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Supporting Information for: Can microsolvation effects be estimated from vacuum computations? A case-study of alcohol decomposition at the H_2O/Pt(111) interface

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Table S1 BEP regression parameters using the data obtained in vacuum, with dispersion corrections (w/ dDsC) and without (w/o dDsC), which are obtained by substracting the dipersion participation to the obtained DFT values

Bond		α	β	R^2	MAE	Max
O-H	w/ dDsC	0.20	0.75	0.47	0.03	0.05
	w/o dDsC	0.14	0.80	0.47	0.02	0.05
C-H_α	w/ dDsC	1.36	0.98	0.56	0.12	0.29
	w/o dDsC	1.18	0.93	0.70	0.11	0.27
C-C	w/ dDsC	0.77	1.44	0.50	0.24	0.52
	w/o dDsC	0.79	1.48	0.49	0.25	0.55
C-O(H)	w/ dDsC	0.71	1.30	0.65	0.29	0.76
	w/o dDsC	0.72	1.32	0.67	0.28	0.74
C-O subset	w/ dDsC	0.79	1.44	0.92	0.15	0.25
	w/o dDsC	0.79	1.47	0.93	0.14	0.24
C-OH subset	w/ dDsC	0.66	1.12	0.53	0.35	0.54
	w/o dDsC	0.67	1.14	0.55	0.34	0.53

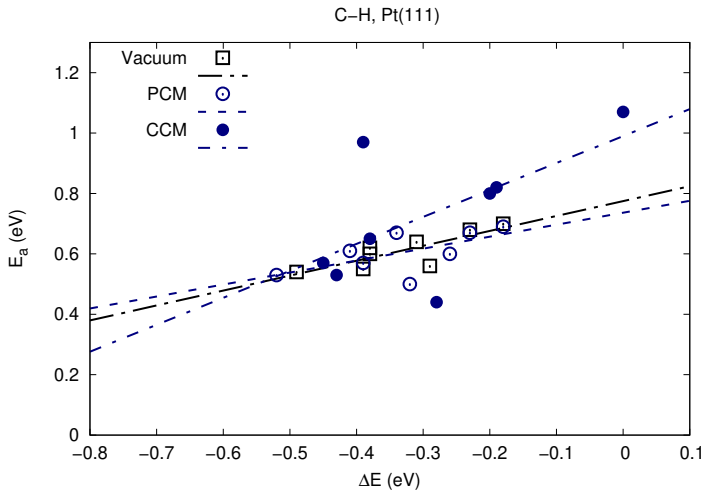

Figure S1 BEP relationships for the C-H_α scission in vaccum, PCM and CCM, without alcoolates species

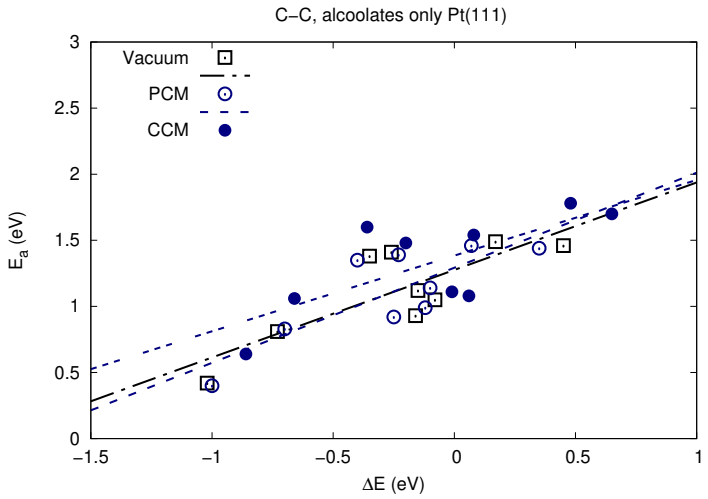

Figure S2 BEP relationships for the C-C scission in vaccum, PCM and CCM, without hydroxyl function containing species

Table S2 Surface reaction considered (initial state (IS) to final states (FS1 & FS2), for C-H$_\alpha$, O-H, C-C and C-O scissions, and the related reaction and activation energy under vacuum, PCM and CCM conditions, in eV

