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

Supplementary Information

Uncovering the multifaceted roles of nitrogen defects in graphitic carbon nitride for selective photocatalytic carbon dioxide reduction: A density functional theory study

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1. FORMATION ENERGY OF DEFECTS

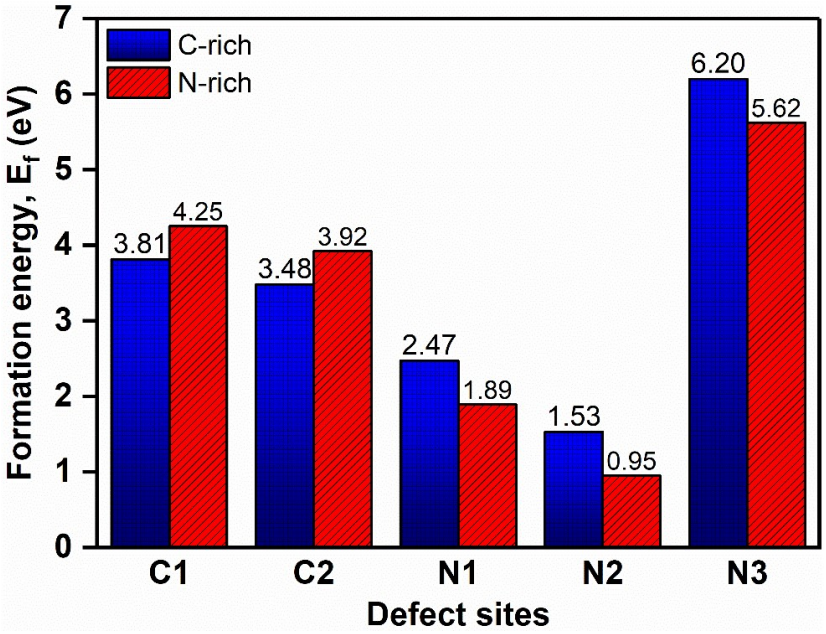

Fig. S1 Formation energy, E_f of defects in g-C_3N_4 at five potential sites under C-rich and N-rich conditions.

