Figure S12 – Entropy of CH_3OH calculated by equations (S1), (S2) and (S4).

S11. Implicit Solvation

Figure S13 shows the free energy of solvation by implicit method in comparison with MSS. Values of F_{imp} are calculated in DFT using the VASPsol method. [3] VASPsol adds a dielectric term to the Hamiltonian that simulates a solvent continuum. The dielectric constant is set to 78.40 for water as solvent. The values for CO calculated by implicit method are closer to free energy of solvation calculated by MSS method specifically at negative electric fields and 0.0 V/Å, however it is significantly different for CH_3OH and COH, suggesting that explicit methods are needed to compute free energies of catalytic species that form hydrogen bonds with H_2O in the presence of fields. Our findings in the main text suggest that explicit H_2O molecules are needed to compute energies and entropies of solvation in the presence of electric fields.

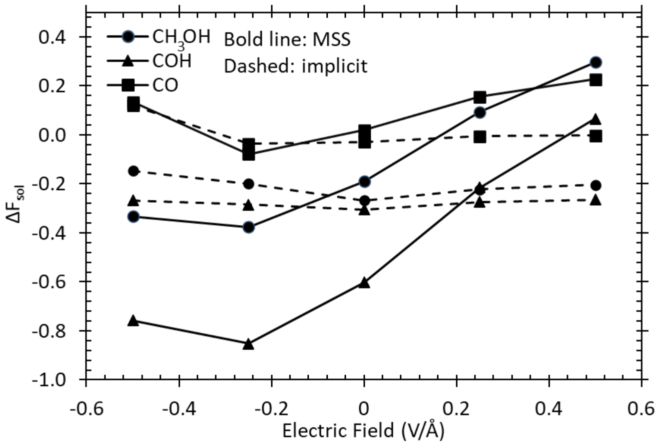


Figure S13 – Free energy of solvation for CH_3OH, COH and CO, calculated by implicit method in DFT in comparison with MSS.

S12. Effects of the Electric Field on Adsorbate-Water Interactions

The applied electric field modifies the water orientation, and this can influence the structure of the solvation shell of the adsorbates. Three parameters were analyzed to describe the influence of the electric field on the solvation shell of water: the adsorbate to water distance for the closest water molecule in the first solvation shell, the average hydrogen bonded water molecules, and the water-adsorbate coordination number. The average distance between the adsorbed species and the closest water molecule in the first solvation shell is shown in Figure S*14*. The influence of the electric field on the oxygen of the adsorbate to oxygen of water was minor for the three adsorbates. The oxygen in the adsorbate to Hydrogen of water distance and hydrogen in the adsorbate to oxygen of water, in the case of CH_3OH were affected by the electric field at -0.5 V/Å, because of the hydrogen down alignment with the electric field, while in the rest of the cases the electric field had minor influence in the adsorbate to water distances.

