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Supporting Information

Elucidating the Role of Aqueous Solvent in an Iron-Based Water Oxidation System by DFT-based Molecular Simulation

Ying-Ying Li, Evert Jan Meijer,* and Rong-Zhen Liao*

Contents

S1. RDF and CNs of O1-H and Cl-H for the equilibrium system

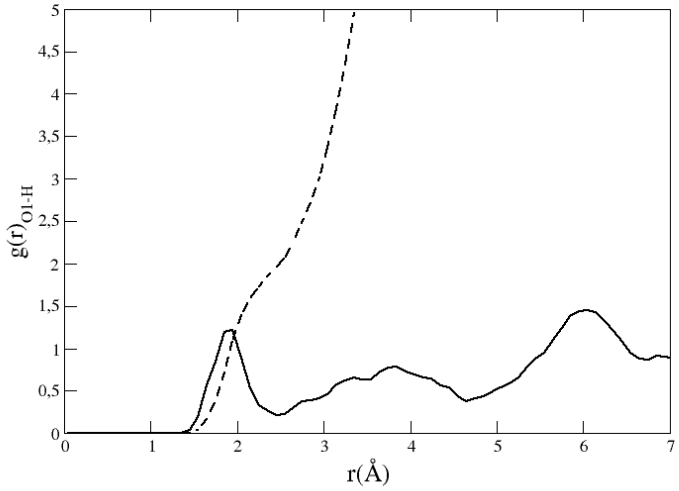


Figure S1. Radial distribution function (RDF) $g(r)_{O1\text{-}H}$ (solid line) and coordinate numbers (CNs) (dash line) between oxo and water protons from the equilibrium run.

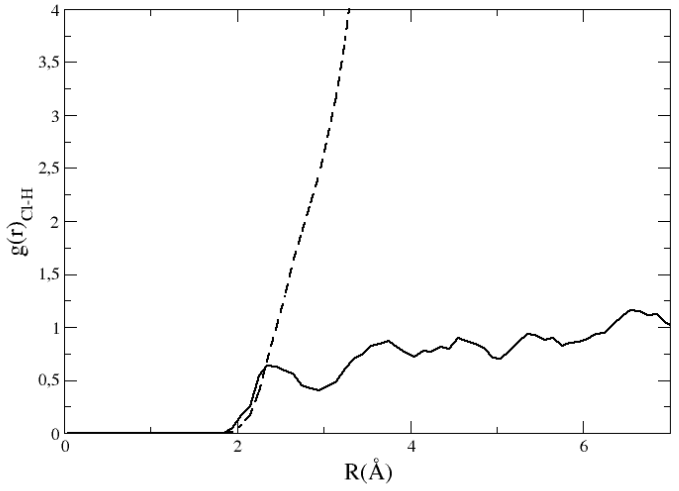


Figure S2. Radial distribution function (RDF) $g(r)_{Cl\text{-}H}$ (solid line) and coordinate numbers (CNs) (dash line) between oxo and water protons from the equilibrium run.

S2. Oxo-H $_{\text{attacking water}}$ distance in R= 2.9 Å run

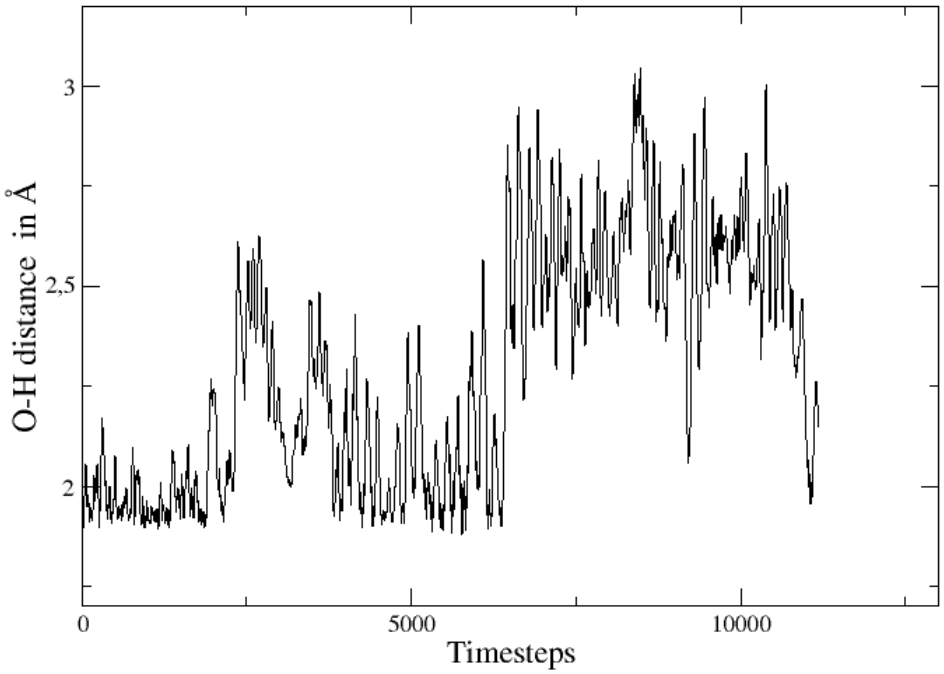


Figure S3. O-H distance of oxo and the proton of attacking water during simulations at R= 2.9 Å