2. SPATIAL DISTRIBUTION OF HOMO-LUMO

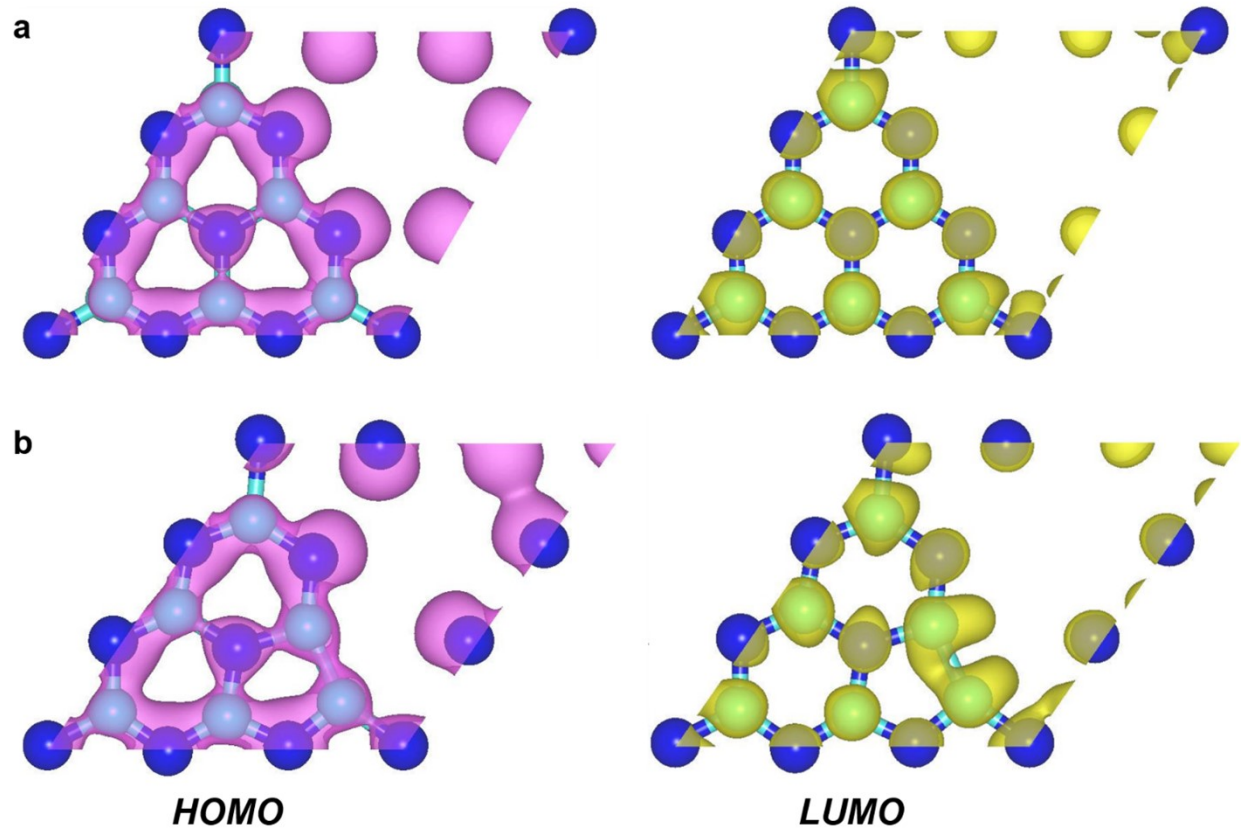

Fig. S2 Spatial distribution of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of (a) GCN and (b) D_{N2}. The isosurface value is set to 0.03 e/Å^3.

3. CO_2 ADSORPTION SIMULATION DETAILS

In this study, nine CO_2 adsorption sites were considered in both parallel and vertical orientations, which were the four atom sites, three bond sites and two interstitial sites. For clarity, the four atom sites were N1, N2, C1 and C2 sites; three bond sites being the intermediate point between C1–N2, N2–C2 and N1–C1 bonds, represented as B1, B2 and B3; lastly, the center of a triazine ring as one interstitial site (I1) and the cavity within the six-fold heptazine ring as another interstitial site (I2). The CO_2 adsorption configurations were illustrated as fixed g-C_3N_4 atoms in Figs. S3–6 to accurately portray the position of the CO_2 molecule on these structures. Optimization of separation distance between CO_2 molecule and g-C_3N_4 surface was performed, and the ideal distance was discovered to be at 2.5 Å.

