Electronic Supplementary Information (ESI)

Radical O-O coupling reaction in diferrate-mediated water oxidation studied with multireference wave function theory

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Molecular geometries (in Å) of diferrate considered in this study (xyz format): optimized at B3LYP/def2-TZVP level of theory for reactant, product, transition states, and potential energy surface scan.

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13
---------- R(O=O) = 1.300 angstrom
Fe       1.513590    0.195743    0.000000
O        0.650006   -1.343363    0.000000
O        2.370367    0.165074   -1.431026
H        2.483839   -0.588137   -2.054553
O        2.370367    0.165074    1.431026
H        2.483839   -0.588137    2.054553
O        0.000000    1.048169    0.000000
Fe      -1.513590    0.195743    0.000000
O       -0.650006   -1.343363    0.000000
O       -2.370367    0.165074   -1.431026
H       -2.483839   -0.588137   -2.054553
O       -2.370367    0.165074    1.431026
H       -2.483839   -0.588137    2.054553
13
---------- R(O=O) = 1.347 angstrom (Product)
Fe       1.515890    0.195410    0.000000
O        0.673708   -1.346171    0.000000
O        2.371976    0.167947   -1.431294
H        2.482768   -0.588065   -2.052673
O        2.371976    0.167947    1.431294
H        2.482768   -0.588065    2.052673
O        0.000000    1.044421    0.000000
Fe      -1.515890    0.195410    0.000000
O       -0.673708   -1.346171    0.000000
O       -2.371976    0.167947   -1.431294
H       -2.482768   -0.588065   -2.052673
O       -2.371976    0.167947    1.431294
H       -2.482768   -0.588065    2.052673
13
---------- R(O=O) = 1.400 angstrom
Fe       1.518740    0.194144    0.000000
O        0.699999   -1.349720    0.000000
O        2.376589    0.173166   -1.429730
H        2.490493   -0.585836   -2.047350
O        2.376589    0.173166    1.429730
H        2.490493   -0.585836    2.047350
O        0.000000    1.037755    0.000000
Fe      -1.518740    0.194144    0.000000
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O        -0.699999   -1.349720    0.000000
O        -2.376589    0.173166   -1.429730
H        -2.490493   -0.585836   -2.047350
O        -2.376589    0.173166    1.429730
H        -2.490493   -0.585836    2.047350
13
----------- R(O=O) = 1.500 angstrom
Fe        1.525032    0.190195    0.000000
O         0.749999   -1.357083    0.000000
O         2.386799    0.185921   -1.427066
H         2.508691   -0.576352   -2.039653
O         2.386799    0.185921    1.427066
H         2.508691   -0.576352    2.039653
O         0.000000    1.022390    0.000000
Fe       -1.525032    0.190195    0.000000
O        -0.749999   -1.357083    0.000000
O        -2.386799    0.185921   -1.427066
H        -2.508691   -0.576352   -2.039653
O        -2.386799    0.185921    1.427066
H        -2.508691   -0.576352    2.039653
13
----------- R(O=O) = 1.600 angstrom
Fe        1.533126    0.184861    0.000000
O         0.799998   -1.361886    0.000000
O         2.400304    0.200198   -1.423802
H         2.534645   -0.564078   -2.031598
O         2.400304    0.200198    1.423802
H         2.534645   -0.564078    2.031598
O         0.000000    1.003423    0.000000
Fe       -1.533126    0.184861    0.000000
O        -0.799998   -1.361886    0.000000
O        -2.400304    0.200198   -1.423802
H        -2.534645   -0.564078   -2.031598
O        -2.400304    0.200198    1.423802
H        -2.534645   -0.564078    2.031598
13
----------- R(O=O) = 1.700 angstrom
Fe        1.542368    0.176790    0.000000
O         0.849996   -1.364572    0.000000
O         2.416690    0.218097   -1.419815
H         2.569545   -0.547680   -2.021390
