Supporting Information

Effect of Explicit Water Molecules on the Electrochemical Hydrogenation of CO_2 on Sn(112)

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1. Computational details

The free energies of the adsorbed intermediates were calculated based on the PBE energies of the optimized structures with the explicit water molecules and implicit solvent effect, Zero Point Energy (ZPE) and entropy (TS) corrections according to the following equation:

$$\Delta G = E_{elec} + \Delta E_{im} + \Delta ZPE - T\Delta S \quad (1)$$

where the ZPE of an adsorbate was calculated from the harmonic frequencies. Vibrational contributions to the entropy of adsorbed species were also calculated at 298.15 K based on the vibrational frequencies[1]. The ZPE and entropy corrections due to the water molecules is proportion to the number of water molecules as shown in Figure S1. The ZPE per water molecule is 0.65 eV and the entropy corrections at 298.15 K is 0.17 eV[2].

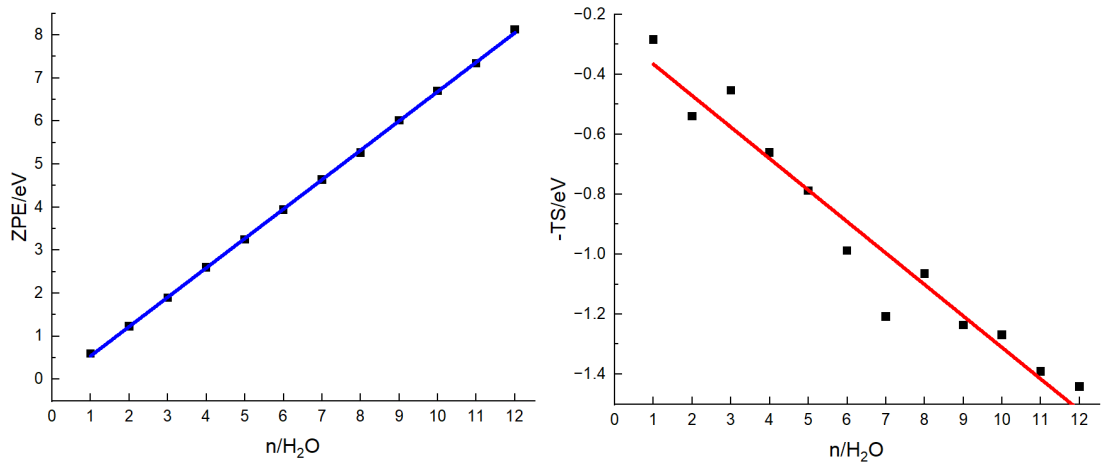


Figure S1 Calculated ZPE and entropy correction as a function of the number of water molecules.

2. Implicit solvent effect

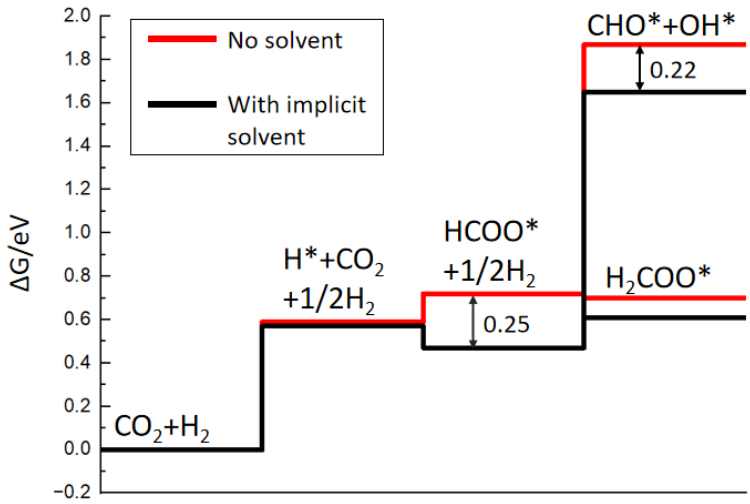
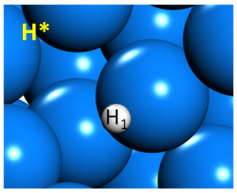
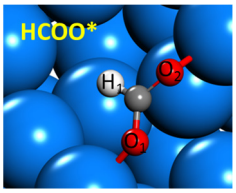
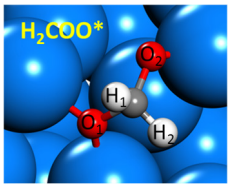
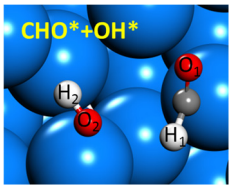


