Supplementary Information for: Topological perturbation to a standard dehydrogenation catalyst, Pt_3Sn

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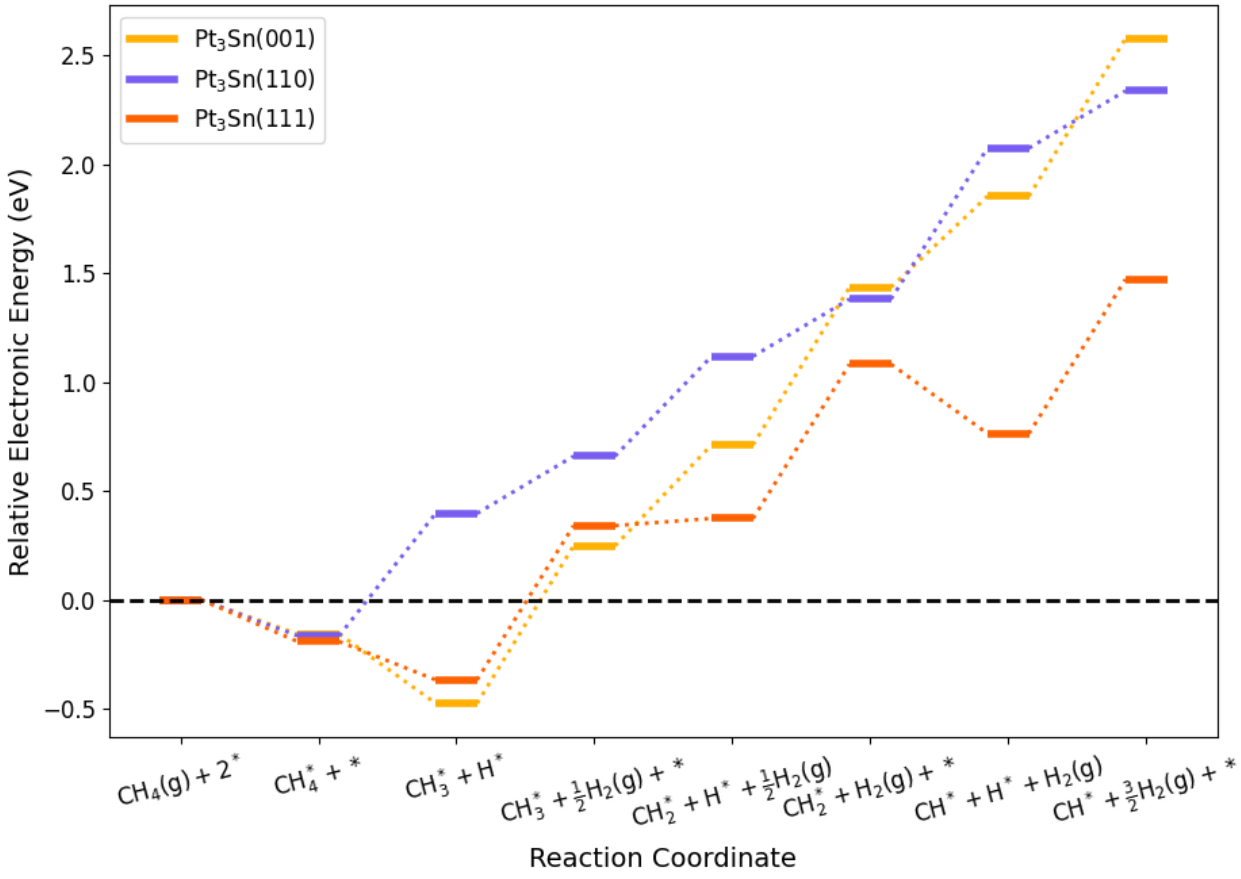

Figure 1: Dehydrogenation profile of methane on Pt_3Sn without thermodynamic correction of gas phase molecules