S3. RDF and CNs of O-H for NNA system at different stages

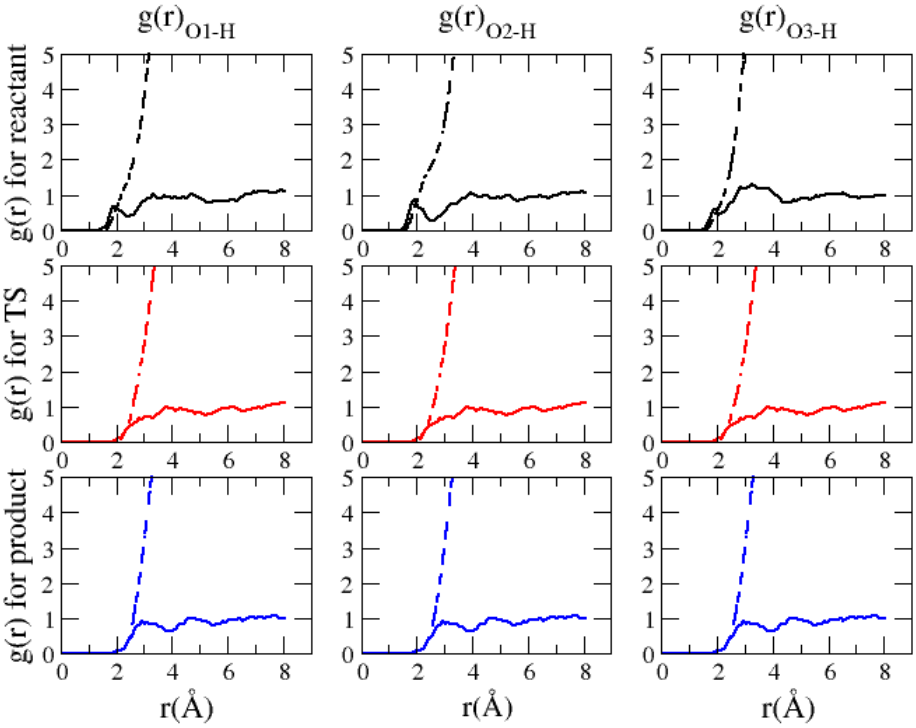
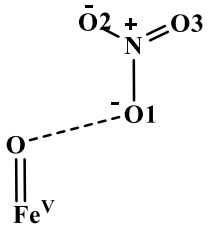


Figure S4. Radial distribution function (RDF) $g(r)_{O\text{-}H}$ (solid lines) and coordinate numbers (CNs) (dash lines) between nitrate and water protons for NNA system at different stages. RDF and CNs of reactant state are shown in black, TSs are shown in red, products are shown in blue. The label of oxygen atoms is shown Scheme S1.



Scheme S1. The labels of oxygen atoms mentioned in Figure S4.

S4. Time-averaged constraint force for the WNA mechanism.

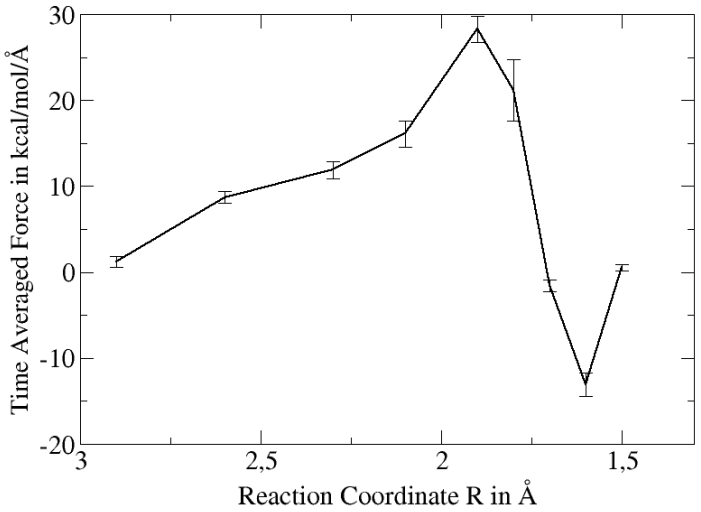


Figure S5. Calculated time-averaged constraint force profile along the reaction pathway for O-O bond formation by WNA mechanism.