Figure S2. Free energy diagram for CO_2 reduction on Sn(112) with and without implicit solvent.

3. Bader Charge Analysis

Table S1. Bader charges of the hydrogen and oxygen atoms in the reaction intermediates with up to 12 water molecules. Specific atoms have been labelled in the figures and the charges are reported in |e|.

														
Atoms		0 H_2O	1 H_2O	2 H_2O	3 H_2O	4 H_2O	5 H_2O	6 H_2O	7 H_2O	8 H_2O	9 H_2O	10 H_2O	11 H_2O	12 H_2O
H*	H_1	-0.32	-0.29	-0.34	-0.38	-0.39	-0.36	-0.35	-0.35	-0.36	-0.35	-0.38	-0.38	-0.36
HCOO*	H_1	+0.10	+0.06	+0.04	+0.11	+0.14	+0.07	+0.07	+0.07	+0.11	+0.11	+0.15	+0.18	+0.13
	O_1	-1.17	-1.14	-1.16	-1.16	-1.19	-1.20	-1.18	-1.19	-1.20	-1.20	-1.20	-1.17	-1.18
	O_2	-1.17	-1.15	-1.20	-1.21	-1.21	-1.22	-1.22	-1.23	-1.22	-1.22	-1.22	-1.22	-1.21
H_2COO*	H_1	+0.06	+0.09	+0.04	+0.07	+0.06	+0.09	+0.10	+0.11	+0.07	+0.03	+0.03	+0.06	+0.07
	H_2	+0.02	+0.04	+0.03	+0.06	+0.05	+0.05	+0.04	+0.04	+0.05	+0.03	+0.03	+0.04	+0.03
	O_1	-1.09	-1.10	-1.12	-1.11	-1.10	-1.12	-1.11	-1.10	-1.11	-1.10	-1.12	-1.11	-1.12
	O_2	-1.12	-1.13	-1.13	-1.15	-1.14	-1.14	-1.13	-1.13	-1.15	-1.14	-1.16	-1.16	-1.14
CHO*+	H_1	+0.13	+0.06	+0.11	+0.09	+0.06	+0.11	+0.09	+0.06	+0.05	+0.06	+0.06	+0.09	+0.06

OH*	H_2	+0.59	+0.57	+0.6	+0.58	+0.65	+0.66	+0.65	+0.67	+0.64	+0.63	+0.63	+0.62	+0.62
	O_1	-1.08	-1.03	-1.09	-1.11	-1.10	-1.11	-1.11	-1.11	-1.12	-1.13	-1.11	-1.12	-1.11
	O_2	-1.19	-1.18	-1.23	-1.28	-1.25	-1.27	-1.25	-1.26	-1.26	-1.25	-1.26	-1.26	-1.26

4. The projected interaction between water molecules and surface ($\Delta E_{H2O/surf}$), and the hydrogen bonding energy as a function of number of water molecules ($\Delta E_{H\text{-}B}$)