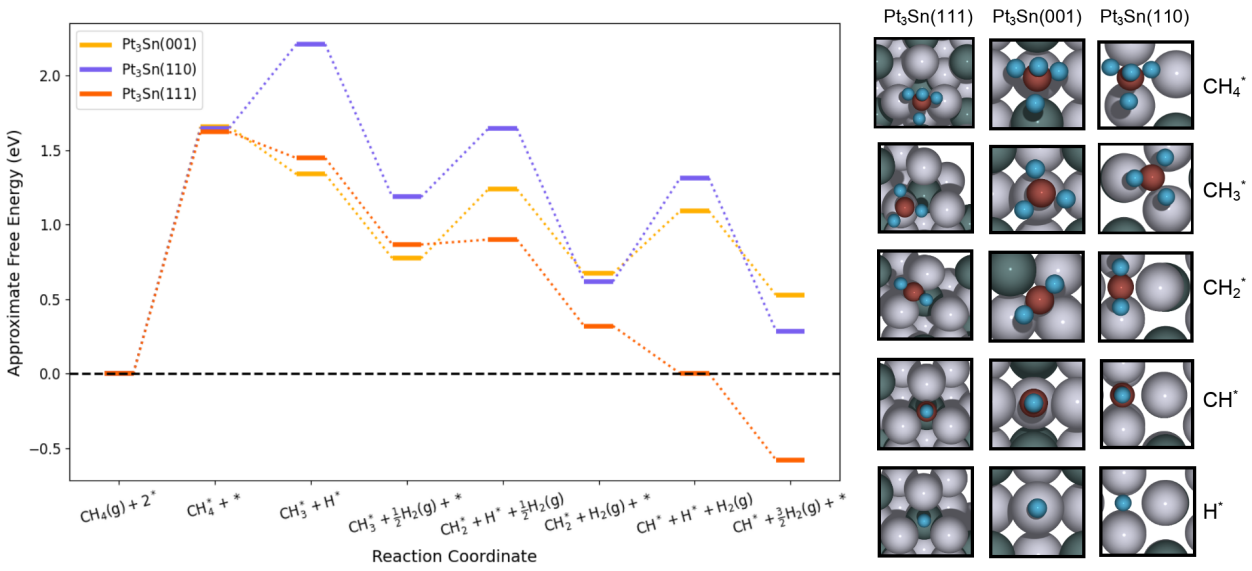

Figure 2: Dehydrogenation profile of methane on Pt_3Sn at 0.2 bar and 873K

Surface Energies and Wulff Constructions

Originally, only the low index surfaces of Pt_3Sn were considered, producing the Wulff construction seen in Figure S5. Our low index model aligns well with both experiment and the general understanding of FCC binary alloys [1, 2, 3, 4]. The closest packed planes are preferentially exposed on FCC nanoparticles. Furthermore, only the surface normals h_{111} and h_{001} of a binary FCC alloy are needed to adequately describe the particle morphology [5].