C-H$_\alpha$			Vacuum (eV)		PCM (eV)		CCM (eV)	
IS	FS1	FS2	ΔE	Ea	ΔE	Ea	ΔE	Ea
CH2CH2CH(OH)CH3	CH2CH2C(OH)CH3	H	-0.39	0.55	-0.39	0.57	-0.39	0.97
CH2C(CH3)(CH2)CH(OH)CH3	CH2C(CH3)(CH2)C(OH)CH3	H	-0.38	0.60	-0.34	0.67	-0.45	0.57
CH2CH2OH	CH2CHOH	H	-0.31	0.64	-0.32	0.50	-0.28	0.44
CH3CHCH2CH2OH	CH3CHCH2CHOH	H	-0.49	0.54	-0.52	0.53	-0.43	0.53
CH3CH2CH2OH	CH3CH2CHOH	H	-0.38	0.62	-0.41	0.61	-0.38	0.65
CH3CH(O)CH3	CH3C(O)CH3	H	-0.67	0.02	-0.73	0.00	-0.54	0.27
CH3CH2O	CH3CHO	H	-0.46	0.08	-0.58	0.03	-0.28	0.39
CH3CH2OH	CH3CHOH	H	-0.29	0.56	-0.26	0.60	-0.20	0.80
CH3CH(OH)CH3	CH3C(OH)CH3	H	-0.18	0.70	-0.18	0.69	0.00	1.07
CH3O	CH2O	H	-0.35	0.22	-0.36	0.18	-0.23	0.43
CH3OH	CH2OH	H	-0.23	0.68	-0.23	0.67	-0.19	0.82

O-H			Vacuum (eV)		PCM (eV)		CCM (eV)	
IS	FS1	FS2	ΔE	Ea	ΔE	Ea	ΔE	Ea
CH2CH2OH	CH2CH2O	H	0.55	0.87	0.62	0.96	0.27	0.75
CH3CH(OH)CH3	CH3CH(O)CH3	H	0.64	0.89	0.66	0.94	0.47	0.79
CH3OH	CH3O	H	0.62	0.86	0.72	0.98	0.44	0.80
CH3CH2OH	CH3CH2O	H	0.62	0.85	0.70	0.95	0.38	0.72
CH2OH	CH2O	H	0.48	0.82	0.58	0.93	0.48	0.75
CH3C(OH)CH3	CH3C(O)CH3	H	0.14	0.81	0.14	0.86	-0.05	0.65
CH3CH(OH)CH2	CH3CH(O)CH2	H	0.62	0.88	0.66	0.93	0.27	0.75
CH3CHOH	CH3CHO	H	0.41	0.79	0.47	0.86	0.34	0.68
CH2CH(OH)CH2	CH2CH(O)CH2	H	0.58	0.91	0.63	0.98	0.26	0.76
CH3CH2CH(OH)CH2	CH3CH2CH(O)CH2	H	0.45	0.81	0.49	0.87	0.34	0.79
CH3CH2CH(OH)CH3	CH3CH2CH(O)CH3	H	0.60	0.92	0.62	0.95	0.46	0.83

C-C			Vacuum (eV)		PCM (eV)		CCM (eV)	
IS	FS1	FS2	ΔE	Ea	ΔE	Ea	ΔE	Ea
CH2CH2O	CH2	CH2O	0.45	1.46	0.35	1.44	0.65	1.70
CH2CH2OH	CH2	CH2OH	0.13	1.44	0.05	1.45	0.23	1.67
CH2CHO	CH2	CHO	-0.08	1.05	-0.12	0.99	-0.01	1.11
CH2CO	CH2	CO	-0.15	1.12	-0.10	1.14	0.08	1.54
CH2COH	CH2	COH	0.10	1.83	-0.09	1.65	-0.09	1.63
CH3CH2O	CH3	CH2O	0.17	1.49	0.07	1.46	0.48	1.78
CH3CHO	CH3	CHO	-0.35	1.38	-0.40	1.35	-0.36	1.60
CH3CHOH	CH3	CHOH	0.20	1.59	0.23	1.65	0.37	1.50
CH3CO	CH3	CO	-0.26	1.41	-0.23	1.39	-0.20	1.48
CH3COH	CH3	COH	-0.17	1.67	-0.39	1.60	-0.37	1.78
CHCH2O	CH	CH2O	-0.16	0.93	-0.25	0.92	0.06	1.08
CHCH2OH	CH	CH2OH	-0.37	1.47	-0.43	1.48	-0.54	1.29
CHCHO	CH	CHO	-1.02	0.42	-1.00	0.40	-0.86	0.64
CHCHOH	CH	CHOH	-0.10	1.04	-0.11	1.04	0.05	0.93
CHCO	CH	CO	-0.73	0.81	-0.70	0.83	-0.66	1.06
CHCOH	CH	COH	-0.53	1.15	-0.61	1.15	-0.26	1.58
CH3CH2OH	CH3	CH2OH	0.12	2.05	0.07	2.07	0.18	1.99