S5. Time-averaged constraint force for the NNA mechanism.

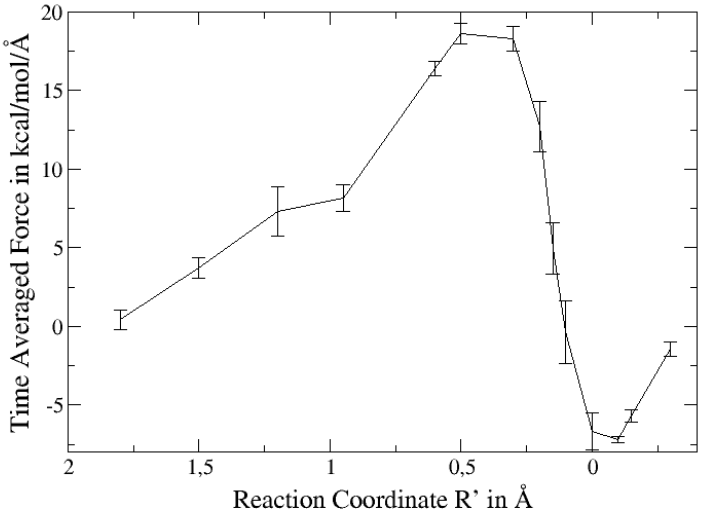


Figure S6. Calculated time-averaged constraint force profile along the reaction pathway for O-O bond formation by NNA mechanism.

S6. Free energy profile for the NNA mechanism with O1-O3 as the reaction coordinate.

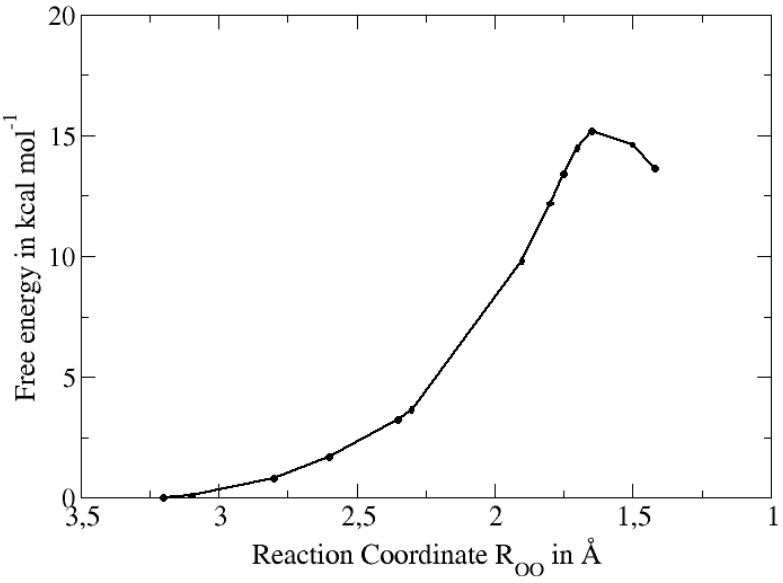


Figure S7. Calculated free energy profile for O-O bond formation via the NNA mechanism with O1-O3 as the reaction coordinate (as is specified in **Scheme 1** in the main text).

S7. Optimized TS for the O-O bond formation by DFT calculations.

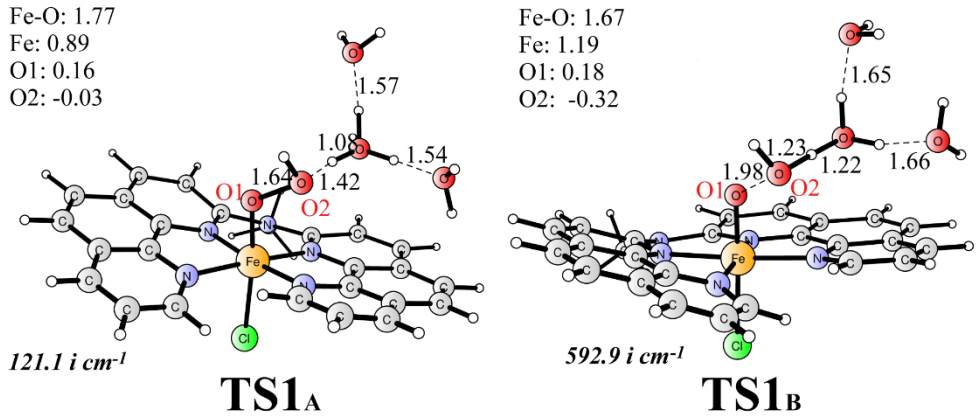


Figure S8. Optimized transition states for WNA mechanism. (Left: from Method-A, right: from Method-B) Distances are shown in Angstrom. Spin densities on selected atoms are shown. The imaginary frequency for both transition states is also shown. All structures were calculated in the doublet state.