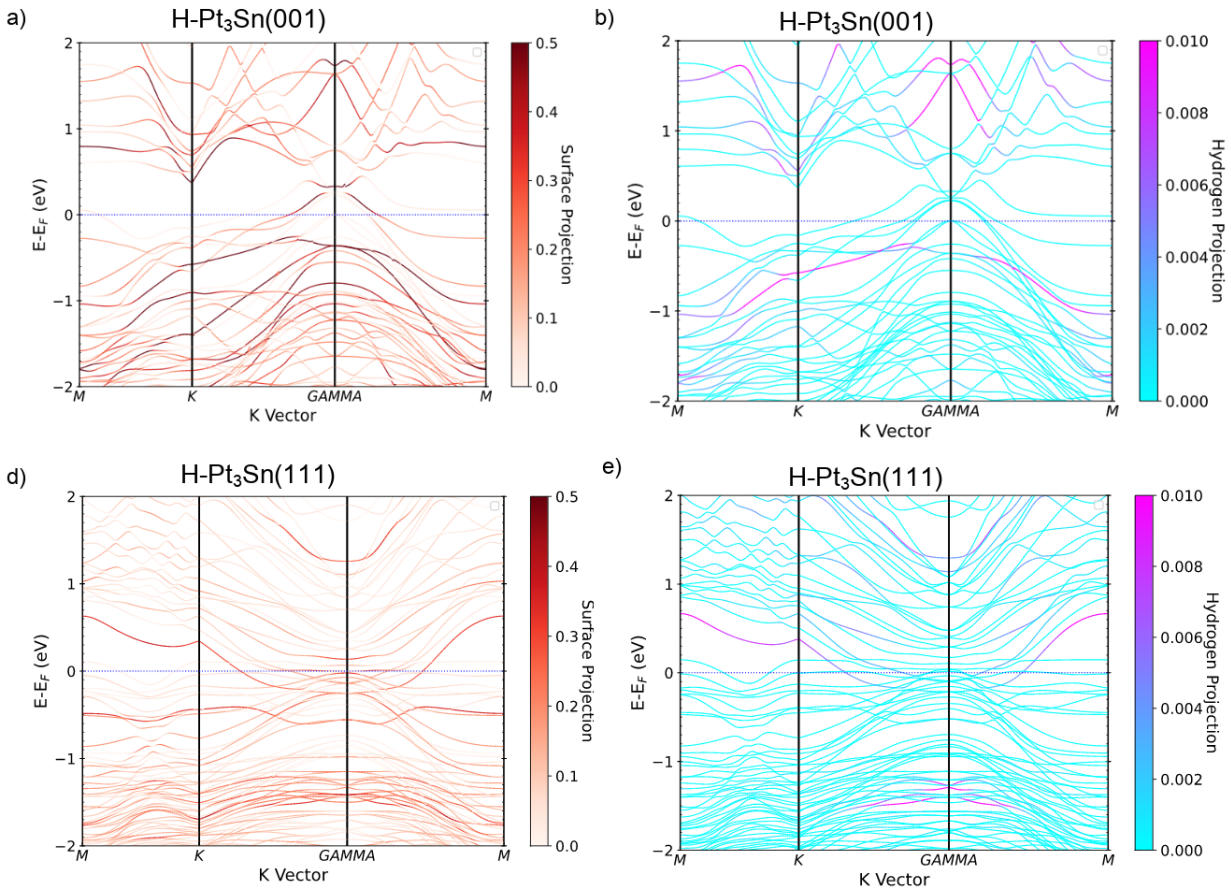

Figure 3: A comparison of the projected band structures of $Pt_3Sn(111)$ and $Pt_3Sn(001)$ with adsorbed H