O         2.416690    0.218097    1.419815
H         2.569545   -0.547680    2.021390
O         0.000000    0.981461    0.000000
Fe       -1.542368    0.176790    0.000000
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O        -0.849996   -1.364572    0.000000
O        -2.416690    0.218097   -1.419815
H        -2.569545   -0.547680   -2.021390
O        -2.416690    0.218097    1.419815
H        -2.569545   -0.547680    2.021390
13
----------- R(O=O) = 1.750 angstrom
Fe        1.547599    0.171200    0.000000
O         0.874998   -1.365623    0.000000
O         2.425704    0.229140   -1.417898
H         2.585372   -0.534789   -2.020180
O         2.425704    0.229140    1.417898
H         2.585372   -0.534789    2.020180
O         0.000000    0.969281    0.000000
Fe       -1.547599    0.171200    0.000000
O        -0.874998   -1.365623    0.000000
O        -2.425704    0.229140   -1.417898
H        -2.585372   -0.534789   -2.020180
O        -2.425704    0.229140    1.417898
H        -2.585372   -0.534789    2.020180
13
----------- R(O=O) = 1.800 angstrom
Fe        1.553269    0.165738    0.000000
O         0.900000   -1.366441    0.000000
O         2.436024    0.240264   -1.415321
H         2.607667   -0.523886   -2.014049
O         2.436024    0.240264    1.415321
H         2.607667   -0.523886    2.014049
O         0.000000    0.956468    0.000000
Fe       -1.553269    0.165738    0.000000
O        -0.900000   -1.366441    0.000000
O        -2.436024    0.240264   -1.415321
H        -2.607667   -0.523886   -2.014049
O        -2.436024    0.240264    1.415321
H        -2.607667   -0.523886    2.014049
13
----------- R(O=O) = 1.850 angstrom
Fe        1.558166    0.159451    0.000000
O         0.925003   -1.369589    0.000000
O         2.442406    0.253086   -1.414326
H         2.617162   -0.506896   -2.017410
O         2.442406    0.253086    1.414326
H         2.617162   -0.506896    2.017410
O         0.000000    0.943852    0.000000
Fe       -1.558166    0.159451    0.000000
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O       -0.925003   -1.369589    0.000000
O       -2.442406    0.253086   -1.414326
H       -2.617162   -0.506896   -2.017410
O       -2.442406    0.253086    1.414326
H       -2.617162   -0.506896    2.017410
13
----------- R(O=O) = 1.893 angstrom (Transition state)
Fe       1.562588    0.154836    0.000000
O        0.946521   -1.372135    0.000000
O        2.448908    0.263342   -1.412794
H        2.634189   -0.496299   -2.013128
O        2.448908    0.263342    1.412794
H        2.634189   -0.496299    2.013128
O        0.000000    0.932612    0.000000
Fe      -1.562588    0.154836    0.000000
O       -0.946521   -1.372135    0.000000
O       -2.448908    0.263342   -1.412794
H       -2.634189   -0.496299   -2.013128
O       -2.448908    0.263342    1.412794
H       -2.634189   -0.496299    2.013128
13
----------- R(O=O) = 2.000 angstrom
Fe       1.571720    0.143286    0.000000
O        1.000000   -1.383391    0.000000
O        2.458538    0.290345   -1.411001
H        2.660387   -0.463927   -2.012802
O        2.458538    0.290345    1.411001
H        2.660387   -0.463927    2.012802
O        0.000000    0.906005    0.000000
Fe      -1.571720    0.143286    0.000000
O       -1.000000   -1.383391    0.000000
O       -2.458538    0.290345   -1.411001
H       -2.660387   -0.463927   -2.012802
O       -2.458538    0.290345    1.411001
H       -2.660387   -0.463927    2.012802
13
----------- R(O=O) = 2.200 angstrom
Fe       1.586274    0.125258    0.000000
O        1.099996   -1.410890    0.000000
O        2.469262    0.338075   -1.408182
H        2.706102   -0.406004   -2.009990