C-O			Vacuum (eV)		PCM (eV)		CCM (eV)	
IS	FS1	FS2	ΔE	Ea	ΔE	Ea	ΔE	Ea
CCHO	O	CCH	1.58	2.44	1.62	2.47	1.70	2.73
CCHOH	OH	CCH	1.67	2.56	1.77	2.68	1.25	2.33
CH2CH2O	O	CH2CH2	-0.13	1.39	-0.08	1.41	0.05	1.61
CH2CH2OH	OH	CH2CH2	0.35	1.86	0.36	1.89	-0.17	1.74
CH2CHOH	OH	CH2CH	0.81	1.57	0.82	1.58	0.24	1.34
CH2CO	O	CH2C	1.18	2.55	1.24	2.58	1.32	2.71
CH3CH2O	O	CH3CH2	-0.09	1.37	-0.08	1.35	0.24	1.90
CH3CH2OH	OH	CH3CH2	0.55	1.86	0.53	1.88	0.14	1.44
CH3CO	O	CH3C	0.36	1.95	0.37	1.95	0.57	2.17
CH3COH	OH	CH3C	0.02	0.78	0.07	0.86	-0.33	0.80
CHCH2O	O	CHCH2	0.79	1.92	0.83	1.94	0.58	1.87
CHCHO	O	CHCH	0.14	1.35	0.16	1.36	0.34	1.39
CHCHOH	OH	CHCH	0.79	1.10	0.72	1.10	0.29	1.11
CHCO	O	CHC	1.94	3.11	1.95	3.11	1.90	3.15
CHCOH	OH	CHC	1.77	2.05	1.80	2.11	1.56	2.21

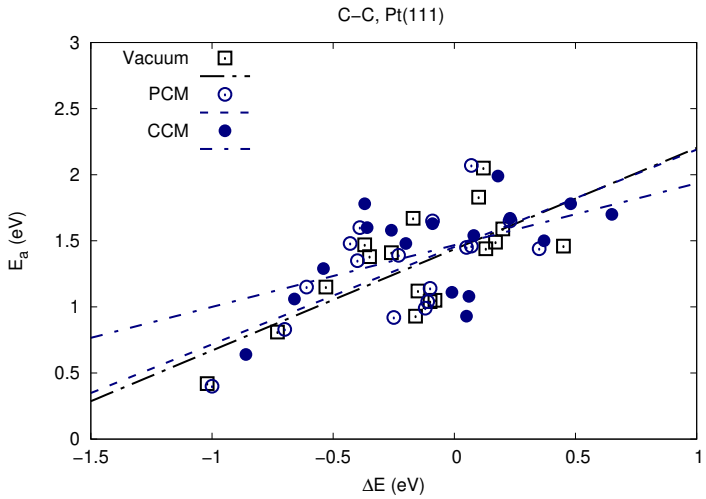

Figure S3 BEP relationships for the C-C scission in vacuum, PCM and CCM.