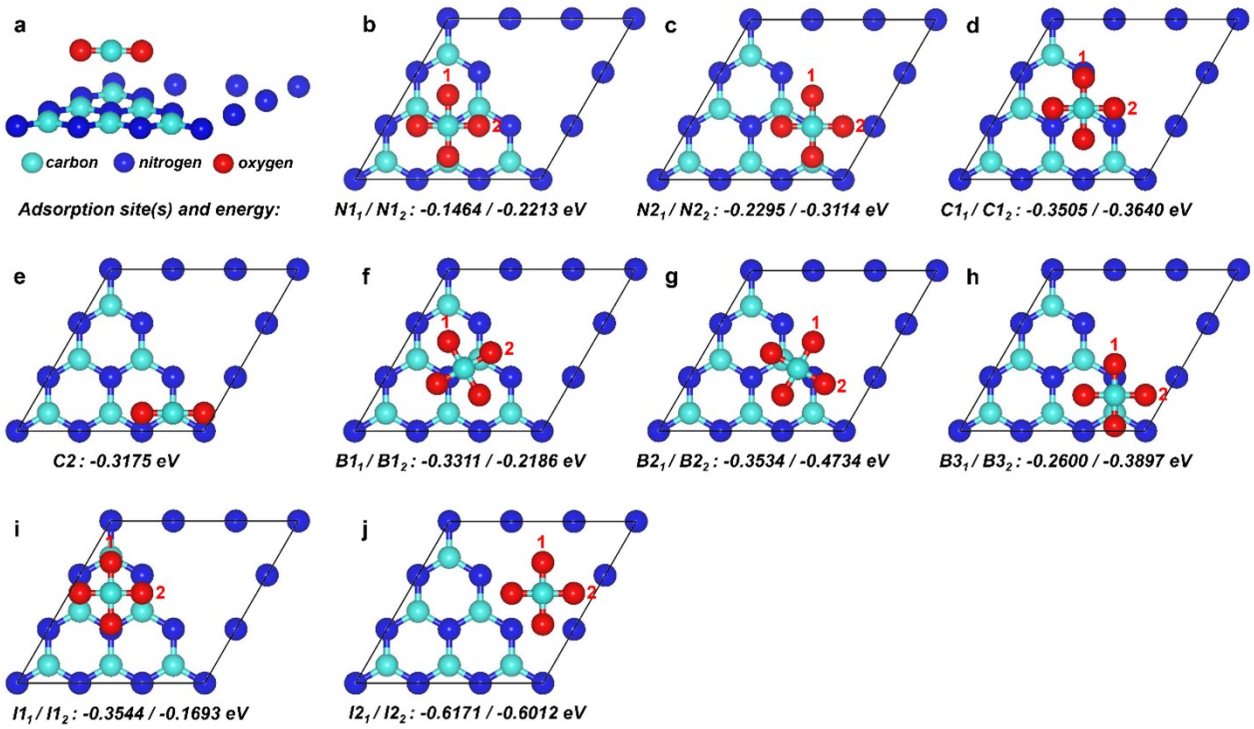

Fig. S3 (a) Side view of CO_2 molecule adsorbed on GCN in parallel orientation. (b-j) Top view of CO_2 molecule adsorbed on GCN in parallel orientation at different adsorption sites with their corresponding adsorption energy, E_{ads}. The number denotes the rotation angle of CO_2 molecule at various points.