O        2.469262    0.338075    1.408182
H        2.706102   -0.406004    2.009990
O        0.000000    0.858305    0.000000
Fe      -1.586274    0.125258    0.000000
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O        -1.099996   -1.410890    0.000000
O        -2.469262    0.338075   -1.408182
H        -2.706102   -0.406004   -2.009990
O        -2.469262    0.338075    1.408182
H        -2.706102   -0.406004    2.009990
13
----------- R(O=O) = 2.400 angstrom
Fe        1.599960    0.111327    0.000000
O         1.199999   -1.438836    0.000000
O         2.477444    0.379786   -1.404744
H         2.747289   -0.354366   -2.005028
O         2.477444    0.379786    1.404744
H         2.747289   -0.354366    2.005028
O         0.000000    0.812085    0.000000
Fe       -1.599960    0.111327    0.000000
O        -1.199999   -1.438836    0.000000
O        -2.477444    0.379786   -1.404744
H        -2.747289   -0.354366   -2.005028
O        -2.477444    0.379786    1.404744
H        -2.747289   -0.354366    2.005028
13
----------- R(O=O) = 2.600 angstrom
Fe        1.612070    0.097489    0.000000
O         1.299993   -1.465942    0.000000
O         2.478255    0.420554   -1.402229
H         2.782355   -0.298780   -2.004084
O         2.478255    0.420554    1.402229
H         2.782355   -0.298780    2.004084
O         0.000000    0.765381    0.000000
Fe       -1.612070    0.097489    0.000000
O        -1.299993   -1.465942    0.000000
O        -2.478255    0.420554   -1.402229
H        -2.782355   -0.298780   -2.004084
O        -2.478255    0.420554    1.402229
H        -2.782355   -0.298780    2.004084
13
----------- R(O=O) = 2.800 angstrom
Fe        1.624872    0.085186    0.000000
O         1.400008   -1.488509    0.000000
O         2.480080    0.457671   -1.398560
H         2.811128   -0.248407   -2.001794
O         2.480080    0.457671    1.398560
H         2.811128   -0.248407    2.001794
O         0.000000    0.716827    0.000000
Fe       -1.624872    0.085186    0.000000
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O        -1.400008   -1.488509    0.000000
O        -2.480080    0.457671   -1.398560
H        -2.811128   -0.248407   -2.001794
O        -2.480080    0.457671    1.398560
H        -2.811128   -0.248407    2.001794
13
----------- R(O=O) = 3.000 angstrom
Fe        1.638883    0.074169    0.000000
O         1.500007   -1.506376    0.000000
O         2.477163    0.491196   -1.398415
H         2.842107   -0.197865   -2.002063
O         2.477163    0.491196    1.398415
H         2.842107   -0.197865    2.002063
O         0.000000    0.664801    0.000000
Fe       -1.638883    0.074169    0.000000
O        -1.500007   -1.506376    0.000000
O        -2.477163    0.491196   -1.398415
H        -2.842107   -0.197865   -2.002063
O        -2.477163    0.491196    1.398415
H        -2.842107   -0.197865    2.002063
13
----------- R(O=O) = 3.226 angstrom (Reactant)
Fe        1.653150    0.061094    0.000000
O         1.612854   -1.522072    0.000000
O         2.471881    0.528338   -1.395950
H         2.873353   -0.142209   -1.997057
O         2.471881    0.528338    1.395950
H         2.873353   -0.142209    1.997057
O         0.000000    0.604783    0.000000
Fe       -1.653150    0.061094    0.000000
O        -1.612854   -1.522072    0.000000
O        -2.471881    0.528338   -1.395950
H        -2.873353   -0.142209   -1.997057
O        -2.471881    0.528338    1.395950
H        -2.873353   -0.142209    1.997057
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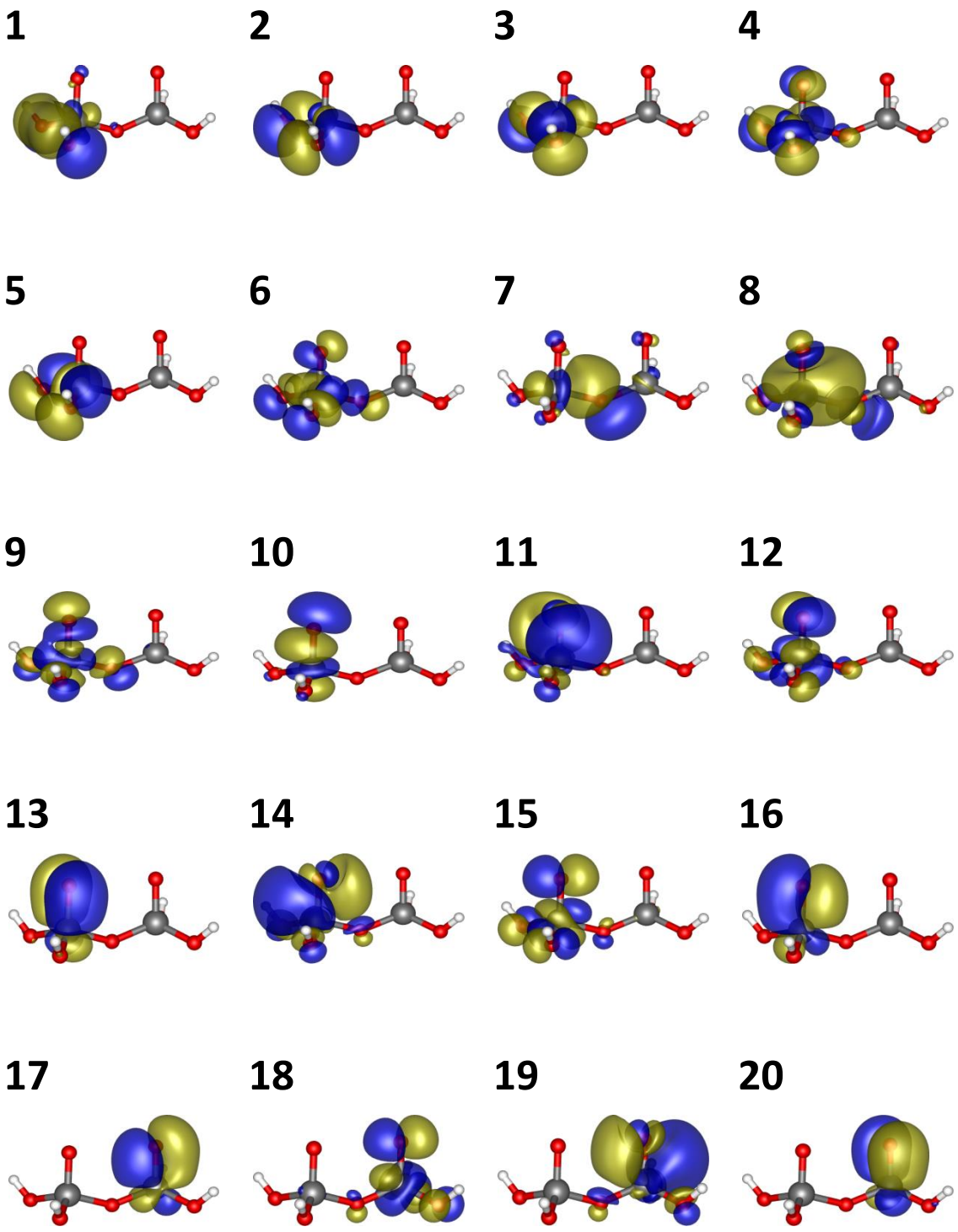
Table S1. Total energies (in Eh) of $[H_4Fe_2O_7]^{2+}$ as a function of R(O-O) in the O-O bond formation pathway.