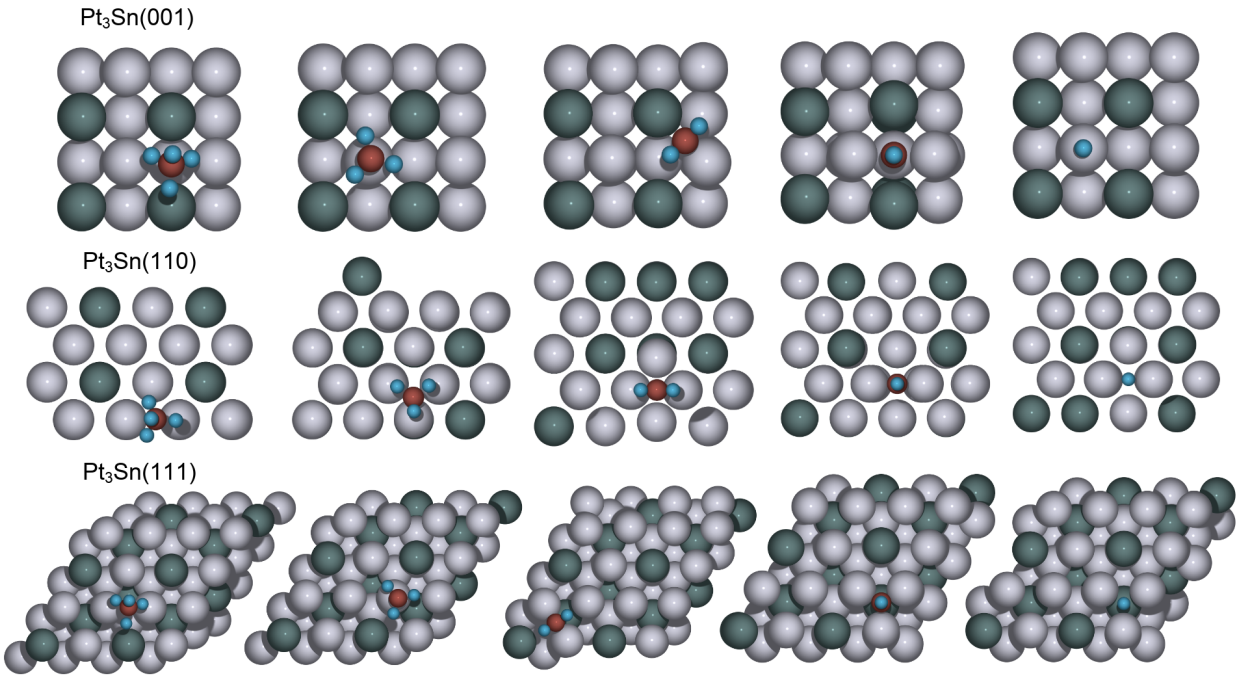

Figure 4: Top down view of the DFT optimized structures used for the dehydrogenation of methane

Table 1: Computed surface energies for various terminations of Pt_3Sn

Surface	**Area** ($\AA^2$)	**Surface Energy** ($eV/\AA^2$)	**Surface Energy** (J/m^2)
001	16.240	0.116	1.858
110	22.960	0.112	1.797
111	28.120	0.091	1.456
210	36.300	0.115	1.843
211	39.770	0.107	1.709
221	48.710	0.103	1.649
310	51.340	0.117	1.869
311	53.850	0.112	1.787
320	58.540	0.117	1.869
321	60.750	0.110	1.764
322	66.940	0.102	1.637
331	70.770	0.108	1.732
332	76.150	0.098	1.575

Pt_3Sn Adsorbate Site Sampling

This section contains results from a sampling procedure for $Pt_3Sn(001)$, $Pt_3Sn(110)$, and $Pt_3Sn(111)$. The first three tables contain the total energies and binding energies of the