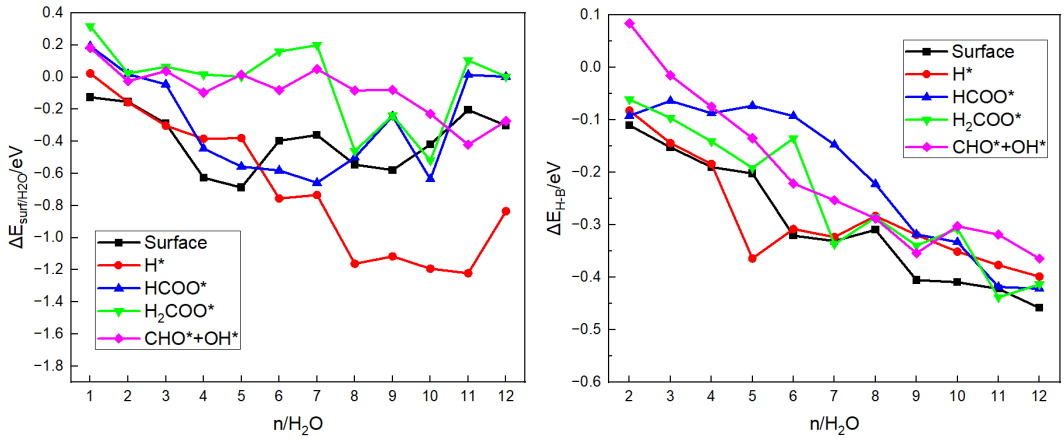


Figure S3. The projected interaction between water molecules and surface (a), and the hydrogen bonding energy inside the water cluster (b) with 1 to 12 water molecules. As one water cannot form hydrogen bond, no hydrogen bonding energy is shown for n=1.

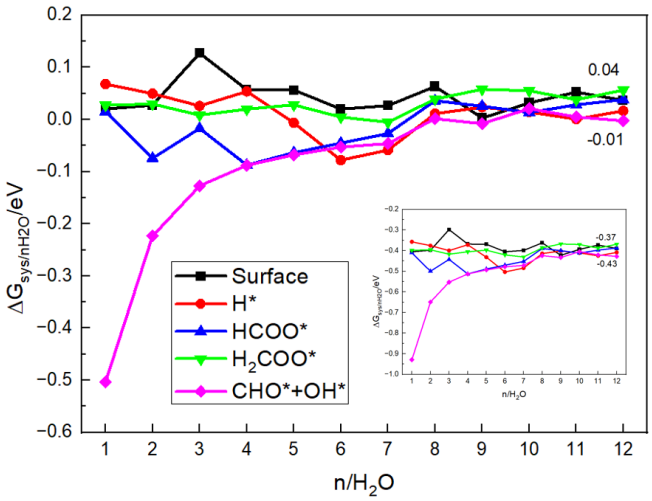


Figure S4. The calculated average contribution of explicit water molecules to different reaction intermediates as a function of the number of the explicit water molecules in the system.