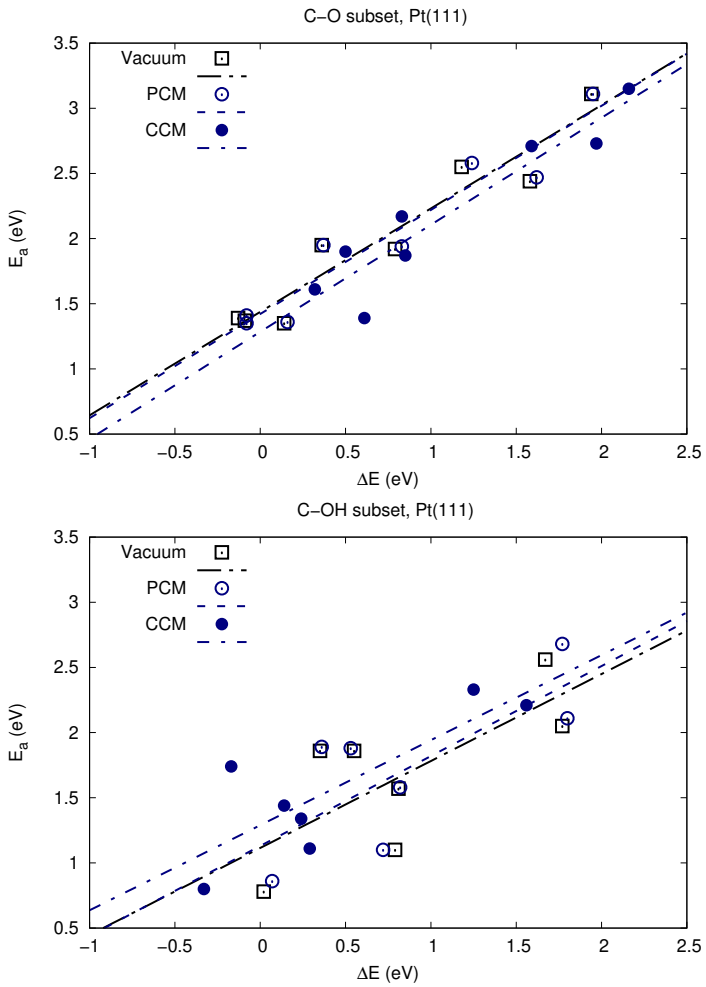

Figure S4 BEP relationships for the C-O scission using the C-O subset (top) and the C-OH subset (bottom) in vacuum, PCM and CCM

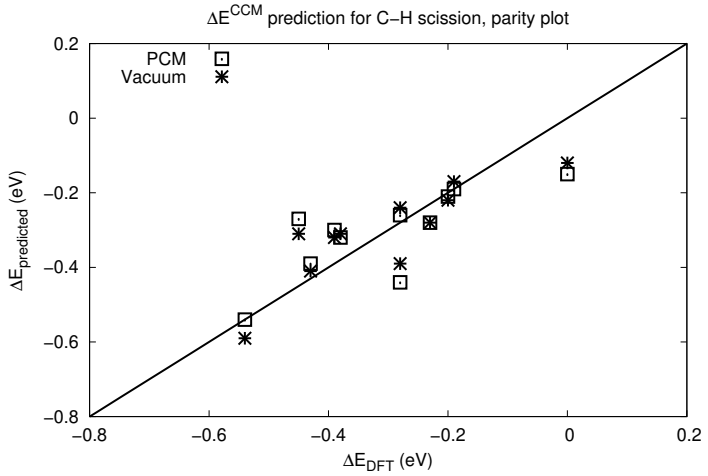

Figure S5 Parity plot for the prediction of ΔE^{CCM} using ΔE^{Vacuum} (squares) or ΔE^{PCM} (stars) for C-H$_\alpha$ scissions

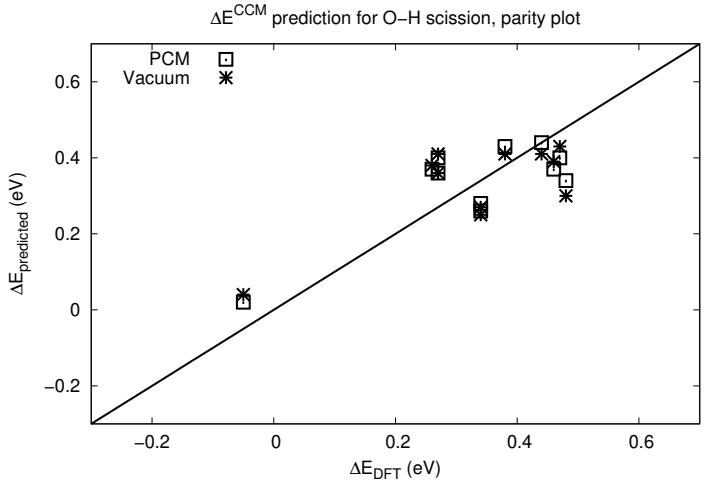

Figure S6 Parity plot for the prediction of ΔE^{CCM} using ΔE^{Vacuum} (stars) or ΔE^{PCM} (squares) for O-H scissions