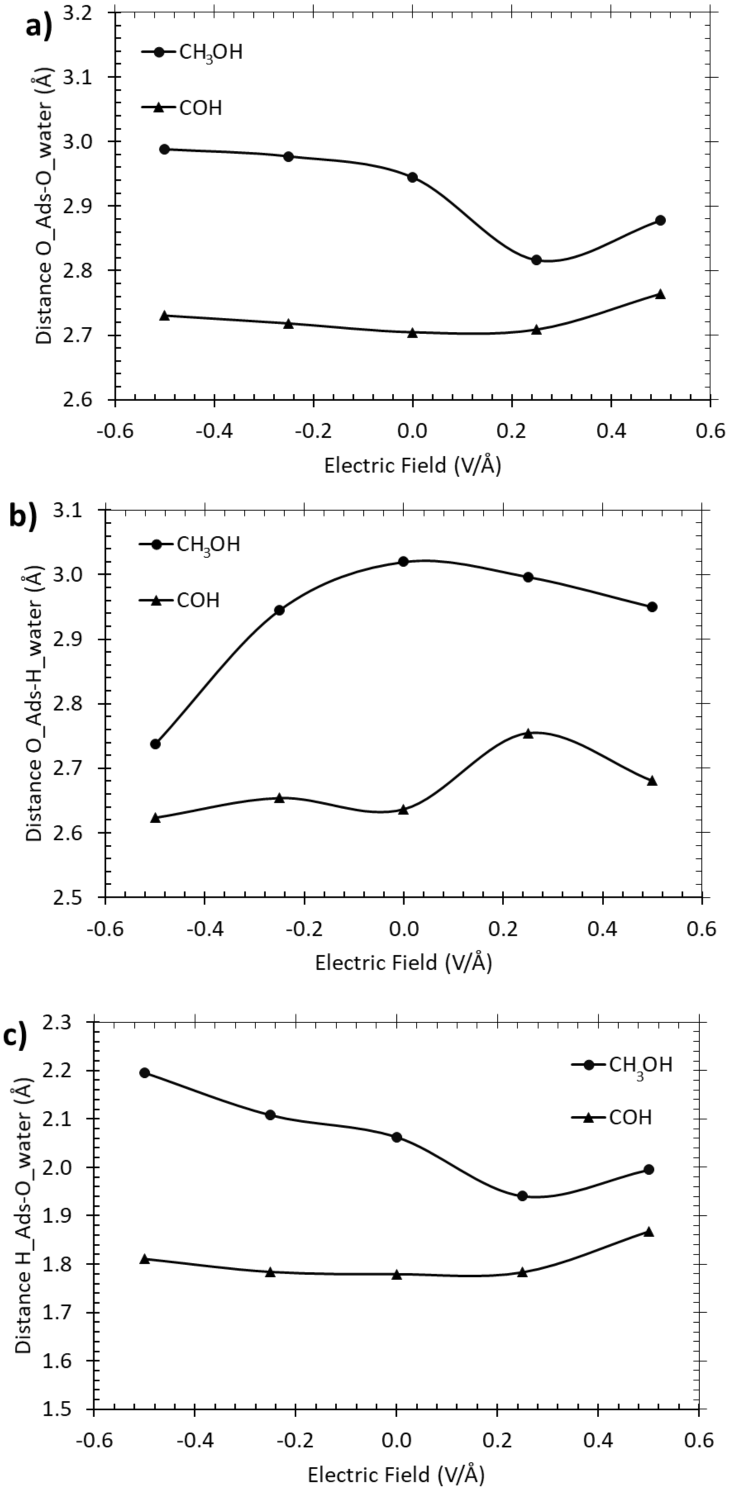


Figure S14 – Effect of the electric field on the adsorbate to water distances calculated with cMD. a) oxygen in the adsorbate to oxygen of water distance b) oxygen of adsorbate to hydrogen of water distance c) hydrogen of adsorbate in the OH group to oxygen of water distance.

In Figure S15, a series plots of the variation of the average number of hydrogen bonds with the electric field is shown. For instance, at -0.5 V/Å COH* forms of hydrogen bonds with an average of ~1.2 water molecules in the cMD trajectory. The donor type hydrogen bond, i.e., where the hydrogen bond is between the H_2O hydrogen and the adsorbate oxygen, in CH_3OH and COH were hindered in the positive electric fields, since H_2O molecules orient oxygen down, and enhanced in negative electric fields, since H_2O molecules orient hydrogen down. The acceptor hydrogen bond, i.e., where the hydrogen bond is between the H_2O oxygen and the adsorbate hydrogen, is the dominant type of hydrogen bond in this work. It did not change significantly with the electric field, which also is reflected in the weak dependence of the total hydrogen bonds on the electric field.