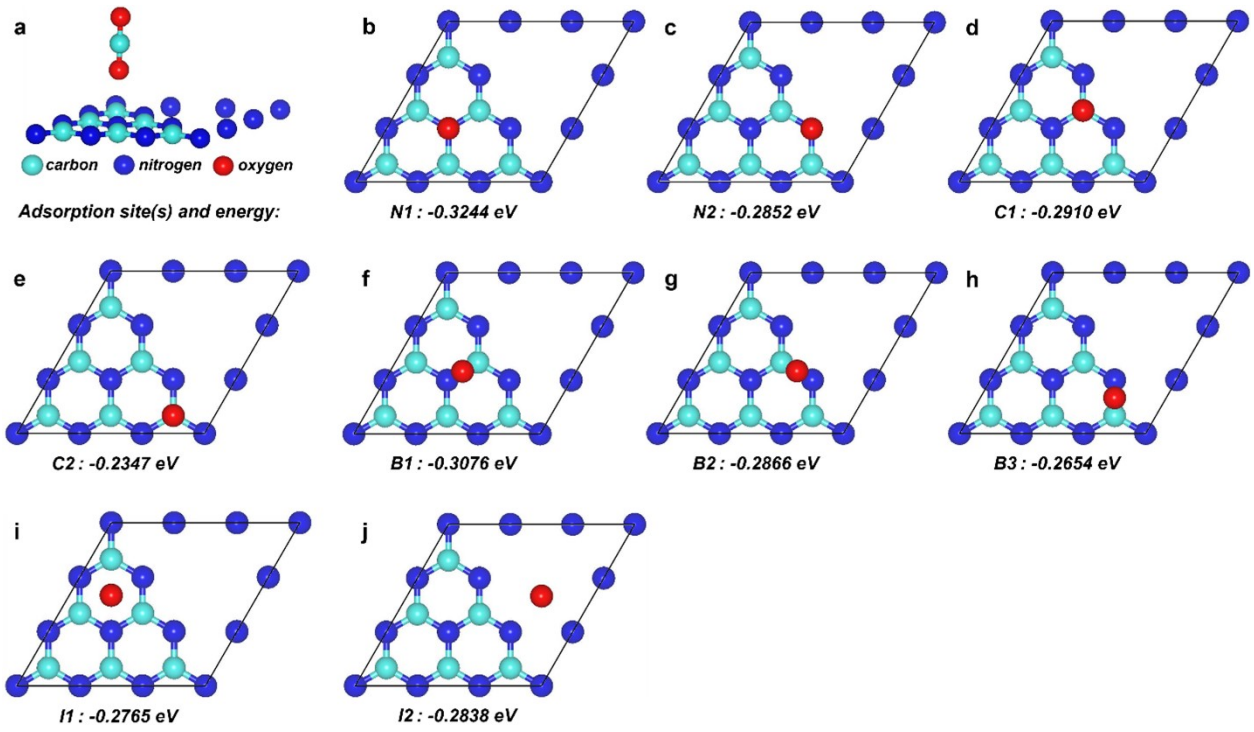

Fig. S4 (a) Side view of CO_2 molecule adsorbed on GCN in vertical orientation. (b-j) Top view of CO_2 molecule adsorbed on GCN in vertical orientation at different adsorption sites with their corresponding adsorption energy, E_{ads}.