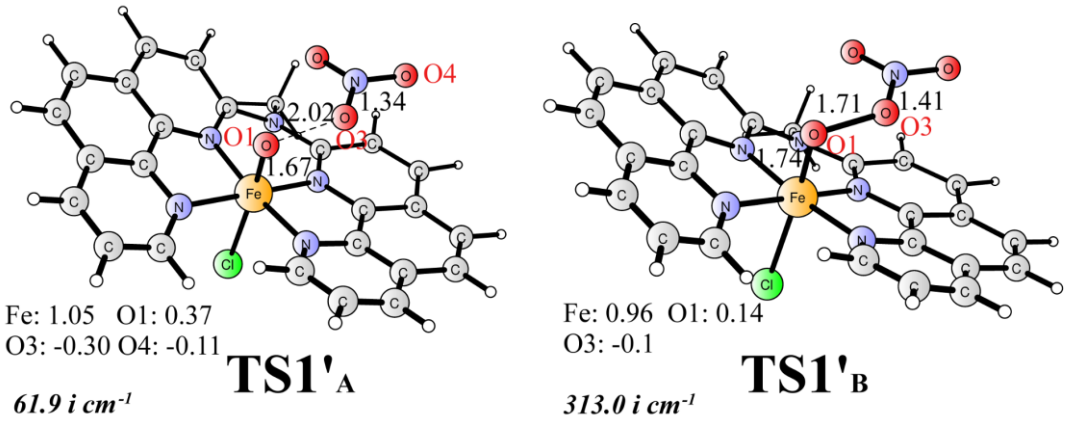


Figure S9. Optimized transition states for NNA mechanism. (Left: from Method-A, right: from Method-B) Distances are shown in Angstrom. Spin densities on selected atoms are shown. The imaginary frequency for both transition states is also shown. All structures were calculated in the doublet state.

S8. Energy barrier for NNA pathway with some water molecules were explicitly incorporated via static DFT calculations.

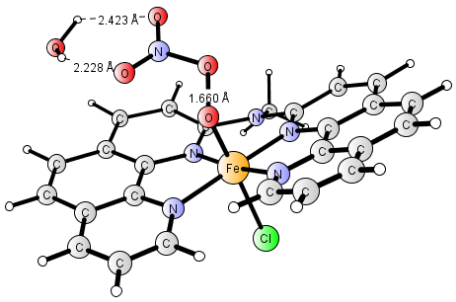
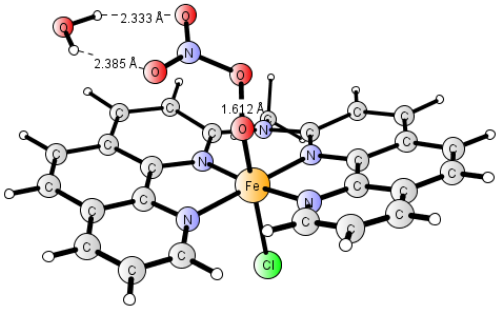
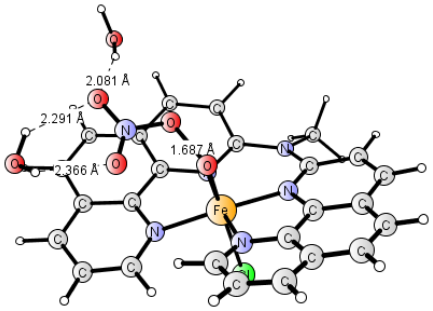
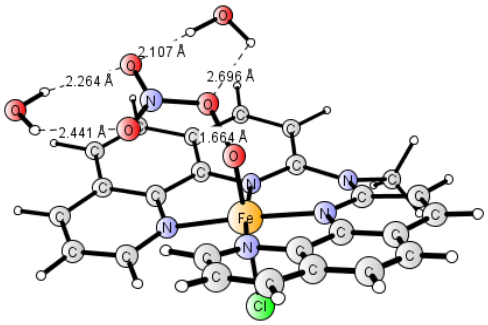
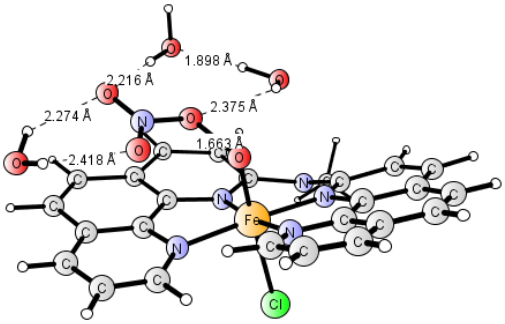
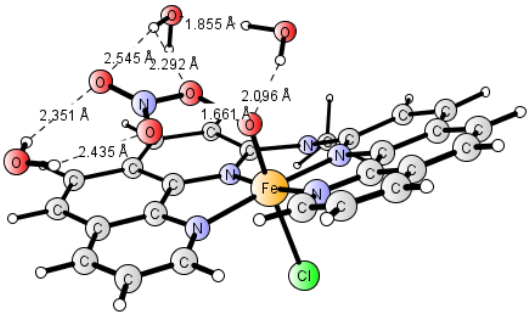
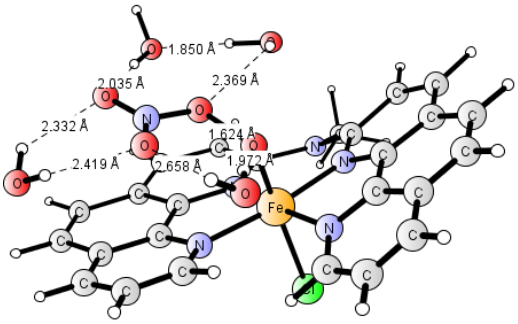
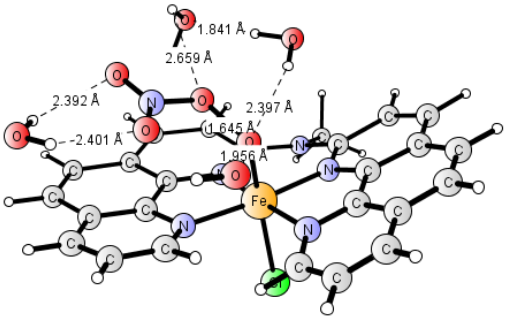
Table S1. Calculated barriers for the NNA pathway with up to four water molecules were considered.[1]