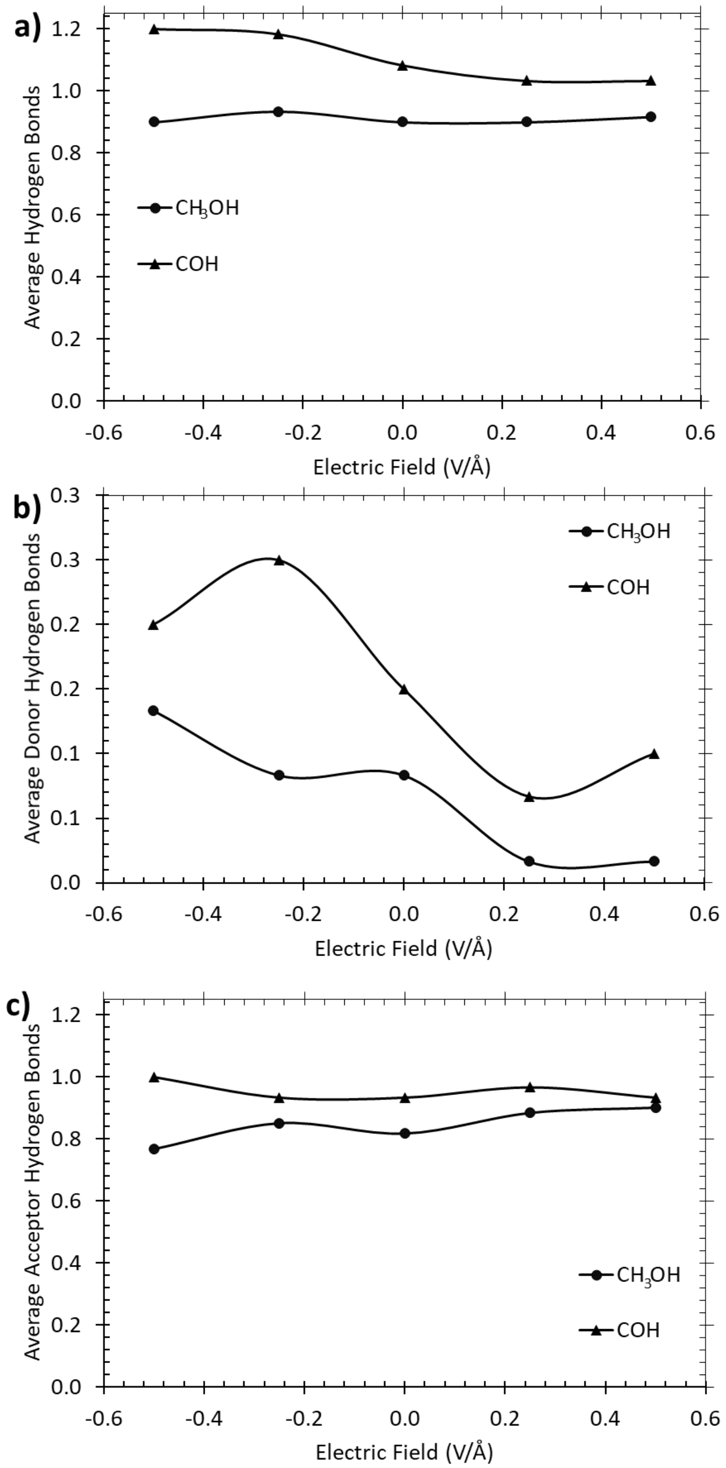


Figure S*15– Effect of the electric field in the average hydrogen bonds of the adsorbates* calculated with cMD*. a)* t*otal hydrogen bond b)* water molecules as d*onor hydrogen bond c)* water molecules as a*cceptor hydrogen bond.* Reported values are averages per frame over 30 uncorrelated configurations of water.

The coordination number was calculated following the method proposed by Qiaoling Li, [4] where the coordination number in the first solvation shell was extracted from those water molecules whose radius between the ion and water does not contain another water molecule. Figure S*16* shows the dependence on the coordination number, the minimum coordination number for all the adsorbates is at 0 V/Å, the application of the electric field causes an increase in the coordination number. These phenomena indicate that the electric field rearranges the water structure and modifies the packing of the water around the adsorbates.

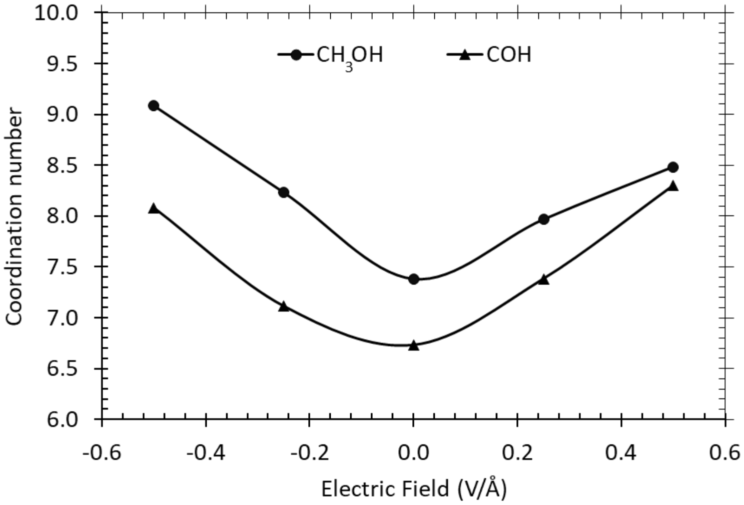


Figure S16– Dependance of the coordination number and electric field for CH_3OH and COH calculated with cMD.