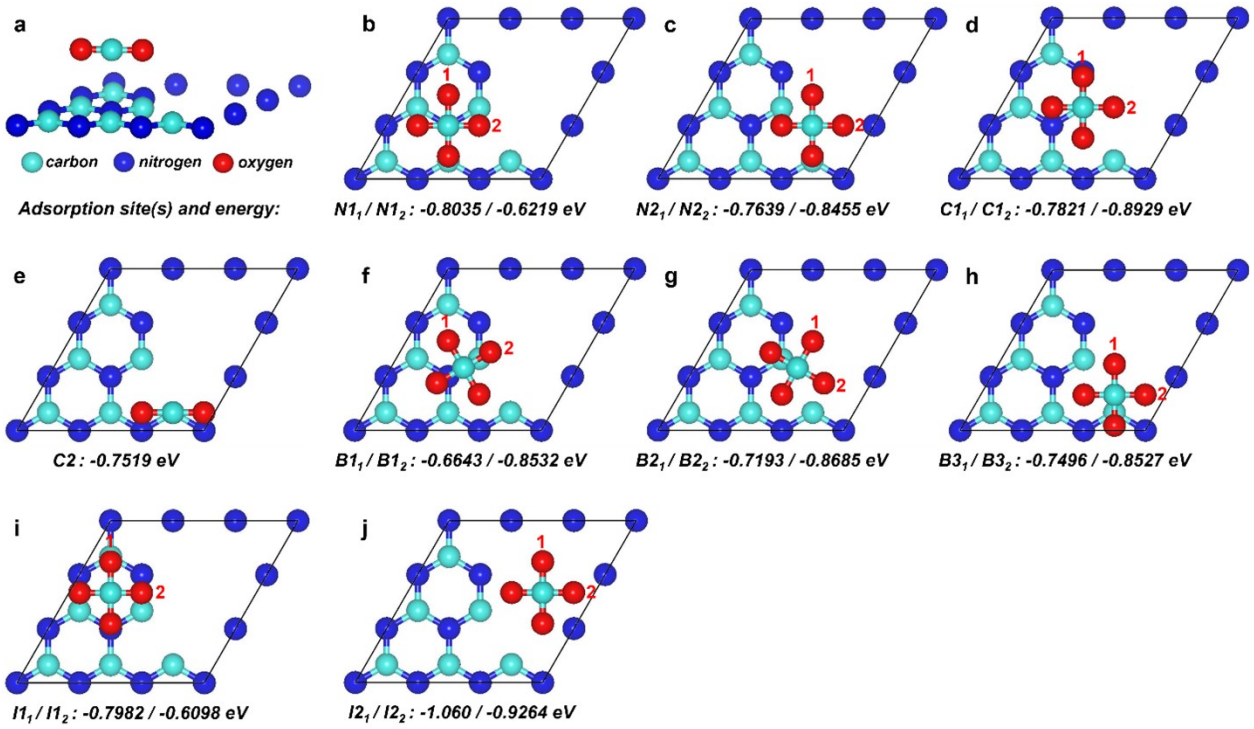

Fig. S5 (a) Side view of CO_2 molecule adsorbed on D_{N2} in parallel orientation. (b-j) Top view of CO_2 molecule adsorbed on D_{N2} in parallel orientation at different adsorption sites with their corresponding adsorption energy, E_{ads}. The number denotes the rotation angle of CO_2 molecule at various points.

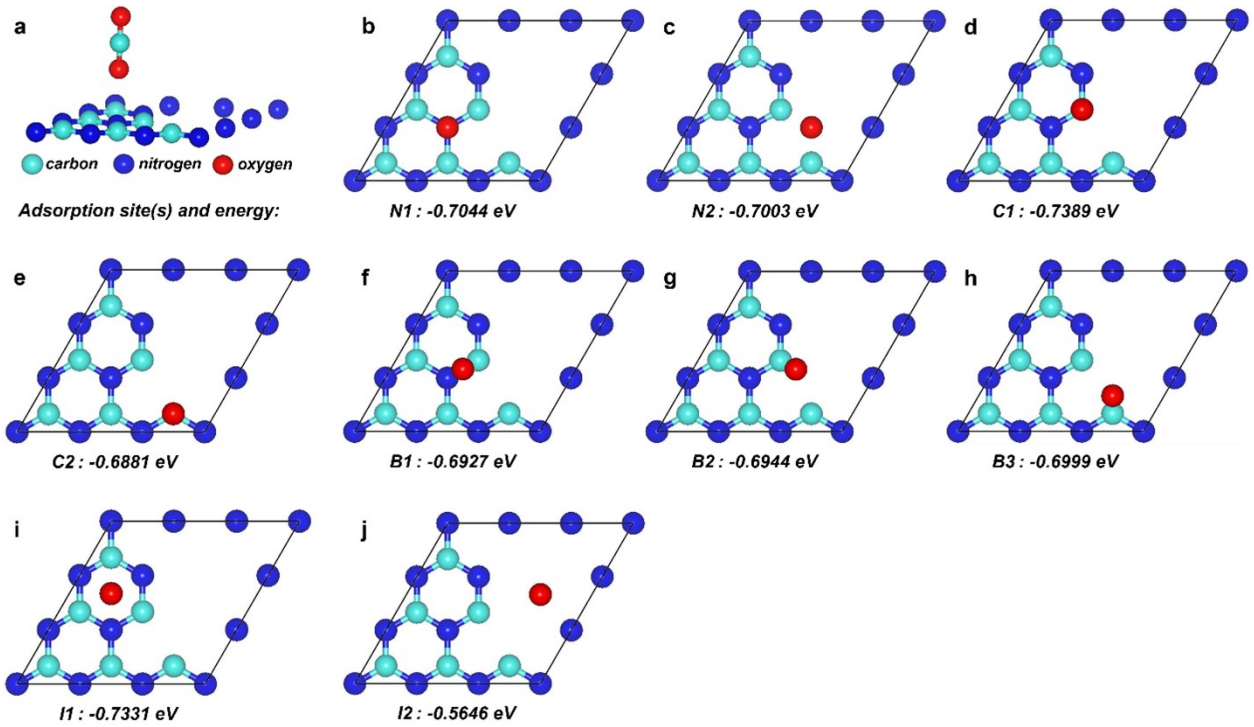

Fig. S6 (a) Side view of CO_2 molecule adsorbed on D_{N2} in vertical orientation. (b-j) Top view of CO_2 molecule adsorbed on D_{N2} in vertical orientation at different adsorption sites with their corresponding adsorption energy, E_{ads}.