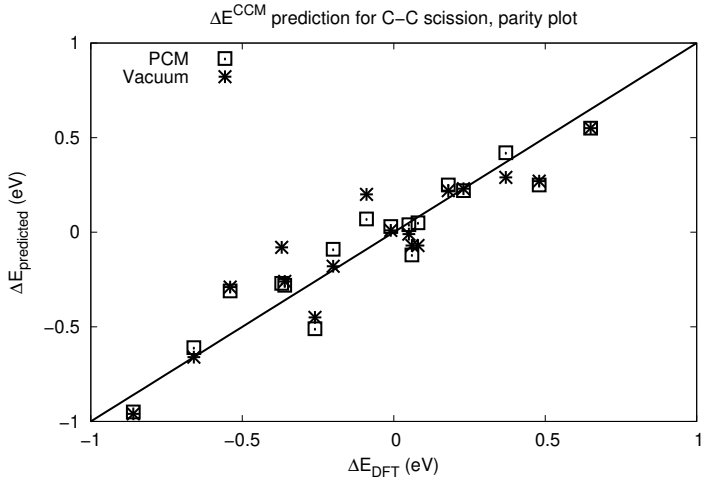

Figure S7 Parity plot for the prediction of ΔE^{CCM} using ΔE^{Vacuum} (stars) or ΔE^{PCM} (squares) for C-C scissions

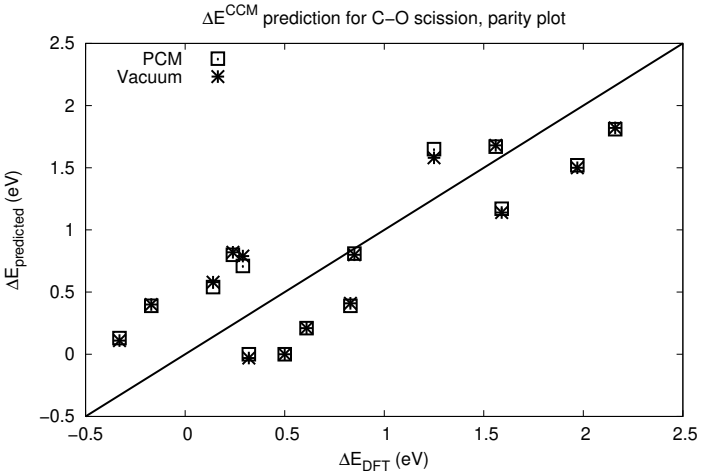

Figure S8 Parity plot for the prediction of ΔE^{CCM} using ΔE^{Vacuum} (stars) or ΔE^{PCM} (squares) for C-O(H) scissions

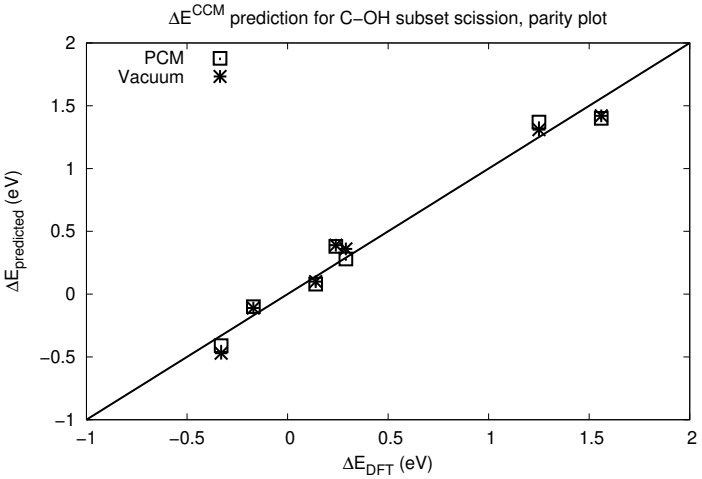

Figure S9 Parity plot for the prediction of ΔE^{CCM} using ΔE^{Vacuum} (stars) or ΔE^{PCM} (squares) for C-OH scissions