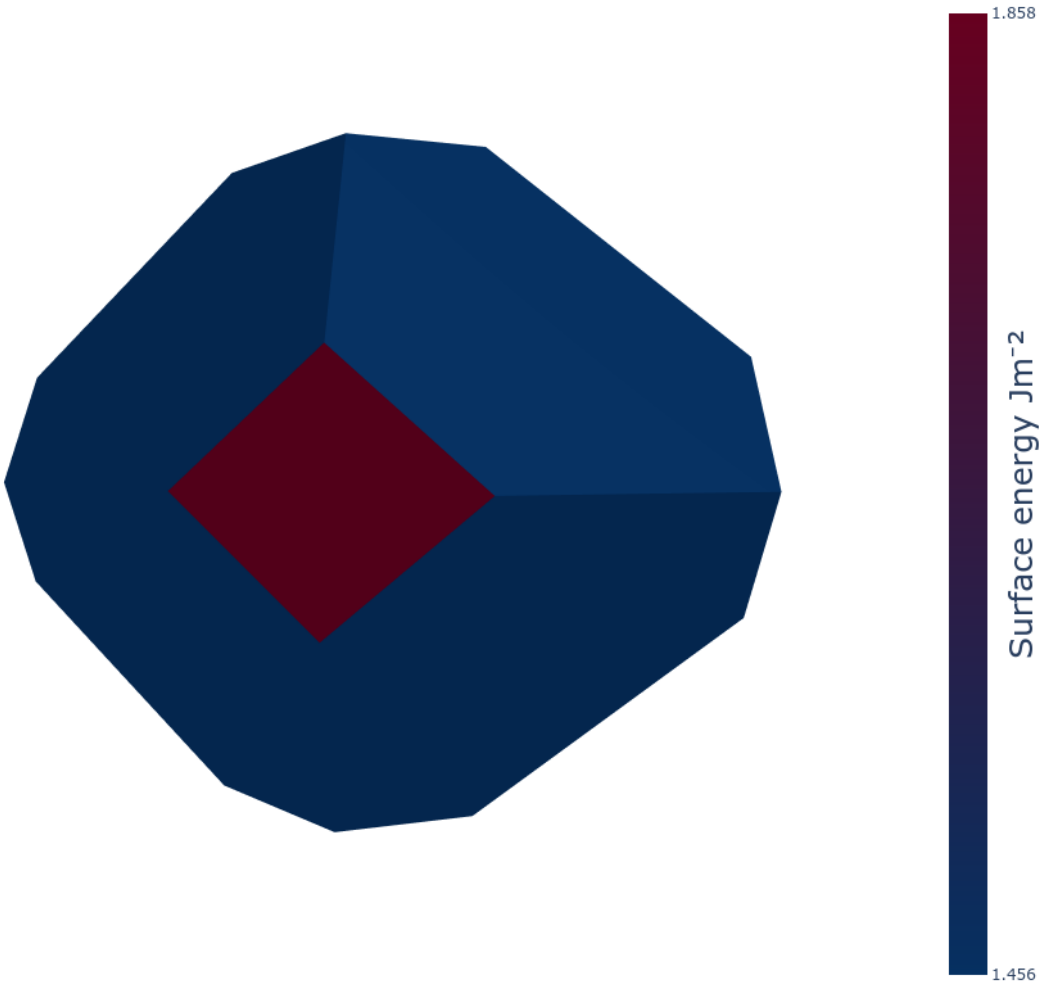

Figure 5: Visualization of the surface energies for the three surface terminations considered. Only $Pt_3Sn(001)$ and $Pt_3Sn(111)$ have non-zero area.