4. GIBBS FREE ENERGY CHANGE

Table S1 The calculated change in Gibbs free energy of all elementary steps for CO_2 reduction pathways on GCN and D_{N2}.

CO Formation								
Elementary Steps	**GCN**				**D_{N2}**			
	ΔE	ΔE_{ZPE}	$T\Delta S$	ΔG	ΔE	ΔE_{ZPE}	$T\Delta S$	ΔG
$*+\ CO_2$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$CO_2^* + H^+ + e^-$	0.32	0.01	0.33	0.64	-0.44	0.01	0.33	-0.12
TS_HCOO^*	2.11	0.26	0.51	2.36	1.53	0.26	0.51	1.78
$HCOO^*$	1.64	0.00	0.11	1.74	1.07	0.00	0.11	1.17
$TS\_(CO^* + OH^*)$	3.73	0.18	0.31	3.86	2.20	0.18	0.31	2.33
$CO^* + OH^*$	3.29	0.11	0.19	3.37	1.75	0.11	0.19	1.83
$CO + OH^* + H^+ + e^-$	0.46	0.05	0.30	0.71	-1.22	0.05	0.30	-0.97
$TS\_(CO + H_2O^*)$	3.27	0.07	0.52	3.72	1.17	0.07	0.52	1.62
$CO + H_2O^*$	0.90	0.29	0.20	0.81	-0.52	0.29	0.20	-0.61
$CO + H_2O + *$	0.79	0.19	0.24	0.84	-0.98	0.19	0.24	-0.93
CH_3OH Formation								
Elementary Steps	**GCN**				**D_{N2}**			
	ΔE	ΔE_{ZPE}	$T\Delta S$	ΔG	ΔE	ΔE_{ZPE}	$T\Delta S$	ΔG
$*+\ CO_2$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$CO_2^* + H^+ + e^-$	0.96	0.01	0.33	0.64	0.20	0.01	0.33	-0.12
TS_HCOO^*	2.61	0.26	0.51	2.36	2.03	0.26	0.51	1.78
$HCOO^*$	1.84	0.00	0.11	1.74	1.27	0.00	0.11	1.17
$HCOO^* + H^+ + e^-$	1.98	0.22	0.09	2.11	0.49	0.22	0.09	0.62
TS_HCOOH^*	1.88	0.61	0.24	2.25	2.53	0.61	0.24	2.90
$HCOOH^*$	1.86	0.06	0.57	1.35	-0.21	0.06	0.57	-0.72
$HCOOH^* + H^+ + e^-$	0.93	0.11	0.21	0.84	-0.34	0.11	0.21	-0.43
$TS\_(HCO^* + H_2O^*)$	2.55	0.30	0.68	2.17	2.68	0.30	0.68	2.30
$HCO^* + H_2O^*$	1.63	0.21	0.54	1.30	0.81	0.21	0.54	0.48
$HCO^* + H_2O^* + H^+ + e^-$	1.95	0.02	0.77	1.20	1.17	0.02	0.77	0.42
$TS\_(CH_2O^*) + H_2O^*$	2.47	0.01	0.40	2.08	2.35	0.01	0.40	1.96
$CH_2O^* + H_2O^*$	2.14	0.25	0.28	2.11	1.61	0.25	0.28	1.58