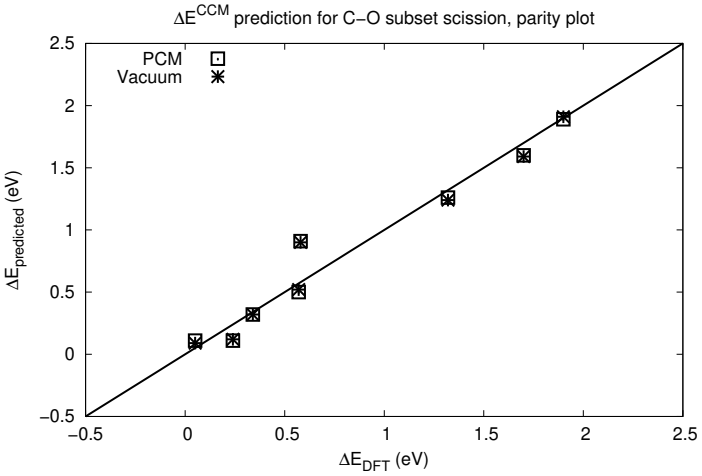

Figure S10 Parity plot for the prediction of ΔE^{CCM} using ΔE^{Vacuum} (stars) or ΔE^{PCM} (squares) for C-O scissions

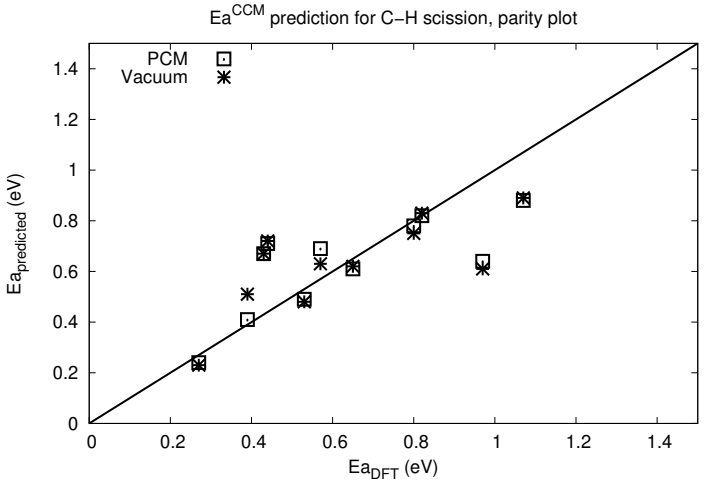

Figure S11 Parity plot for the prediction of E_a^{CCM} using ΔE^{Vacuum} (stars) or ΔE^{PCM} (squares) for C-H$_\alpha$ scissions

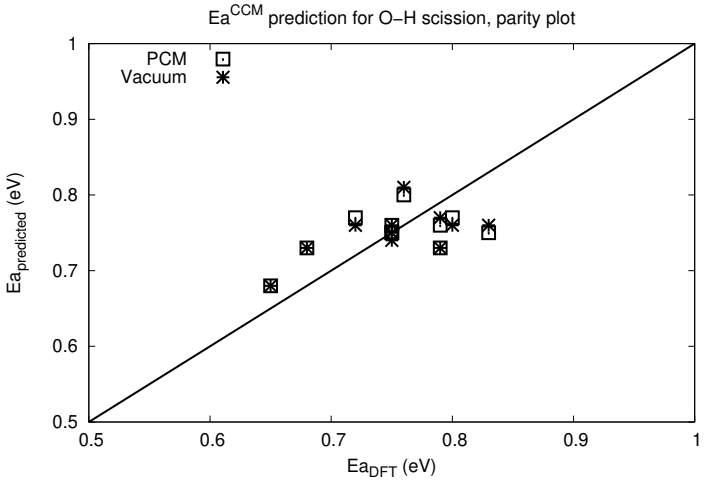

Figure S12 Parity plot for the prediction of E_a^{CCM} using ΔE^{Vacuum} (stars) or ΔE^{PCM} (squares) for O-H scissions

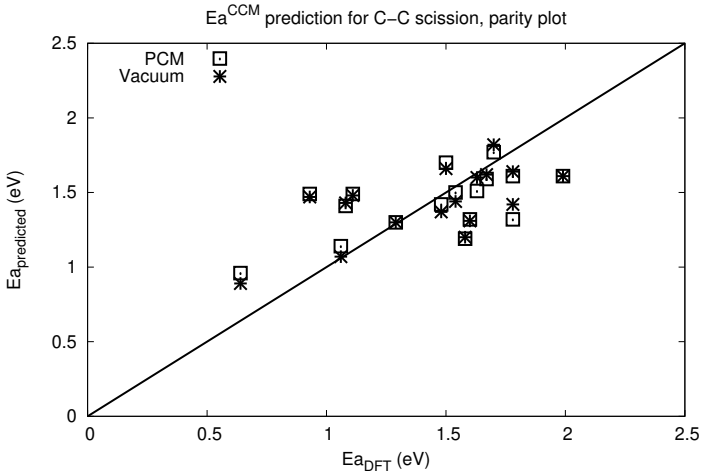

Figure S13 Parity plot for the prediction of E_a^{CCM} using ΔE^{Vacuum} (stars) or ΔE^{PCM} (squares) for C-C scissions