S13. Configuration and Partial Charges of Adsorbate on Pt Surface

Figure S17 shows the geometry parameters in CH_3OH and COH adsorption. The partial charges of hydrogen on hydroxyl group are also reported in Table S6. Partial charges of all other atoms for CH_3OH, COH and CO are shown in Table S7, Table S8 and Table S9, respectively.

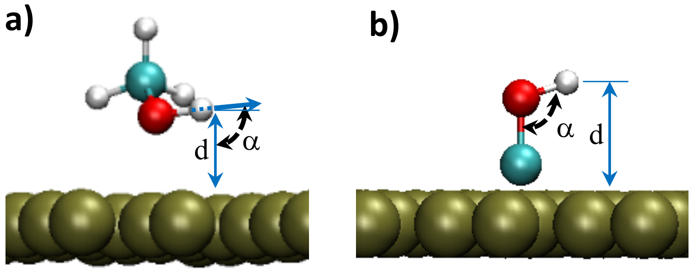


Figure S17 – schematic of a) CH_3OH and b) COH adsorption on Pt (111)

Table S6 – The values of ‘α’ and ‘d’ in Figure S17 at -0.5, 0.0 and +0.5 V/Å calculated with DFT. Partial charge of hydrogen on hydroxyl group is also reported.

Adsorbate	Description	-0.5 V/Å	0.0 V/Å	+0.5 V/Å
COH	d(Å)	2.94	2.79	2.86
	α(°)	112.33	109.19	106.48
	Hydrogen in (OH) partial charge	0.42	0.40	0.37
CH_3OH	d(Å)	2.40	2.37	2.32
	α(°)	103.78	100.44	94.11
	Hydrogen in (OH) partial charge	0.36	0.34	0.32

Table S7 – Methanol on platinum partial charges calculated with DFT

		Potential (V/Å)				
No.	**Atom type**	**-0.50**	**-0.25**	**0.0**	**+0.25**	**+0.50**
1	Pt	-0.063124	-0.05117	-0.04156	-0.02709	-0.01488
2	Pt	-0.063727	-0.05178	-0.04214	-0.02778	-0.01562
3	Pt	-0.062354	-0.05043	-0.04081	-0.02624	-0.01412
4	Pt	-0.062664	-0.05083	-0.04125	-0.0269	-0.01486
5	Pt	-0.062277	-0.05061	-0.04119	-0.02688	-0.01508
6	Pt	-0.060262	-0.04856	-0.0391	-0.02485	-0.01298
7	Pt	-0.057629	-0.04602	-0.03682	-0.02273	-0.011
8	Pt	-0.061415	-0.04977	-0.04042	-0.02597	-0.01414
9	Pt	-0.059585	-0.04745	-0.03767	-0.02299	-0.01078
10	Pt	-0.058585	-0.04663	-0.03682	-0.02219	-0.00993
11	Pt	-0.061875	-0.05014	-0.04076	-0.02647	-0.01458
12	Pt	-0.059152	-0.04721	-0.03758	-0.02302	-0.01088
13	Pt	-0.056396	-0.04479	-0.03554	-0.02134	-0.00981
14	Pt	-0.063459	-0.0517	-0.04222	-0.02802	-0.01616
15	Pt	-0.062122	-0.05033	-0.04083	-0.02662	-0.01469
16	Pt	-0.058222	-0.04659	-0.03723	-0.02295	-0.01117
17	Pt	0.081146	0.080521	0.079847	0.078613	0.077384
18	Pt	0.079786	0.079099	0.078309	0.076967	0.07573
19	Pt	0.08896	0.088167	0.087086	0.085624	0.083987
20	Pt	0.081883	0.080861	0.079754	0.078263	0.076814
21	Pt	0.085898	0.085495	0.084971	0.083868	0.082827
22	Pt	0.078278	0.077903	0.077413	0.076605	0.07575
23	Pt	0.078485	0.078258	0.077936	0.077253	0.076567
24	Pt	0.081081	0.08059	0.079945	0.078929	0.077948
25	Pt	0.083694	0.083157	0.082667	0.081474	0.080488
26	Pt	0.080132	0.079612	0.078917	0.077986	0.077077
27	Pt	0.077989	0.077725	0.077316	0.076624	0.075719
28	Pt	0.079593	0.079305	0.078912	0.078162	0.077347
29	Pt	0.058263	0.057565	0.057254	0.056595	0.056111
30	Pt	0.079529	0.079163	0.078846	0.077914	0.077066
31	Pt	0.050401	0.049477	0.048546	0.047335	0.046572
32	Pt	0.049274	0.048295	0.047714	0.046749	0.046046
33	Pt	-0.122017	-0.13346	-0.1422	-0.15484	-0.16304
34	Pt	-0.059492	-0.06638	-0.06964	-0.07576	-0.07906
35	Pt	-0.050958	-0.05673	-0.06055	-0.06667	-0.07046
36	Pt	-0.076255	-0.08513	-0.0926	-0.10316	-0.11107
37	Pt	0.121402	0.120622	0.118064	0.115172	0.110629
38	Pt	-0.02752	-0.03784	-0.04608	-0.05838	-0.06797
39	Pt	-0.025628	-0.03517	-0.04189	-0.05286	-0.06142