	TS1'-H_2O	TS1'-3H_2O	TS1'-3H_2O	TS1'-4H_2O
Method-A	*10.3*	*11.5*	*11.5*	*13.4*[2]
	12.1	**13.1**	**12.0**	**11.7**[3]
Method-B	*13.4*	*11.9*	*12.1*	*12.7*[2]
	13.3	**12.5**	**12.5**	**11.1**[3]

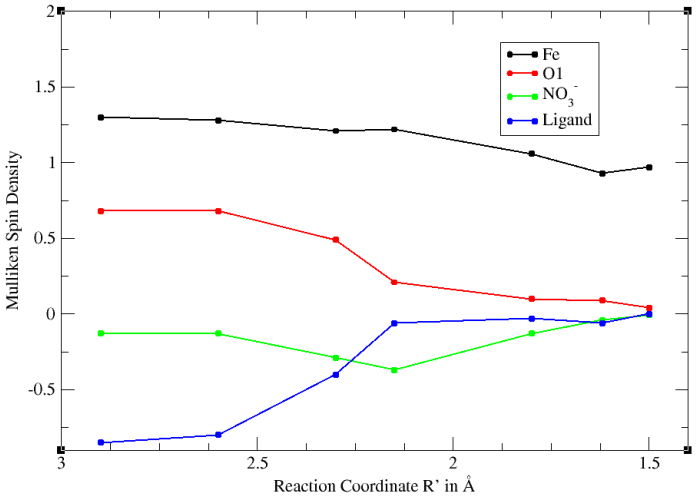
[1]All energies are given in kcal/mol.
[2]The barriers of this row are that the energies of TS subtract the energy of **3** and the energy of n×H_2O and the energy of a NO_3^-.(n means the number of water molecules)
[3]The barriers of this row are that the energies of TS subtract the energy of **3** and the energy of nH_2O and NO_3^- complex. (n means the number of water molecules)

S9. Optimized transition states for NNA pathway when water molecules were incorporated explicitly.

Table S2. Optimized transition states for NNA pathway.

 TS1'-H_2O-Method-A	 TS1'-H_2O-Method-B
 TS1'-2H_2O-Method-A	 TS1'-2H_2O-Method-B
 TS1'-3H_2O-Method-A	 TS1'-3H_2O-Method-B
 TS1'-4H_2O-Method-A	 TS1'-4H_2O-Method-B

S10. Mulliken spin density on selected atoms during the O-O bond formation for TS1'-4H_2O-Method-B.