R(O-O) / Å		DMRG-CASSCF (36e,32o)	DMRG-CASPT2 (36e,32o)	DMRG-CASPT2 ref.weight	DMRG-MRCI (36e,32o)	DMRG-MRCI+Q (36e,32o)
3.226	**R**	-3069.05541	-3071.64100	0.636	-3070.94311	-3071.30568
3.00		-3069.05491				
2.80		-3069.05383				
2.60		-3069.05193				
2.40		-3069.04905	-3071.63769			
2.20		-3069.04476	-3071.63569			
2.00		-3069.04005	-3071.63289			
1.893	**TS**	-3069.03896	-3071.63173	0.632	-3070.93164	-3071.29611
1.80		-3069.03892	-3071.63137		-3070.93176	-3071.29640
1.70		-3069.04074	-3071.62914		-3070.93268	-3071.29714
1.60		-3069.04476	-3071.63075		-3070.93647	-3071.30083
1.50		-3069.04995	-3071.63490			
1.40		-3069.05434	-3071.64050			
1.347	**P**	-3069.05529	-3071.64159	0.634	-3070.94790	-3071.31202
1.30		-3069.05407				

R(O-O) / Å		CASSCF (4,4)	CASPT2 (4,4)	CASPT2(4,4) ref.weight	MRCI (4,4)	MRCI+Q (4,4)	CASSCF (20,14)	CASPT2 (20,14)	CASPT2(20,14) ref.weight
3.226	**R**	-3068.23550	-3071.39165	0.540	-3070.33558	-3070.91956	-3068.40079	-3071.66899	0.511
3.00		-3068.23652	-3071.39517	0.540	-3070.33712	-3070.92141	-3068.40055	-3071.67237	0.511
2.80		-3068.23693	-3071.39801	0.539	-3070.33818	-3070.92280	-3068.39954	-3071.67544	0.510
2.60		-3068.23853	-3071.40108	0.539	-3070.34009	-3070.92487	-3068.39804	-3071.67712	0.510
2.40		-3068.24055	-3071.40425	0.539	-3070.34238	-3070.92727	-3068.39533	-3071.67982	0.509
2.20		-3068.24332	-3071.40721	0.539	-3070.34534	-3070.93022	-3068.39114	-3071.68253	0.508
2.00		-3068.25031	-3071.41209	0.539	-3070.35217	-3070.93680	-3068.38638	-3071.68683	0.506
1.893	**TS**	-3068.25875	-3071.41715	0.540	-3070.36023	-3070.94450	-3068.38530	-3071.68997	0.505
1.80		-3068.27102	-3071.42412	0.541	-3070.37186	-3070.95557	-3068.38572	-3071.68829	0.506
1.70		-3068.28947	-3071.43465	0.543	-3070.38944	-3070.97226	-3068.39021	-3071.68930	0.506
1.60		-3068.31020	-3071.44820	0.545	-3070.40962	-3070.99162	-3068.39717	-3071.68839	0.508
1.50		-3068.33295	-3071.46421	0.547	-3070.43199	-3071.01306	-3068.40698	-3071.68569	0.511
1.40		-3068.35659	-3071.48098	0.549	-3070.45520	-3071.03509	-3068.41892	-3071.67982	0.515
1.347	**P**	-3068.36819	-3071.48879	0.550	-3070.46651	-3071.04567	-3068.42506	-3071.67523	0.518
1.30		-3068.37720	-3071.49431	0.551	-3070.47528	-3071.05370	-3068.42977	-3071.66974	0.521

R(O-O) / Å		B3LYP	B3LYP-D	TPSSh	TPSSh-D	BP86	BP86-D	CAM-B3LYP	CAM-B3LYP-D
3.226	**R**	-3055.74968	-3055.76192	-3055.80101	-3055.81325	-3056.28473	-3056.29697	-3055.59712	-3055.60936
3.00		-3055.74944	-3055.76197	-3055.80079	-3055.81332	-3056.28432	-3056.29686	-3055.59704	-3055.60958
2.80		-3055.74875	-3055.76152	-3055.80012	-3055.81290	-3056.28358	-3056.29635	-3055.59655	-3055.60932
2.60		-3055.74741	-3055.76030	-3055.79890	-3055.81179	-3056.28256	-3056.29545	-3055.59536	-3055.60824
2.40		-3055.74519	-3055.75811	-3055.79701	-3055.80993	-3056.28123	-3056.29415	-3055.59320	-3055.60612
2.20		-3055.74184	-3055.75481	-3055.79436	-3055.80733	-3056.27979	-3056.29277	-3055.58979	-3055.60277
2.00		-3055.73796	-3055.75091	-3055.79147	-3055.80442	-3056.27903	-3056.29199	-3055.58557	-3055.59853
1.893	**TS**	-3055.73696	-3055.74985	-3055.79085	-3055.80375	-3056.27953	-3056.29243	-3055.58428	-3055.59717
1.80		-3055.73824	-3055.75106	-3055.79197	-3055.80480	-3056.28072	-3056.29354	-3055.58535	-3055.59817
1.70		-3055.74340	-3055.75614	-3055.79590	-3055.80865	-3056.28288	-3056.29562	-3055.59103	-3055.60377
1.60		-3055.75150	-3055.76414	-3055.80223	-3055.81487	-3056.28650	-3056.29914	-3055.60108	-3055.61372
1.50		-3055.75976	-3055.77227	-3055.80923	-3055.82175	-3056.29130	-3056.30381	-3055.61094	-3055.62346
1.40		-3055.76570	-3055.77808	-3055.81463	-3055.82701	-3056.29557	-3056.30795	-3055.61756	-3055.62994
1.347	**P**	-3055.76674	-3055.77906	-3055.81562	-3055.82794	-3056.29644	-3056.30876	-3055.61858	-3055.63090
1.30		-3055.76565	-3055.77791	-3055.81458	-3055.82683	-3056.29548	-3056.30773	-3055.61739	-3055.62964