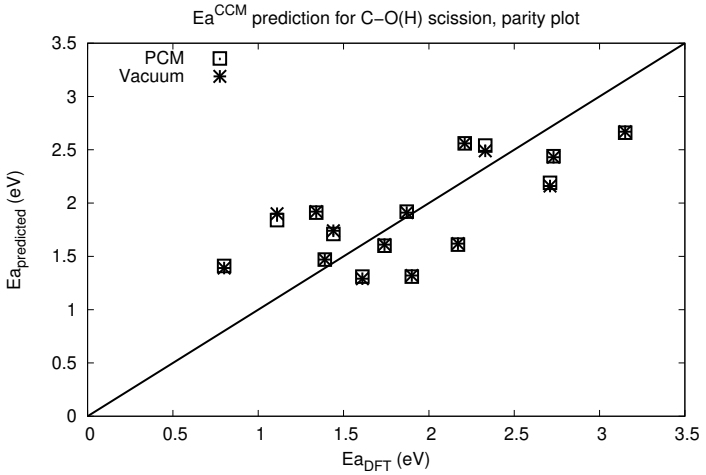

Figure S14 Parity plot for the prediction of E_a^{CCM} using ΔE^{Vacuum} (stars) or ΔE^{PCM} (squares) for C-O(H) scissions

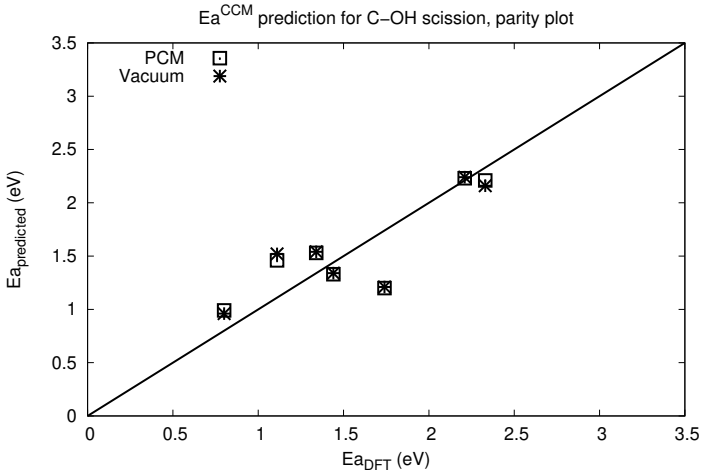

Figure S15 Parity plot for the prediction of E_a^{CCM} using ΔE^{Vacuum} (stars) or ΔE^{PCM} (squares) for C-OH scissions

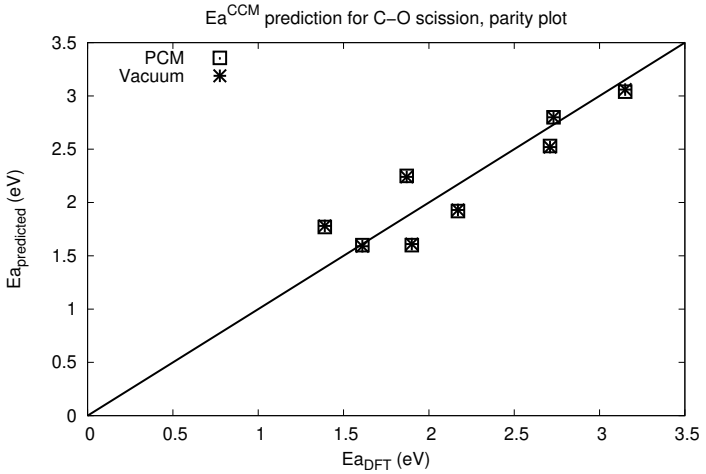

Figure S16 Parity plot for the prediction of E_a^{CCM} using ΔE^{Vacuum} (stars) or ΔE^{PCM} (squares) for C-O scissions