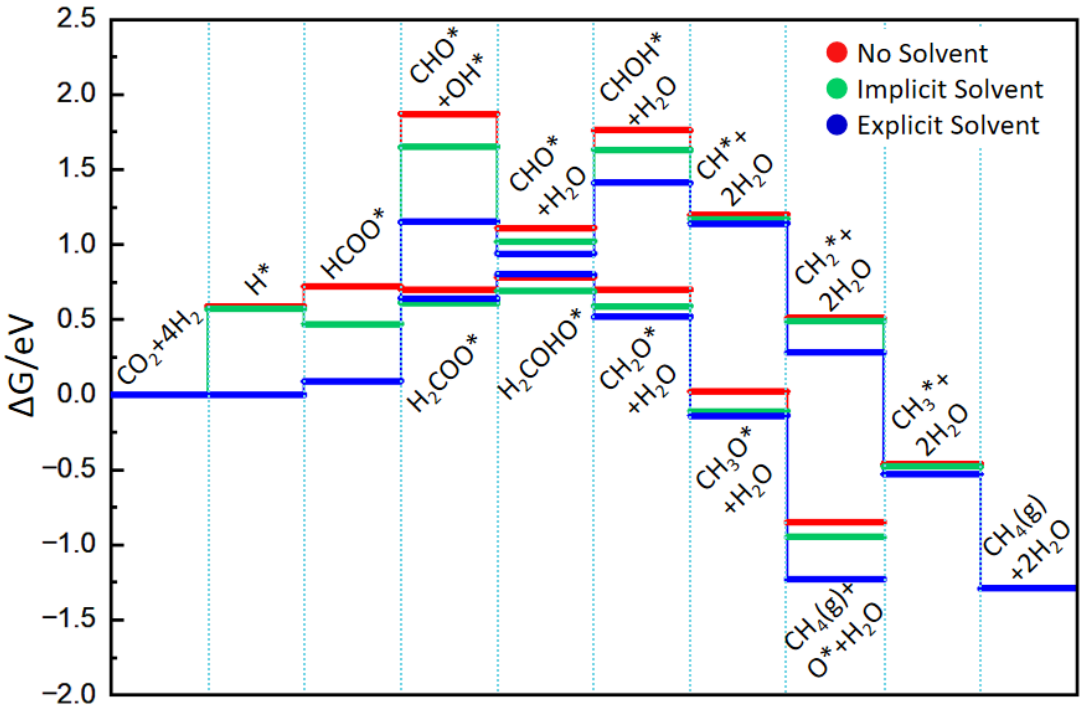
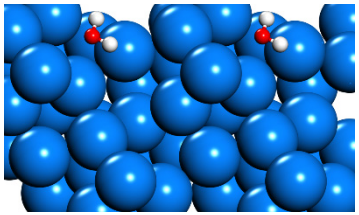
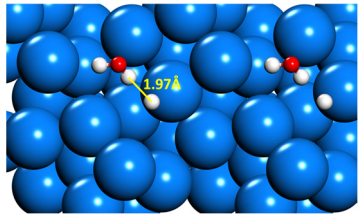
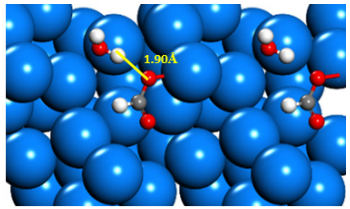
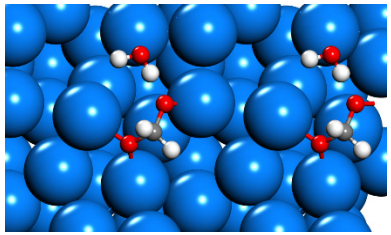
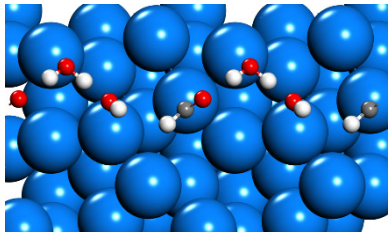
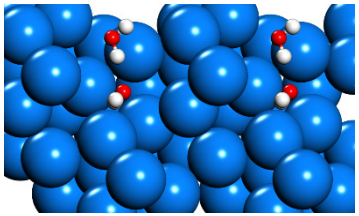
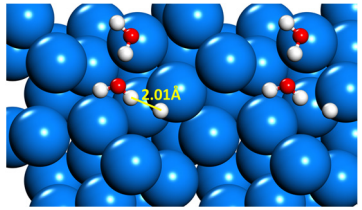
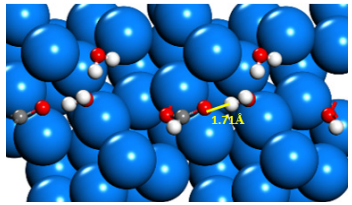
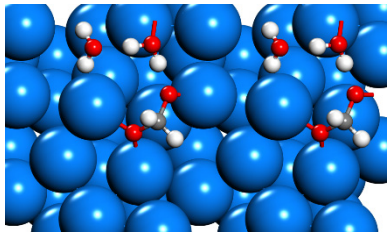
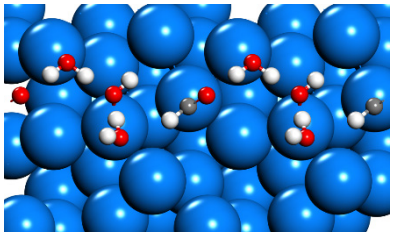
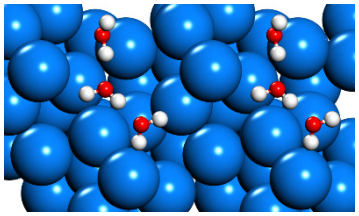