Fig. S1. Localized orbital used in DMRG-CASSCF(36e,32o) in the ordering of the DMRG lattice sites for **R** (reactant: O-O = 3.226 Å)



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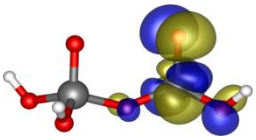

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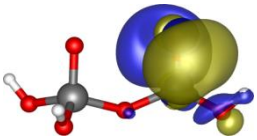

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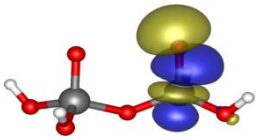

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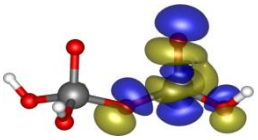

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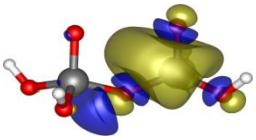

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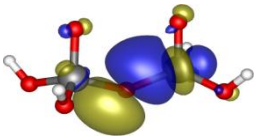

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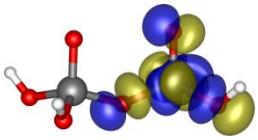

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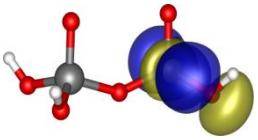

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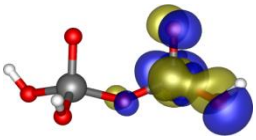

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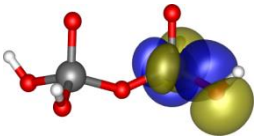

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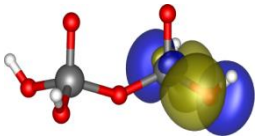

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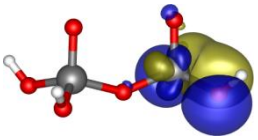


Fig. S2. Natural orbitals and occupation numbers obtained by DMRG-CASSCF(20e,14o) for **TS** (transition state: O-O = 1.893 Å)