40	Pt	-0.054302	-0.06372	-0.07095	-0.0818	-0.08943
41	Pt	-0.04147	-0.05177	-0.05974	-0.07143	-0.08055
42	Pt	-0.034246	-0.045	-0.05352	-0.06574	-0.07543
43	Pt	-0.030006	-0.04001	-0.04772	-0.05886	-0.06785
44	Pt	-0.036946	-0.04707	-0.05471	-0.06603	-0.07505
45	Pt	-0.025467	-0.03553	-0.04362	-0.05505	-0.06438
46	Pt	-0.040537	-0.05082	-0.05864	-0.07053	-0.0795
47	Pt	-0.024827	-0.03528	-0.04347	-0.05593	-0.0658
48	Pt	-0.032162	-0.04223	-0.05005	-0.0614	-0.07073
-	C	-0.131208	-0.13118	-0.13282	-0.13076	-0.12674
-	O	-0.283345	-0.28977	-0.29208	-0.29817	-0.31276
-	H	0.121785	0.120093	0.11715	0.112467	0.107987
-	H	0.103336	0.098395	0.095275	0.090338	0.085565
-	H	0.150819	0.134886	0.122405	0.10133	0.080969
-	H	0.357498	0.351896	0.343883	0.331138	0.323313
-	Methanol (total)	0.318885	0.284312	0.253819	0.206347	0.158338