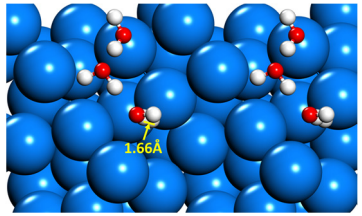
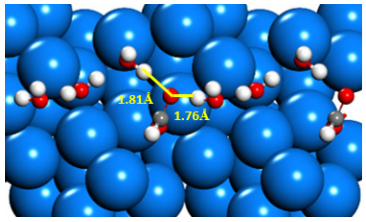
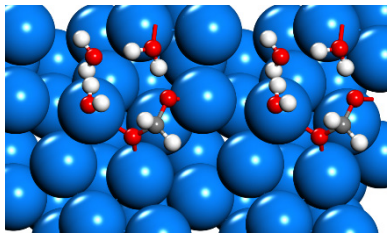
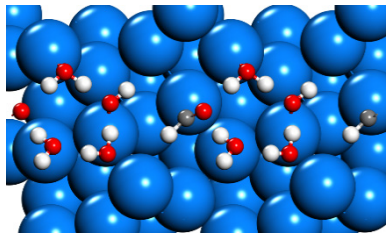
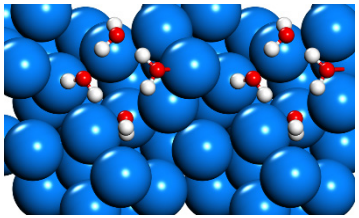
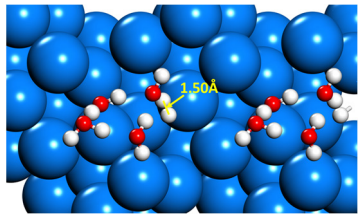
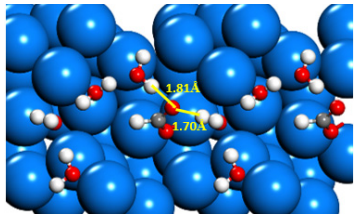
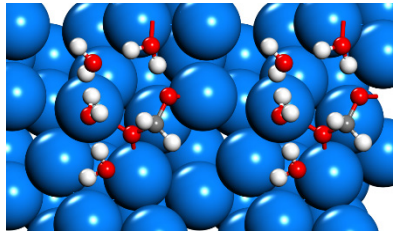
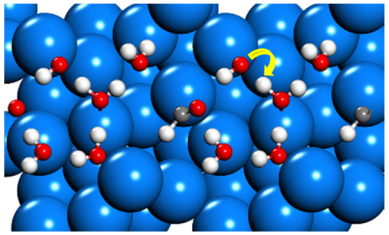
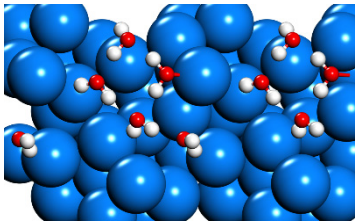
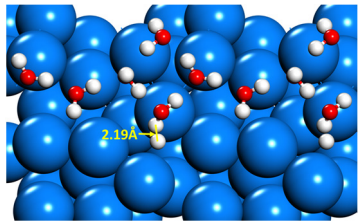
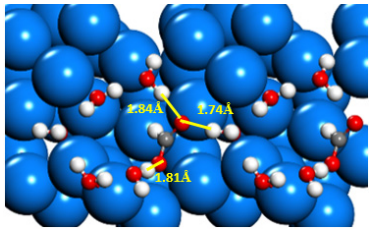