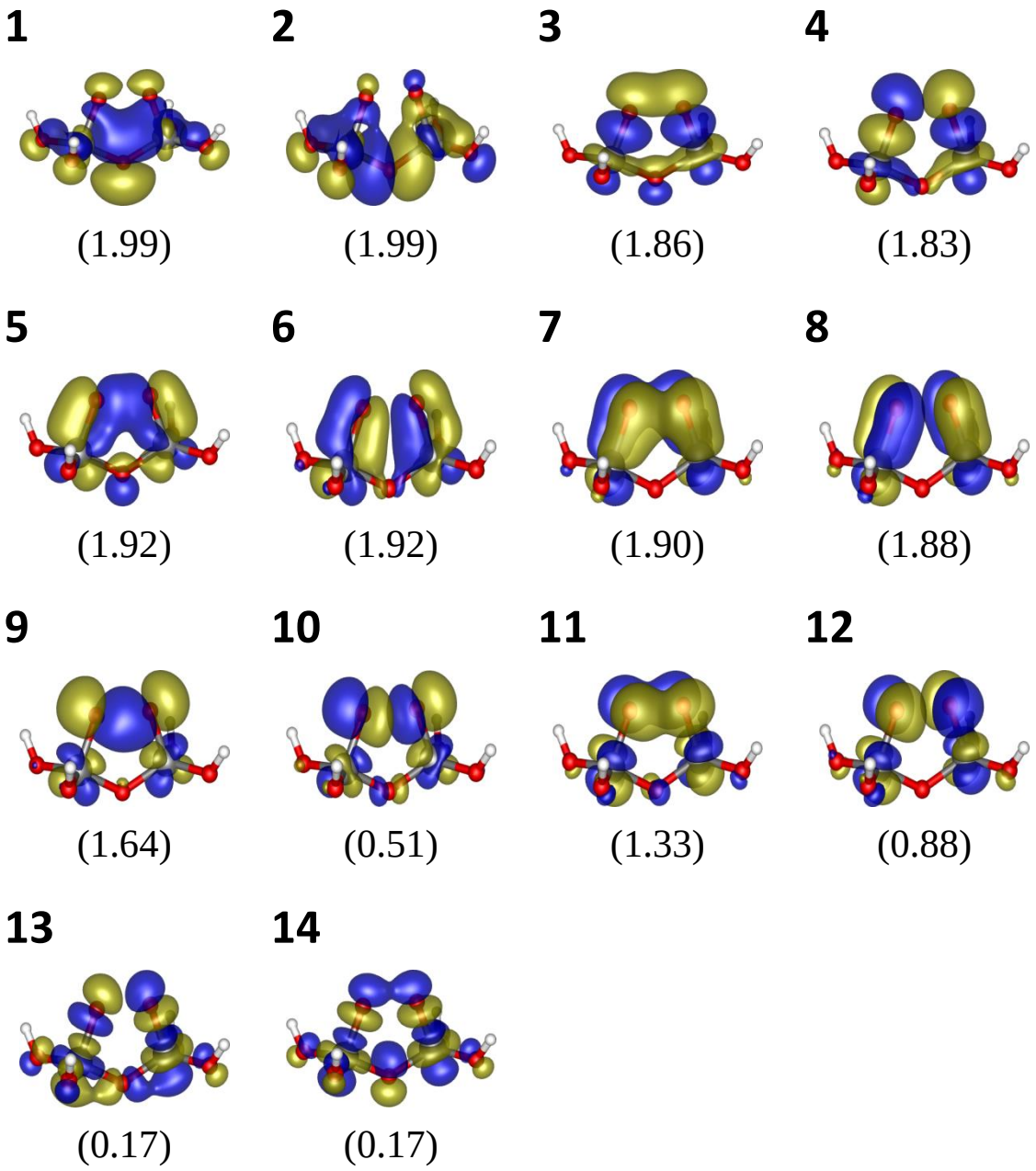


Fig. S3. Natural orbitals and occupation numbers obtained by DMRG-CASSCF(20e,14o) for **P** (product: O-O = 1.347 Å)