Table S8 – COH on platinum partial charges calculated with DFT

		Potential (V/Å)				
No.	**Atom type**	**-0.50**	**-0.25**	**0.0**	**+0.25**	**+0.50**
1	Pt	-0.05836	-0.04635	-0.03551	-0.0222	-0.01008
2	Pt	-0.05988	-0.0481	-0.03745	-0.02436	-0.01244
3	Pt	-0.06203	-0.05027	-0.0396	-0.02649	-0.01459
4	Pt	-0.05597	-0.04413	-0.03331	-0.0201	-0.00802
5	Pt	-0.0625	-0.05068	-0.04002	-0.02691	-0.01501
6	Pt	-0.06883	-0.05725	-0.04659	-0.03352	-0.02168
7	Pt	-0.0557	-0.04376	-0.03282	-0.01948	-0.00724
8	Pt	-0.05368	-0.04205	-0.03151	-0.01849	-0.00668
9	Pt	-0.05542	-0.04355	-0.0327	-0.01948	-0.00735
10	Pt	-0.05447	-0.04256	-0.03175	-0.01847	-0.00638
11	Pt	-0.06065	-0.04894	-0.03831	-0.02528	-0.01343
12	Pt	-0.06802	-0.05641	-0.04583	-0.03288	-0.02105
13	Pt	-0.05856	-0.04662	-0.03577	-0.02248	-0.01045
14	Pt	-0.06036	-0.04869	-0.03801	-0.02498	-0.01309
15	Pt	-0.0725	-0.06088	-0.05036	-0.03735	-0.02555
16	Pt	-0.05536	-0.04345	-0.0326	-0.01929	-0.00723
17	Pt	0.084343	0.084353	0.084309	0.084115	0.083745
18	Pt	0.057421	0.05644	0.05528	0.053759	0.052442
19	Pt	0.078666	0.078383	0.07816	0.077802	0.077348
20	Pt	0.04536	0.043403	0.041483	0.038929	0.036586
21	Pt	0.077603	0.077396	0.0771	0.076711	0.076328
22	Pt	0.079097	0.07904	0.07886	0.078507	0.078113
23	Pt	0.079411	0.07941	0.079267	0.079046	0.078641
24	Pt	0.087177	0.087336	0.087357	0.087184	0.086841
25	Pt	0.049437	0.048437	0.047504	0.046237	0.044817
26	Pt	0.087549	0.087648	0.087639	0.087376	0.087024
27	Pt	0.073901	0.073699	0.07339	0.072974	0.072504
28	Pt	0.078392	0.078156	0.077838	0.077387	0.076986
29	Pt	0.045295	0.043348	0.041537	0.03936	0.037024
30	Pt	0.079061	0.078783	0.078515	0.078058	0.077579
31	Pt	0.056165	0.055033	0.053888	0.052673	0.051385
32	Pt	0.053202	0.051412	0.049518	0.047157	0.044931
33	Pt	-0.03279	-0.04296	-0.05216	-0.06372	-0.07433
34	Pt	-0.03527	-0.04634	-0.05641	-0.06849	-0.0795
35	Pt	0.004297	0.002721	0.002667	0.002947	0.002142
36	Pt	0.057419	0.05557	0.053941	0.051769	0.051009
37	Pt	0.021991	0.021052	0.020409	0.018579	0.017809
38	Pt	-0.01732	-0.0278	-0.03731	-0.04921	-0.0599
39	Pt	-0.04145	-0.05265	-0.06277	-0.07439	-0.08556

40	Pt	-0.07468	-0.08768	-0.09888	-0.11206	-0.12261
41	Pt	-0.0468	-0.05887	-0.06935	-0.08205	-0.09309
42	Pt	-0.03916	-0.0504	-0.06063	-0.07282	-0.08356
43	Pt	-0.01881	-0.02934	-0.03902	-0.05088	-0.06142
44	Pt	-0.03388	-0.04477	-0.05464	-0.06669	-0.07775
45	Pt	-0.01912	-0.02978	-0.03959	-0.05161	-0.06225
46	Pt	-0.03482	-0.04451	-0.05338	-0.0641	-0.07449
47	Pt	-0.01868	-0.0293	-0.0391	-0.05105	-0.06171
48	Pt	-0.0334	-0.04419	-0.05405	-0.06599	-0.07707
	C	0.077234	0.072677	0.06667	0.061314	0.055221
	O	-0.27958	-0.29572	-0.31162	-0.33137	-0.34736
	H	0.414985	0.403684	0.395711	0.384279	0.372362
	COH (total)	0.212636	0.180642	0.150758	0.114228	0.08022