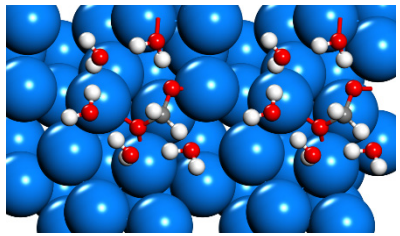
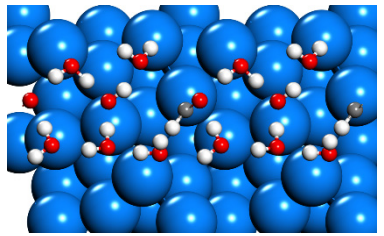
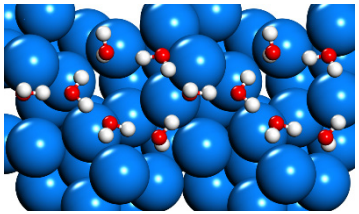
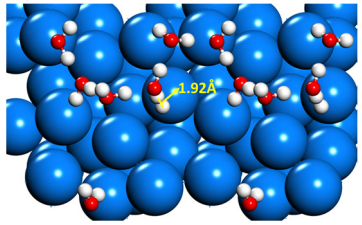
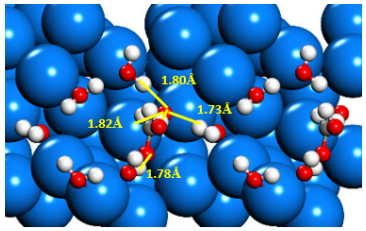
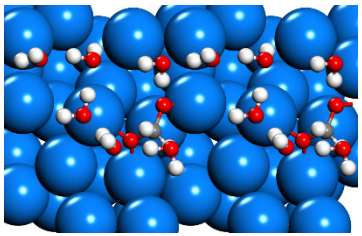
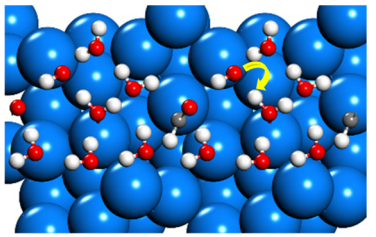
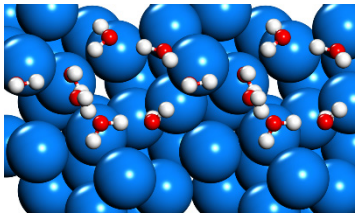
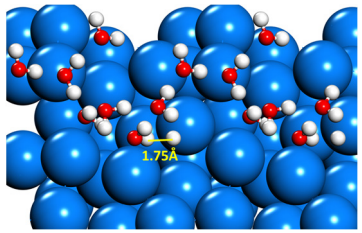
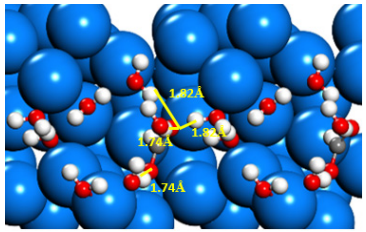
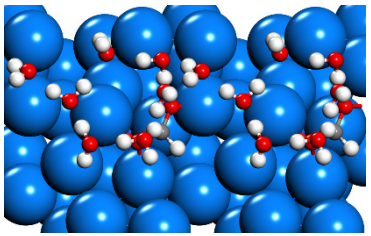
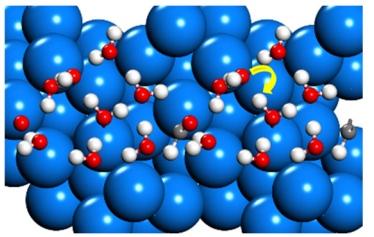