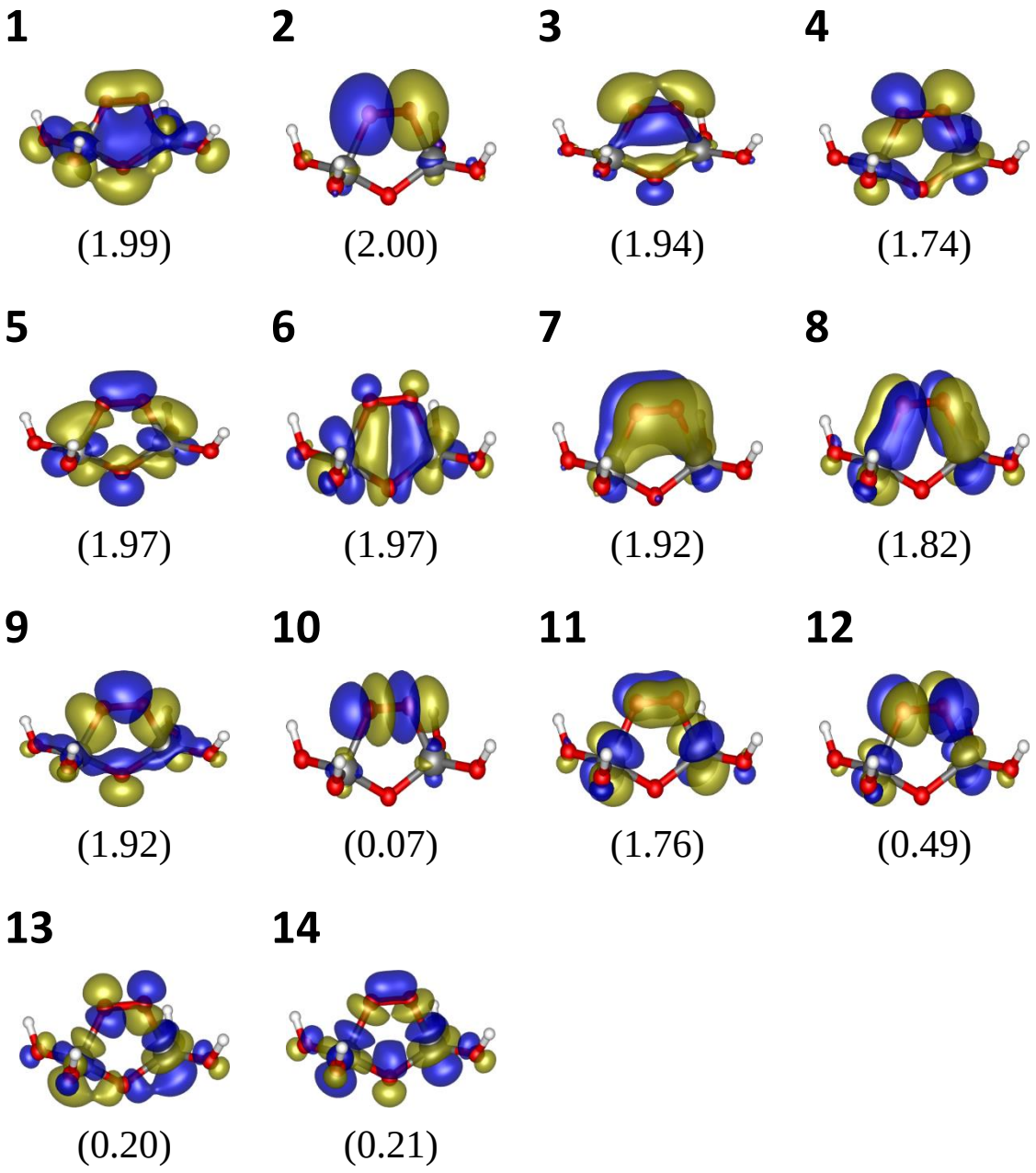
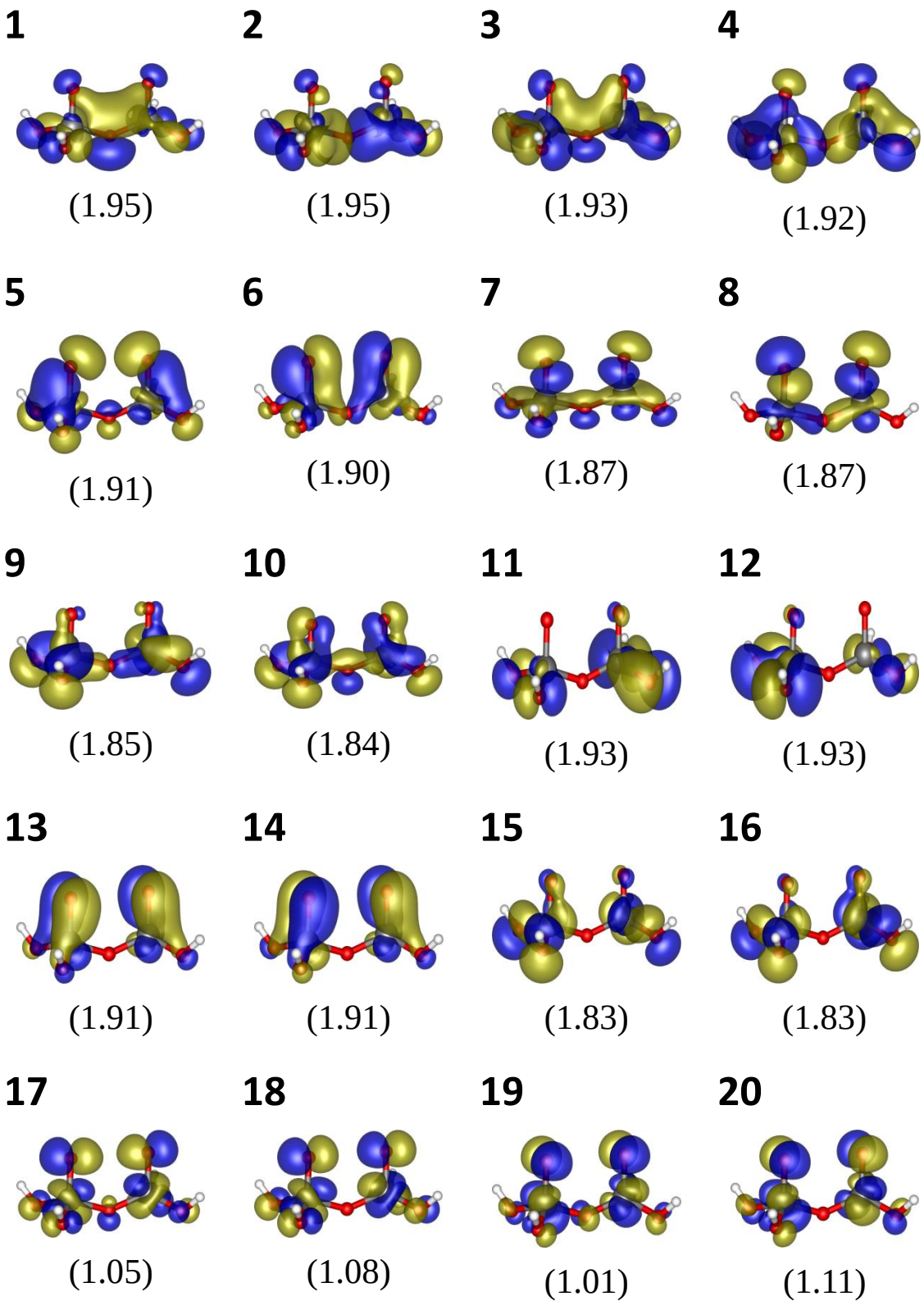


Fig. S4. Natural orbitals and occupation numbers obtained by DMRG-CASSCF(36e,32o) for **R** (reactant: O-O = 3.226 Å)



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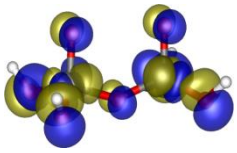

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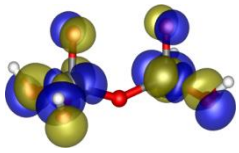

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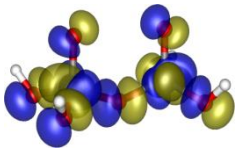

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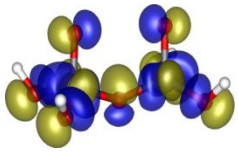

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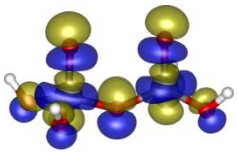