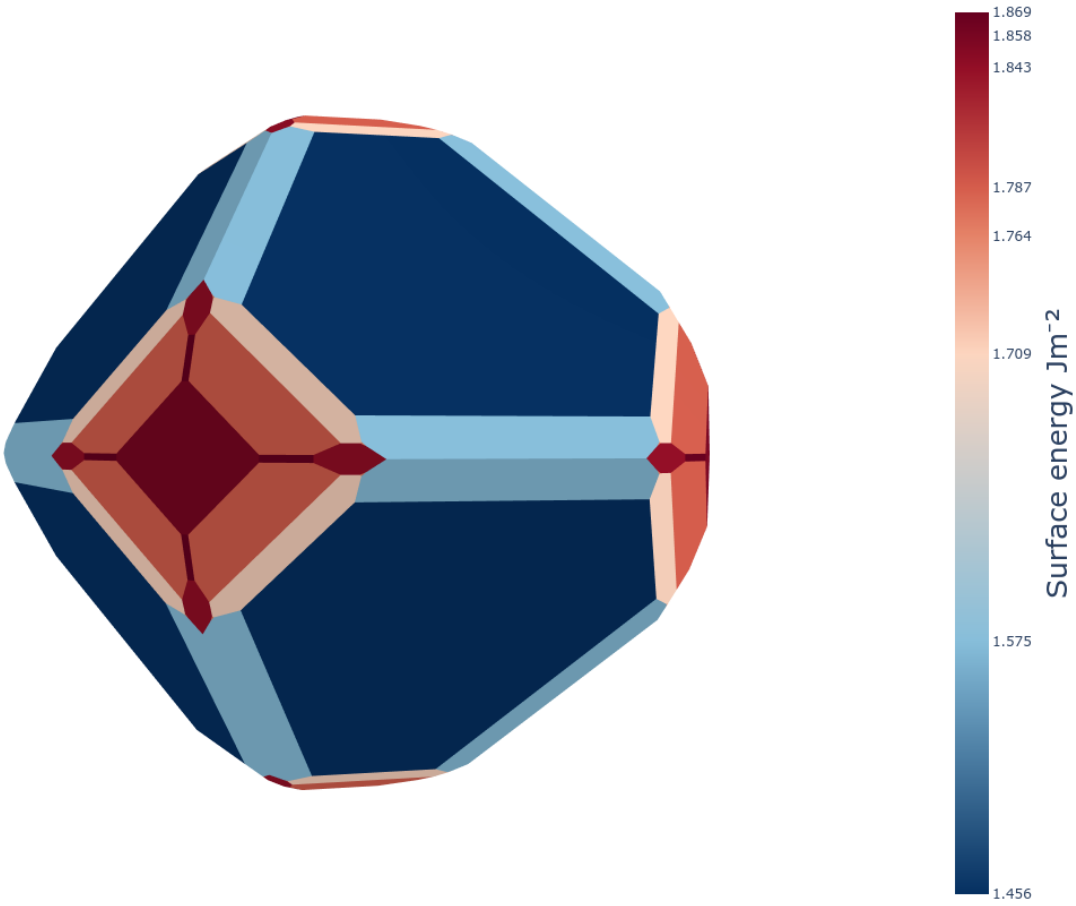

Figure 6: Visualization of the surface energies for the all miller $\{h, k, l\} \leq 3$ index terminations of Pt_3Sn

preferred sites for each adsorbate. The last three tables contain the complete sampling data - with the initial site placement of the adsorbate and the final site after relaxation.

Table 2: Electronic energies for adsorbates on the $Pt_3Sn(111)$ surface.

Adsorbate	Preferred Site	Binding Energy (eV)	Total Energy (eV)
CH_4	phys	−0.1914	−604.6268
CH_3	Pt atop	−2.7703	−600.7089
CH_2	Pt-Pt bridging hcp	−4.8234	−596.5823
CH	Pt-Pt-Pt hollow hcp	−6.8094	−592.8070
H	Pt-Pt-Pt hollow hcp	−0.7079	−584.4870
Bare	–		−580.3934

Table 3: Electronic energies for adsorbates on the $Pt_3Sn(001)$ surface.

Adsorbate	Preferred Site	Binding Energy (eV)	Total Energy (eV)
CH_4	phys	−0.1570	−309.1442
CH_3	Pt atop	−2.8628	−305.3533
CH_2	Pt-Sn bridge	−4.4704	−300.7812
CH	Pt-Sn-Pt-Sn hollow	−5.7041	−296.2536
H	Pt atop	−0.7233	−289.0542
Bare	–		−284.9452

Table 4: Electronic energies for adsorbates on the $Pt_3Sn(110)$ surface.

Adsorbate	Preferred Site	Binding Energy (eV)	Total Energy (eV)
CH_4	phys	−0.1653	−504.2841
CH_3	Pt atop	−2.4514	−500.0734
CH_2	Pt-Pt bridging	−4.5243	−495.9667
CH	Pt-Pt bridging	−5.9438	−491.6249
H	Pt-Pt bridging	−0.2629	−483.7255
Bare	–		−480.0769

Table 5: Gas-phase electronic energies of adsorbates considered in the dehydrogenation of methane.

Species	$E_{\sigma\to 0}$ (eV)	Energy - Entropy (eV)	Free Energy (eV)
H	−6.771 451 94	−6.771 451 94	−6.771 451 94
CH	−5.604 280 25	−5.595 292 17	−5.613 268 33
CH_2	−11.365 506 51	−11.365 506 51	−11.365 506 51
CH_3	−17.545 214 92	−17.539 573 02	−17.550 856 81
CH_4	−24.041 956 61	−24.041 956 61	−24.041 956 61

Table 6: Uncorrected Electronic Total and Binding Energies of $Pt_3Sn(001)$

Adsorbate	Initial Site	Final Site	Total Energy (eV)	Binding Energy (eV)
CH	Sn atop	Sn atop	-293.539665	-2.990144
CH	Pt atop	Pt atop	-295.079279	-4.529758
CH	Pt-Sn bridge	Pt-Sn bridge	-295.826314	-5.276793
CH	Pt-Sn-Pt-Sn hollow	Pt-Sn-Pt-Sn hollow	-296.253609	-5.704088
CH2	Sn atop	Pt-Sn bridge	-300.781192	-4.470444
CH2	Pt atop	Pt atop	-300.272615	-3.961868
CH2	Pt-Sn bridge	Pt-Sn bridge	-300.779046	-4.468299
CH2	Pt-Sn-Pt-Sn hollow	Pt-Sn-Pt-Sn hollow	-300.138586	-3.827839
CH3	Sn atop	Sn atop	-304.592098	-2.101642
CH3	Pt atop	Pt atop	-305.353258	-2.862803
CH3	Pt-Sn bridge	Pt atop	-305.349080	-2.858624
CH3	Pt-Sn-Pt-Sn hollow	Pt atop	-305.348982	-2.858526
CH4	Sn atop	phys	-309.139936	-0.152738
CH4	Pt atop	phys	-309.139757	-0.152560
CH4	Pt-Sn bridge	phys	-309.144175	-0.156977
CH4	Pt-Sn-Pt-Sn hollow	phys	-309.143843	-0.156645
H	Sn atop	Sn atop	-287.772062	0.558905
H	Pt atop	Pt atop	-289.054238	-0.723271
H	Pt-Sn bridge	Pt atop	-289.053378	-0.722411
H	Pt-Sn-Pt-Sn hollow	Pt-Sn-Pt-Sn hollow	-288.083422	0.247545