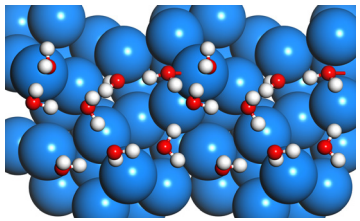
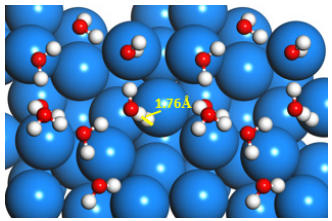
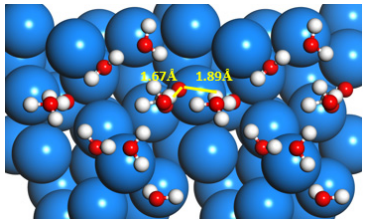
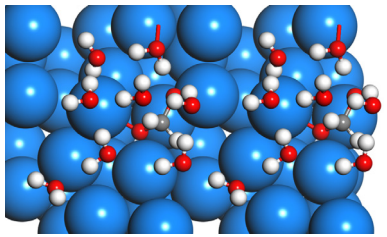
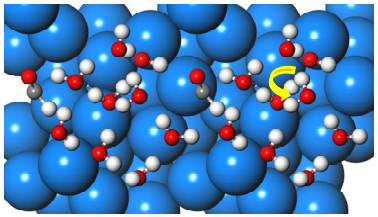
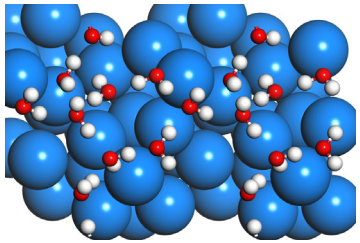
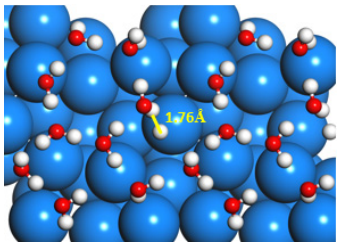
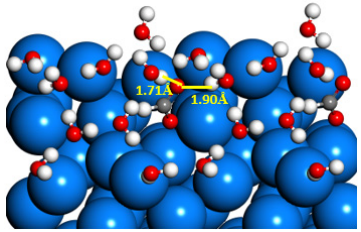
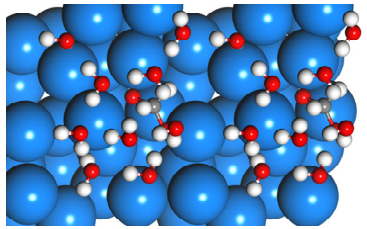
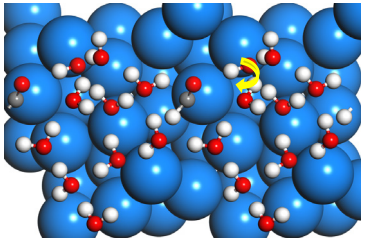
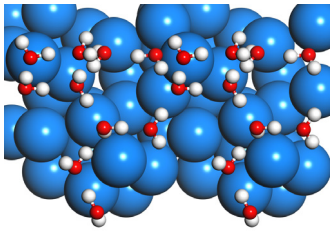
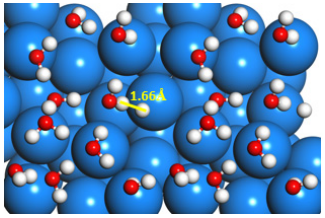
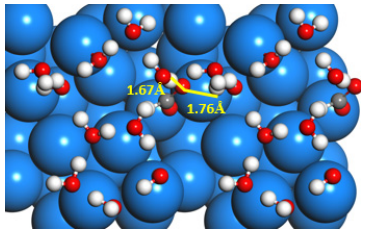
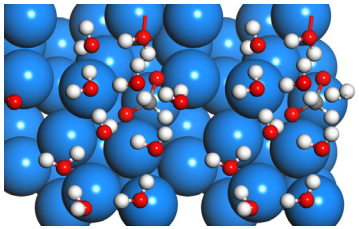
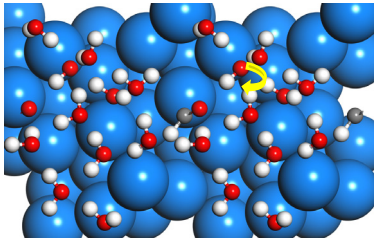
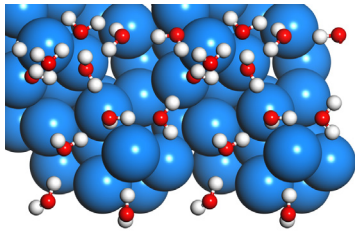
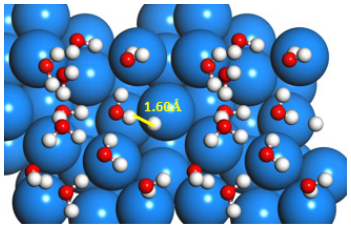
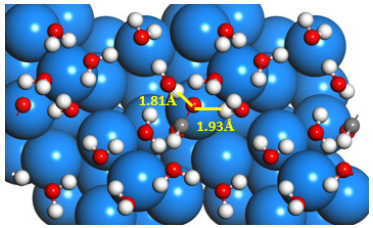
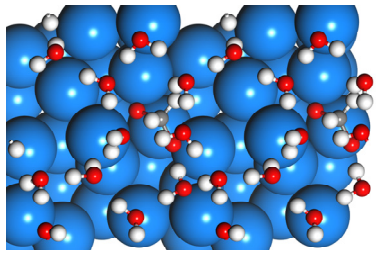
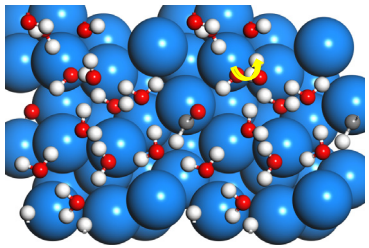
Figure S5. Comparison of electrochemical hydrogenation of CO_2 on Sn(112) under different solvent conditions. The red line shows the mechanism with no solvent. The green line shows the pathway with the implicit solvent model. The blue line shows the route with six explicit water molecules as the solvation shell.