Figures S10. Mulliken spin density on selected atoms at specified reaction coordinate during the O-O bond formation for TS1'-4H_2O-Method-B, during which four water molecules were explicitly considered.

S11. Calculated vertical ionization energy of NO_3^- ion hydrated by the different number of water molecules.

Table S2

	NO_3^-	NO_3^--H_2O	NO_3^--$2H_2O$	NO_3^--$3H_2O$	NO_3^--$4H_2O$
Energy	146.4	151.1	155.4	157.7	158.6

Energies are given in kcal/mol.

S12. Coordinates for all structures via DFT calculations

TS_A E= -2200.8698942 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	26	0	0.413971	0.496824	-0.238591
2	17	0	0.660058	0.913583	-2.472109
3	7	0	2.126273	1.594628	0.005012
4	7	0	1.698177	-0.998016	-0.321449
5	7	0	-1.080251	-0.694200	-0.718013
6	7	0	-1.042631	1.879873	-0.080939
7	7	0	0.211070	-2.665363	-1.204747
8	6	0	2.365960	2.911794	-0.096399
9	1	0	1.538932	3.533669	-0.432890
10	6	0	3.636461	3.474369	0.173556
11	1	0	3.766740	4.553855	0.085296
12	6	0	4.695605	2.646819	0.540233
13	1	0	5.679598	3.064008	0.766370
14	6	0	4.497611	1.238612	0.571549
15	6	0	3.185669	0.762469	0.271487
16	6	0	5.537988	0.275519	0.837715
17	1	0	6.533509	0.640731	1.098768
18	6	0	5.295740	-1.078019	0.736858
19	1	0	6.094987	-1.798415	0.923815
20	6	0	4.000386	-1.571221	0.343710
21	6	0	2.949042	-0.640973	0.125327
22	6	0	3.677985	-2.941159	0.133381
23	1	0	4.421620	-3.715217	0.336064
24	6	0	2.422283	-3.293283	-0.337600
25	1	0	2.180105	-4.343800	-0.486391
26	6	0	1.437320	-2.287364	-0.608017
27	6	0	-1.009825	-1.988164	-1.116486
28	6	0	-2.217414	-2.683716	-1.476138
29	1	0	-2.183981	-3.746627	-1.701807
30	6	0	-3.431619	-2.025310	-1.517510
31	1	0	-4.338404	-2.567976	-1.794353
32	6	0	-3.498351	-0.639902	-1.196983
33	6	0	-2.283120	-0.030160	-0.789769
34	6	0	-4.701927	0.153525	-1.237234
35	1	0	-5.627400	-0.317213	-1.577926
36	6	0	-4.689969	1.486052	-0.865588

37	1	0	-5.605341	2.080906	-0.908103
38	6	0	-3.465596	2.124543	-0.445043
39	6	0	-2.261183	1.357565	-0.439282
40	6	0	-3.375050	3.480987	-0.026530
41	1	0	-4.265209	4.114556	-0.031097
42	6	0	-2.145951	3.978857	0.397643
43	1	0	-2.042835	5.006117	0.750117
44	6	0	-1.002934	3.144448	0.365938
45	1	0	-0.041398	3.505228	0.722835
46	6	0	0.260457	-3.869095	-2.096680
47	1	0	-0.404088	-3.708568	-2.953408
48	1	0	1.275930	-3.971205	-2.493283
49	1	0	-0.024313	-4.791859	-1.568146
50	8	0	0.419663	0.168116	1.504072
51	8	0	-0.949094	0.507501	2.350909
52	1	0	-0.499909	0.560567	3.223469
53	1	0	-1.715768	-0.680160	2.239816
54	8	0	-2.402842	-1.504468	2.106436
55	1	0	-3.348115	-1.094067	2.030768
56	1	0	-2.363288	-2.121618	2.927799
57	8	0	-4.736065	-0.440492	1.917594
58	1	0	-5.069801	0.154883	2.615082
59	1	0	-4.957699	-0.013921	1.061668
60	8	0	-2.191460	-2.941465	4.254607
61	1	0	-1.842818	-3.851685	4.189120
62	1	0	-2.932766	-2.995663	4.888832

TS_B E= -2201.995107 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	26	0	-0.371179	-0.018580	-0.422937
2	17	0	-0.757683	0.688691	-2.619899
3	7	0	-1.633242	-1.564324	-0.798953
4	7	0	-2.043530	0.878280	0.178323
5	7	0	0.634800	1.680132	-0.191628
6	7	0	1.445028	-0.765487	-0.941560
7	7	0	-1.220926	3.125112	0.320068
8	6	0	-1.470205	-2.701841	-1.491873
9	1	0	-0.552359	-2.808499	-2.063794
10	6	0	-2.455764	-3.715867	-1.512680
11	1	0	-2.258936	-4.624653	-2.082110