Table 7: Uncorrected Electronic Total and Binding Energies of $Pt_3Sn(110)$

Adsorbate	Initial Site	Final Site	Total Energy (eV)	Binding Energy (eV)
CH	Sn atop	Sn atop	-487.749906	-2.068773
CH	Pt atop	Pt atop	-490.058055	-4.376922
CH	Sn-Sn bridging	Sn-Sn bridging	-488.922992	-3.241859
CH	Pt-Sn 4 fold hollow	Pt-Sn bridging	-490.600401	-4.919268
CH	Pt-Pt bridging	Pt-Pt bridging	-491.624919	-5.943786
CH	Pt-Sn bridging	Pt-Pt bridging	-491.460288	-5.779155
CH2	Sn atop	Pt-Sn bridging	-495.320299	-3.877940
CH2	Pt atop	Pt atop	-495.053272	-3.610913
CH2	Sn-Sn bridging	Sn-Sn bridging	-494.558849	-3.116490
CH2	Pt-Sn 4 fold hollow	Pt-Sn bridging	-495.319722	-3.877362
CH2	Pt-Sn bridging	Pt-Sn bridging	-495.315107	-3.872748
CH2	Pt-Pt bridging	Pt-Pt bridging	-495.966708	-4.524349
CH3	Sn atop	Sn atop	-499.897525	-2.275457
CH3	Pt atop	Pt atop	-500.073239	-2.451172
CH3	Sn-Sn bridging	Sn atop	-499.904281	-2.282213
CH3	Pt-Sn 4 fold hollow	Pt atop	-500.073446	-2.451378
CH3	Pt-Sn bridging	Pt atop	-500.073111	-2.451043
CH3	Pt-Pt bridging	Pt atop	-500.072624	-2.450556
CH4	Sn atop	phys	-504.254809	-0.136000
CH4	Pt atop	phys	-504.270080	-0.151271
CH4	Sn-Sn bridging	phys	-504.276977	-0.158167
CH4	Pt-Sn 4 fold hollow	phys	-504.261463	-0.142654
CH4	Pt-Sn bridging	phys	-504.276604	-0.157794
CH4	Pt-Pt bridging	phys	-504.284116	-0.165307
H	Sn atop	Sn atop	-482.883272	0.579307
H	Pt atop	Pt atop	-483.272943	0.189636
H	Sn-Sn bridging	Sn-Sn bridging	-482.316623	1.145956
H	Pt-Sn 4 fold hollow	Pt atop	-483.274713	0.187866
H	Pt-Pt bridging	Pt-Pt bridging	-483.719549	-0.256970
H	Pt-Sn bridging	Pt-Pt bridging	-483.725454	-0.262875