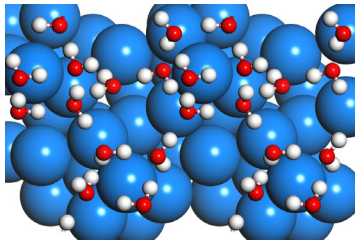
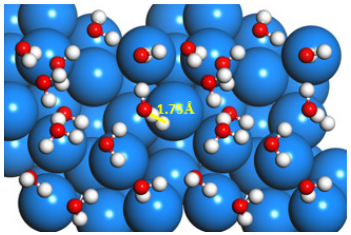
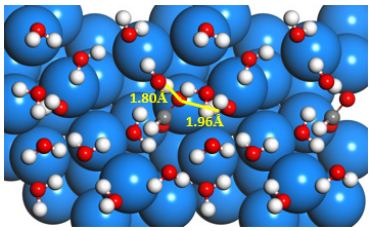
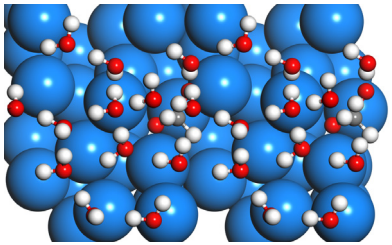
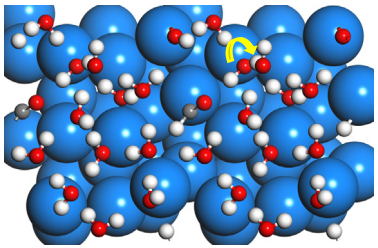
5. **Optimized structures**

Table S2. Top view of the optimized configurations for every intermediate with one to seven water molecules. Hydrogen hopping pathways are shown as yellow arrows in CHO*+OH* with more than four water molecules. Every structure is shown in two unit-cells.

Spec.	Clean Surface	H*	HCOO*	H_2COO*	CHO*+OH*
$1H_2O$					
$2H_2O$					
$3H_2O$					

$4H_2O$					
$5H_2O$					
$6H_2O$					
$7H_2O$					

$8H_2O$					
$9H_2O$					
$10H_2O$					
$11H_2O$					

$12H_2O$					

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