Table S9 – CO on platinum partial charges calculated with DFT

		Potential (V/Å)				
No.	**Atom type**	**-0.50**	**-0.25**	**0.0**	**+0.25**	**+0.50**
1	Pt	-0.06454	-0.0527	-0.04036	-0.02904	-0.01669
2	Pt	-0.05973	-0.04802	-0.0357	-0.02447	-0.01238
3	Pt	-0.06019	-0.04839	-0.03576	-0.02446	-0.01284
4	Pt	-0.05382	-0.0418	-0.02909	-0.01763	-0.00587
5	Pt	-0.06151	-0.04968	-0.03742	-0.0262	-0.01424
6	Pt	-0.05748	-0.04582	-0.03302	-0.02163	-0.01043
7	Pt	-0.05452	-0.04262	-0.02998	-0.01851	-0.00625
8	Pt	-0.05763	-0.04597	-0.03367	-0.02239	-0.01038
9	Pt	-0.05803	-0.04601	-0.03333	-0.02183	-0.0097
10	Pt	-0.06104	-0.04937	-0.03698	-0.02574	-0.01327
11	Pt	-0.0601	-0.04834	-0.03605	-0.02474	-0.0128
12	Pt	-0.06849	-0.05686	-0.04447	-0.03326	-0.02154
13	Pt	-0.05871	-0.04676	-0.03398	-0.02243	-0.01042
14	Pt	-0.06064	-0.04894	-0.03678	-0.02555	-0.01327
15	Pt	-0.0686	-0.0571	-0.04471	-0.03349	-0.02189
16	Pt	-0.05178	-0.03993	-0.02703	-0.01551	-0.00378
17	Pt	0.077334	0.077427	0.077225	0.077062	0.077185
18	Pt	0.071851	0.07182	0.0721	0.071935	0.070088
19	Pt	0.07409	0.07367	0.07294	0.072358	0.072676
20	Pt	0.053527	0.052249	0.050589	0.049234	0.046969
21	Pt	0.073221	0.072833	0.071934	0.071279	0.071567
22	Pt	0.077045	0.077221	0.077256	0.07718	0.07687
23	Pt	0.073265	0.073145	0.072857	0.072653	0.072554
24	Pt	0.079162	0.079237	0.079319	0.079234	0.079051
25	Pt	0.05272	0.051743	0.050374	0.049336	0.047834
26	Pt	0.078475	0.078533	0.078489	0.078271	0.078277
27	Pt	0.072942	0.073013	0.0729	0.07275	0.072336
28	Pt	0.075013	0.074995	0.074736	0.074522	0.07426
29	Pt	0.04501	0.042536	0.03933	0.036926	0.034477
30	Pt	0.076335	0.076448	0.076391	0.076207	0.075821
31	Pt	0.053211	0.052162	0.050883	0.049677	0.04833
32	Pt	0.052136	0.050775	0.049195	0.047667	0.045444
33	Pt	-0.01187	-0.01958	-0.02654	-0.03367	-0.04522
34	Pt	-0.02329	-0.03485	-0.04677	-0.05729	-0.0693
35	Pt	-0.00111	-0.00905	-0.01823	-0.02584	-0.02859
36	Pt	0.020731	0.020523	0.020696	0.019738	0.02014
37	Pt	0.022873	0.021903	0.023245	0.022581	0.022635
38	Pt	-0.01109	-0.02224	-0.03388	-0.04453	-0.05547
39	Pt	-0.02439	-0.03601	-0.04853	-0.0597	-0.07122

40	Pt	-0.02325	-0.03477	-0.04687	-0.05765	-0.06768
41	Pt	-0.01678	-0.02808	-0.0396	-0.05017	-0.06215
42	Pt	-0.01568	-0.02686	-0.03849	-0.04913	-0.06109
43	Pt	-0.01394	-0.02549	-0.03762	-0.04844	-0.05883
44	Pt	-0.02173	-0.03287	-0.04444	-0.05487	-0.06679
45	Pt	-0.01532	-0.02677	-0.03911	-0.05002	-0.06042
46	Pt	-0.02494	-0.03649	-0.0487	-0.05959	-0.06987
47	Pt	-0.01023	-0.02143	-0.03298	-0.04349	-0.05484
48	Pt	-0.02274	-0.03422	-0.04673	-0.05783	-0.06907
	C	0.167048	0.167104	0.16412	0.167365	0.167204
	O	-0.10285	-0.13033	-0.15778	-0.18686	-0.21746
	CO (total)	0.064194	0.036778	0.006339	-0.0195	-0.05026

S14. Influence of Hydrogen Bonding Criteria

Figure S18 shows the comparison between the θ (please see the main text for definition) for CH_3OH and COH at a) -0.5 b) 0.0 and c) +0.5 V/Å, respectively. This data is the same as presented in the main text but comparing adsorbates at constant field instead of fields for the same adsorbate.