$CH_2O^* + H_2O^* + H^+ + e^-$	2.23	0.24	0.54	1.93	1.34	0.24	0.54	1.04
$TS\_(CH_2OH^*) + H_2O^*$	2.97	0.23	0.23	2.97	3.40	0.23	0.23	3.40
$CH_2OH^* + H_2O^*$	1.03	0.04	0.38	0.70	0.11	0.04	0.38	-0.22
$CH_2OH^* + H_2O^* + H^+ + e^-$	1.03	0.14	0.31	0.86	-0.80	0.14	0.31	-0.97
$TS\_(CH_3OH^*) + H_2O^*$	1.88	0.65	0.48	2.05	0.00	0.65	0.48	0.17
$CH_3OH^* + H_2O^*$	0.62	0.29	0.60	0.31	-0.49	0.29	0.60	-0.80
$CH_3OH^* + H_2O$	0.04	0.03	0.34	-0.27	-1.30	0.03	0.34	-1.61
$CH_3OH + H_2O + *$	-0.18	0.06	0.18	-0.30	-2.00	0.06	0.18	-2.12
CH_4 Formation								
Elementary Steps	**GCN**				**D_{N2}**			
	ΔE	ΔE_{ZPE}	$T\Delta S$	ΔG	ΔE	ΔE_{ZPE}	$T\Delta S$	ΔG
$*+ CO_2$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$CO_2^* + H^+ + e^-$	0.56	0.41	0.33	0.64	-0.20	0.41	0.33	-0.12
TS_HCOO^*	2.61	0.26	0.51	2.36	2.03	0.26	0.51	1.78
$HCOO^*$	1.84	0.00	0.11	1.74	1.27	0.00	0.11	1.17
$HCOO^* + H^+ + e^-$	1.98	0.22	0.09	2.11	0.49	0.22	0.09	0.62
TS_HCOOH^*	1.88	0.61	0.24	2.25	2.53	0.61	0.24	2.90
$HCOOH^*$	1.86	0.06	0.57	1.35	-0.21	0.06	0.57	-0.72
$HCOOH^* + H^+ + e^-$	0.93	0.11	0.21	0.84	-0.34	0.11	0.21	-0.43
$TS\_(HCO^* + H_2O^*)$	2.55	0.30	0.68	2.17	2.68	0.30	0.68	2.30
$HCO^* + H_2O^*$	1.63	0.21	0.54	1.30	0.81	0.21	0.54	0.48
$HCO^* + H_2O^* + H^+ + e^-$	1.95	0.02	0.77	1.20	1.17	0.02	0.77	0.42
$TS\_(CH_2O^*) + H_2O^*$	2.47	0.01	0.40	2.08	2.35	0.01	0.40	1.96
$CH_2O^* + H_2O^*$	2.14	0.25	0.28	2.11	1.61	0.25	0.28	1.58
$CH_2O^* + H_2O^* + H^+ + e^-$	2.23	0.24	0.54	1.93	1.34	0.24	0.54	1.04
$TS\_(CH_2OH^*) + H_2O^*$	2.97	0.23	0.23	2.97	3.40	0.23	0.23	3.40
$CH_2OH^* + H_2O^*$	1.03	0.04	0.38	0.70	0.11	0.04	0.38	-0.22
$CH_2OH^* + H□_2O + H^+ + e^-$	3.15	0.16	0.47	2.84	1.46	0.16	0.47	1.15
$TS\_(CH_2^* + H_2O^*)$	4.30	0.11	0.44	3.97	2.56	0.11	0.44	2.23
$CH_2^* + H_2O^*$	1.51	0.43	0.35	1.59	-0.05	0.43	0.35	0.03
$CH_2^* + H_2O^* + H^+ + e^-$	2.13	0.03	0.52	1.64	0.19	0.03	0.52	-0.30

$TS\_(CH_3^*) + H_2O^*$	2.77	0.24	0.28	2.73	0.80	0.24	0.28	0.76
$CH_3^* + H_2O^*$	0.63	0.20	0.35	0.48	-1.21	0.20	0.35	-1.36
$CH_3^* + H_2O^* + H^+ + e^-$	0.61	0.17	0.22	0.56	-1.43	0.17	0.22	-1.48
$TS\_(CH_4^*) + H_2O^*$	2.00	0.00	0.29	1.71	-0.01	0.00	0.29	-0.30
$CH_4^* + H_2O^*$	-0.85	0.30	0.19	-0.75	-2.77	0.30	0.19	-2.67
$CH_4^* + H_2O$	-0.70	0.10	0.22	-0.82	-2.74	0.10	0.22	-2.86
$CH_4 + H_2O + *$	-0.67	0.13	0.30	-0.84	-2.74	0.13	0.30	-2.91