Table 8: Uncorrected Electronic Total and Binding Energies of $Pt_3Sn(111)$

Adsorbate	Initial Site	Final Site	Total Energy (eV)	Binding Energy (eV)
CH	Sn atop	Sn atop	-588.192904	-2.195267
CH	Pt atop	Pt-Pt-Pt hollow hcp	-592.752498	-6.754861
CH	Pt-Sn bridging	Pt-Pt-Pt hollow hcp	-592.751252	-6.753615
CH	Pt-Pt bridging hcp	Pt-Pt-Pt hollow hcp	-592.806989	-6.809352
CH	Pt-Pt bridging fcc	Pt-Pt-Pt hollow fcc	-592.672475	-6.674838
CH	Pt-Pt-Sn hollow fcc	Pt-Pt-Pt hollow hcp	-592.749044	-6.751407
CH	Pt-Pt-Pt hollow hcp	Pt-Pt-Pt hollow hcp	-592.754839	-6.757202
CH	Pt-Pt-Sn hollow hcp	Pt-Pt-Sn hollow hcp	-591.826217	-5.828580
CH	Pt-Pt-Pt hollow fcc	Pt-Pt-Pt hollow fcc	-592.672781	-6.675144
CH2	Sn atop	Pt-Sn bridging	-595.621043	-3.862179
CH2	Pt atop	Pt-Pt bridging hcp	-596.582301	-4.823438
CH2	Pt-Sn bridging	Pt-Pt bridging hcp	-596.578189	-4.819326
CH2	Pt-Pt bridging hcp	Pt-Pt bridging hcp	-595.619648	-3.860785
CH2	Pt-Pt bridging fcc	Pt-Sn bridging fcc	-596.350659	-4.591795
CH2	Pt-Pt-Sn hollow fcc	Pt-Pt bridging hcp	-596.581065	-4.822202
CH2	Pt-Pt-Pt hollow hcp	Pt-Pt bridging hcp	-596.581242	-4.822378
CH2	Pt-Pt-Sn hollow hcp	Pt-Pt bridging fcc	-596.352418	-4.593555
CH2	Pt-Pt-Pt hollow fcc	Pt-Pt bridging fcc	-596.352126	-4.593263
CH3	Sn atop	Sn atop	-599.907373	-1.968802
CH3	Pt atop	Pt atop	-600.698055	-2.759483
CH3	Pt-Sn bridging	Pt atop	-600.706886	-2.768314
CH3	Pt-Pt bridging hcp	Pt atop	-600.706444	-2.767873
CH3	Pt-Pt bridging fcc	Pt atop	-600.702071	-2.763499
CH3	Pt-Pt-Sn hollow fcc	Pt atop	-600.708692	-2.770120
CH3	Pt-Pt-Pt hollow hcp	Pt atop	-600.708850	-2.770278
CH3	Pt-Pt-Sn hollow hcp	Pt atop	-600.702059	-2.763487
CH3	Pt-Pt-Pt hollow fcc	Pt atop	-600.702007	-2.763435
CH4	Sn atop	phys	-604.608027	-0.172713
CH4	Pt atop	phys	-604.605872	-0.170559
CH4	Pt-Sn bridging	phys	-604.593957	-0.158643
CH4	Pt-Pt bridging hcp	phys	-604.606695	-0.171381
CH4	Pt-Pt bridging fcc	phys	-604.614731	-0.179417
CH4	Pt-Pt-Sn hollow fcc	phys	-604.585420	-0.150106
CH4	Pt-Pt-Pt hollow hcp	phys	-604.599670	-0.164356
CH4	Pt-Pt-Sn hollow hcp	phys	-604.609323	-0.174009
CH4	Pt-Pt-Pt hollow fcc	phys	-604.626752	-0.191438
H	Sn atop	Sn-atop	-582.903331	0.875752
H	Pt atop	Pt-Pt-Pt hollow hcp	-584.482621	-0.703538
H	Pt-Sn bridging	Pt-Pt-Pt hollow hcp	-584.485361	-0.706278
H	Pt-Pt bridging hcp	Pt-Pt-Pt hollow hcp	-584.486987	-0.707904
H	Pt-Pt bridging fcc	Pt-Pt-Pt hollow fcc	-584.206731	-0.427648
H	Pt-Pt-Sn hollow fcc	Pt-Pt-Pt hollow hcp	-584.485123	-0.706040
H	Pt-Pt-Pt hollow hcp	Pt-Pt-Pt hollow hcp	-584.482920	-0.703837
H	Pt-Pt-Sn hollow hcp	Pt-Pt-Pt hollow fcc	-584.205809	-0.426726
H	Pt-Pt-Pt hollow fcc	Pt-Pt-Pt hollow fcc	-584.207787	-0.428704