12	6	0	-3.645857	-3.540260	-0.812322
13	1	0	-4.412698	-4.317854	-0.801554
14	6	0	-3.880441	-2.312622	-0.134278
15	6	0	-2.837709	-1.339672	-0.174342
16	6	0	-5.106164	-1.983386	0.547380
17	1	0	-5.889610	-2.742106	0.598029
18	6	0	-5.295727	-0.734649	1.100642
19	1	0	-6.230806	-0.484167	1.605709
20	6	0	-4.280455	0.280511	1.003093
21	6	0	-3.050995	-0.036795	0.371340
22	6	0	-4.409652	1.611754	1.491661
23	1	0	-5.310542	1.905111	2.034234
24	6	0	-3.396012	2.529985	1.285243
25	1	0	-3.492796	3.538081	1.681158
26	6	0	-2.199908	2.153928	0.587102
27	6	0	0.152795	2.896394	0.152960
28	6	0	1.067192	3.987447	0.343224
29	1	0	0.698778	4.943567	0.704618
30	6	0	2.418738	3.825322	0.107915
31	1	0	3.104975	4.659698	0.265228
32	6	0	2.924062	2.568162	-0.326018
33	6	0	1.977510	1.517198	-0.446443
34	6	0	4.307646	2.306038	-0.617087
35	1	0	5.020606	3.127072	-0.518379
36	6	0	4.724625	1.050820	-1.003095
37	1	0	5.776155	0.850491	-1.217515
38	6	0	3.785139	-0.032697	-1.122842
39	6	0	2.404477	0.216142	-0.854794
40	6	0	4.151499	-1.360601	-1.471100
41	1	0	5.196439	-1.592028	-1.688977
42	6	0	3.177196	-2.352720	-1.494249
43	1	0	3.426123	-3.391046	-1.712608
44	6	0	1.833283	-2.022147	-1.208007
45	1	0	1.075176	-2.796898	-1.170747
46	6	0	-1.689129	4.545472	0.251220
47	1	0	-1.086294	5.079638	-0.490856
48	1	0	-2.724272	4.556401	-0.104102
49	1	0	-1.621764	5.049520	1.225732
50	8	0	-0.134123	-0.434946	1.174624
51	8	0	0.498454	-2.281045	1.529746
52	1	0	0.066442	-2.244788	2.412697
53	1	0	1.632105	-1.859632	1.726614
54	8	0	2.749613	-1.397694	1.880658
55	1	0	3.402073	-2.075143	1.497827

56	1	0	2.968511	-1.435563	2.872945
57	8	0	4.553067	-3.246205	1.251701
58	1	0	5.215668	-2.781366	0.701178
59	1	0	4.958172	-3.245777	2.144328
60	8	0	3.552871	-1.702998	4.391069
61	1	0	4.304162	-1.076355	4.437825
62	1	0	3.995107	-2.566733	4.255116

TS_A' E= -2175.7677204 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	26	0	0.197534	0.525945	-0.213653
2	17	0	0.247506	0.807446	-2.509220
3	7	0	1.904325	1.665500	-0.199897
4	7	0	1.502750	-0.957089	-0.282703
5	7	0	-1.295716	-0.728550	-0.484261
6	7	0	-1.293114	1.900730	-0.032563
7	7	0	0.001488	-2.703699	-0.922901
8	6	0	2.108748	2.972594	-0.412699
9	1	0	1.250975	3.548018	-0.755198
10	6	0	3.378850	3.574038	-0.240426
11	1	0	3.485318	4.645537	-0.415199
12	6	0	4.465319	2.793856	0.148541
13	1	0	5.448760	3.242902	0.306080
14	6	0	4.296724	1.389810	0.301405
15	6	0	2.983822	0.870474	0.091081
16	6	0	5.360529	0.467548	0.611136
17	1	0	6.358421	0.866644	0.805098
18	6	0	5.133577	-0.892219	0.638412
19	1	0	5.948691	-1.584077	0.862105
20	6	0	3.833510	-1.435670	0.339817
21	6	0	2.761105	-0.543657	0.077702
22	6	0	3.524152	-2.823595	0.269023
23	1	0	4.285589	-3.565571	0.519892
24	6	0	2.258792	-3.233248	-0.114932
25	1	0	2.020764	-4.294432	-0.139971
26	6	0	1.243841	-2.269044	-0.429101
27	6	0	-1.228915	-2.054759	-0.742925
28	6	0	-2.438806	-2.820300	-0.830959
29	1	0	-2.388999	-3.900408	-0.939621
30	6	0	-3.673026	-2.209942	-0.709806