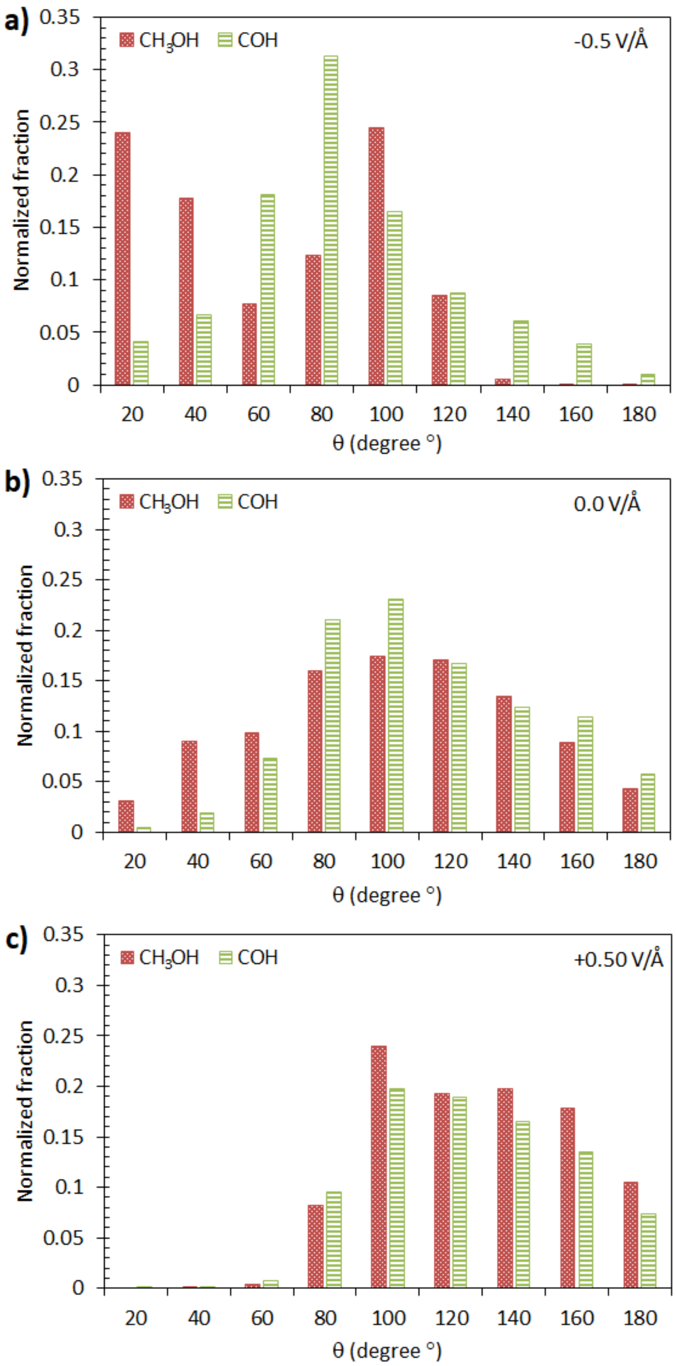


Figure S18 – Orientations of H_2O molecules hydrogen bonded with CH_3OH and COH at (a) –0.5 (b) 0.0 and (c) +0.5 V/Å, respectively calculated with cMD.

S15. VASP INCAR File

Here is a sample of INCAR file for CH_3OH at -0.5 V/Å

```
System  = Geometry Optimization
NWRITE  = 1
LCHARG  = .TRUE.
LVTOT   = .TRUE.
LAECHG = .TRUE.
LWAVE = .TRUE.

Electronic Relaxation
ENCUT   = 400
ALGO    = Fast
ISMEAR  = 0
SIGMA   = 0.100
PREC    = Accurate
LREAL   = Auto
ROPT    = 2e-4 2e-4 2e-4 2e-4
ISTART  = 2
NELM    = 10000
NELMDL  = -8
EDIFF   = 1e-5
ISPIN   = 1

EFIELD = -0.5
LDIPOL = .TRUE.
IDIPOL = 3

Ionic Relaxation
NSW     = 1000
ISIF    = 2
IBRION  = 1
NFREE   = 10
POTIM   = 0.35
EDIFFG  = -0.03

Dispersion
LVDW    = .TRUE.
VDW_C6  = 42.440 1.750 0.700 0.140
```

VDW_R0 = 1.750 1.452 1.342 1.002

Density of States
RWIGS = 1.300 0.770 0.730 0.320

References

1. R. P. Hardikar, U. Mondal, F. M. Thakkar, S. Roy and P. Ghosh, *Physical Chemistry Chemical Physics*, 2019, **21**, 24345-24353.
2. X. Zhang, R. S. DeFever, S. Sarupria and R. B. Getman, *Journal of Chemical Information and Modeling*, 2019, **59**, 2190-2198.
3. K. Mathew, R. Sundararaman, K. Letchworth-Weaver, T. A. Arias and R. G. Hennig, *The Journal of Chemical Physics*, 2014, **140**, 084106.
4. Y. Liu, H. Lu, Y. Wu, T. Hu and Q. Li, *The Journal of Chemical Physics*, 2010, **132**, 124503.