31	1	0	-4.584564	-2.810099	-0.749985
32	6	0	-3.756578	-0.805509	-0.505366
33	6	0	-2.523060	-0.113014	-0.393949
34	6	0	-4.988334	-0.074039	-0.370028
35	1	0	-5.929702	-0.620859	-0.457454
36	6	0	-4.987090	1.280569	-0.119735
37	1	0	-5.926310	1.825958	-0.006284
38	6	0	-3.748663	2.003347	0.013449
39	6	0	-2.518140	1.295634	-0.147411
40	6	0	-3.663129	3.388221	0.322790
41	1	0	-4.577384	3.972682	0.449602
42	6	0	-2.412117	3.975237	0.488308
43	1	0	-2.310419	5.027665	0.756559
44	6	0	-1.245154	3.193904	0.315968
45	1	0	-0.259252	3.619991	0.484558
46	6	0	-0.012939	-4.013912	-1.634196
47	1	0	-0.771245	-3.981143	-2.425147
48	1	0	0.957682	-4.160734	-2.120785
49	1	0	-0.218112	-4.856666	-0.954872
50	8	0	0.288714	0.486862	1.455124
51	8	0	-1.358756	-0.201446	2.402961
52	7	0	-1.435564	-1.538604	2.354352
53	8	0	-2.590589	-1.974093	2.566784
54	8	0	-0.431994	-2.229135	2.096573

TS_B' E= -2175.8447263 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	26	0	0.171490	0.495348	-0.245382
2	17	0	0.193239	0.756545	-2.564808
3	7	0	1.848049	1.669222	-0.228059
4	7	0	1.507166	-0.960882	-0.304227
5	7	0	-1.296690	-0.798803	-0.458434
6	7	0	-1.344293	1.835377	-0.071954
7	7	0	0.030311	-2.763398	-0.861828
8	6	0	2.020128	2.985463	-0.426267
9	1	0	1.150627	3.556237	-0.742428
10	6	0	3.276754	3.613955	-0.258518
11	1	0	3.349822	4.689958	-0.419761
12	6	0	4.386418	2.859143	0.111457
13	1	0	5.360132	3.328209	0.267889

14	6	0	4.253335	1.450489	0.250857
15	6	0	2.953387	0.899550	0.045239
16	6	0	5.342440	0.555011	0.546874
17	1	0	6.329968	0.983014	0.730683
18	6	0	5.148728	-0.810025	0.575675
19	1	0	5.978231	-1.486719	0.790812
20	6	0	3.858419	-1.382405	0.292893
21	6	0	2.765473	-0.516747	0.033180
22	6	0	3.580155	-2.777656	0.243461
23	1	0	4.364731	-3.496713	0.486878
24	6	0	2.318023	-3.221145	-0.108692
25	1	0	2.107490	-4.287925	-0.122975
26	6	0	1.274466	-2.286155	-0.415159
27	6	0	-1.207835	-2.133226	-0.683186
28	6	0	-2.404446	-2.924014	-0.743062
29	1	0	-2.333768	-4.004521	-0.832052
30	6	0	-3.649136	-2.333483	-0.642166
31	1	0	-4.550527	-2.948703	-0.671426
32	6	0	-3.759045	-0.924103	-0.482117
33	6	0	-2.539722	-0.206010	-0.388267
34	6	0	-5.004476	-0.211987	-0.376747
35	1	0	-5.932468	-0.781774	-0.456682
36	6	0	-5.028194	1.149756	-0.165490
37	1	0	-5.974513	1.686341	-0.073568
38	6	0	-3.803503	1.896348	-0.043215
39	6	0	-2.560943	1.206379	-0.179160
40	6	0	-3.744472	3.289205	0.235252
41	1	0	-4.670787	3.857927	0.340197
42	6	0	-2.504863	3.899089	0.399320
43	1	0	-2.419454	4.957806	0.646056
44	6	0	-1.321678	3.137881	0.252876
45	1	0	-0.349942	3.593786	0.421134
46	6	0	0.026525	-4.107917	-1.518682
47	1	0	-0.748606	-4.119842	-2.292870
48	1	0	0.989245	-4.254075	-2.018948
49	1	0	-0.148196	-4.918962	-0.797290
50	8	0	0.308030	0.461130	1.490650
51	8	0	-1.142102	0.102045	2.316554
52	7	0	-1.276254	-1.292148	2.487829
53	8	0	-2.431409	-1.601555	2.816168
54	8	0	-0.306952	-2.032161	2.307206