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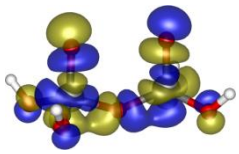

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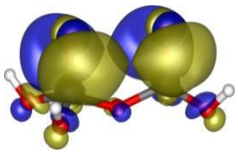

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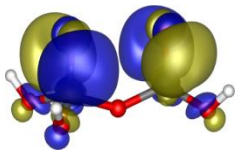

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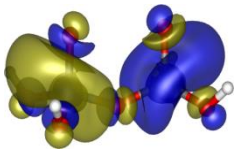

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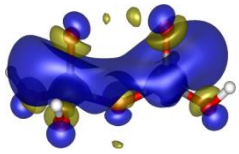

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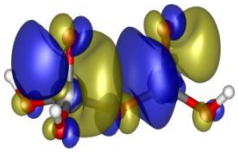

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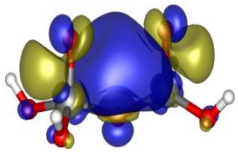

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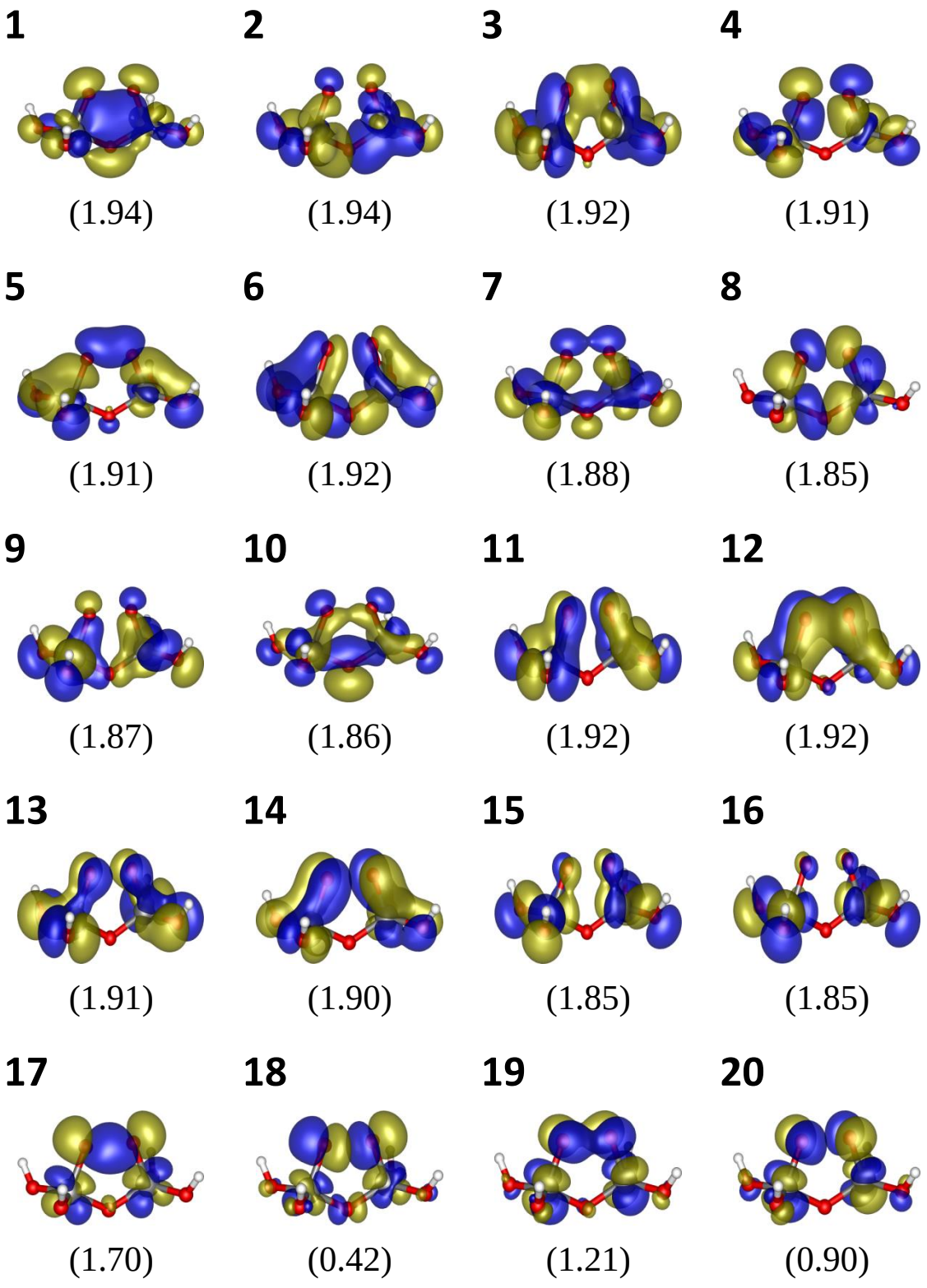
Fig. S5. Natural orbitals and occupation numbers obtained by DMRG-CASSCF(36e,32o) for **TS** (transition state: O-O = 1.893 Å)



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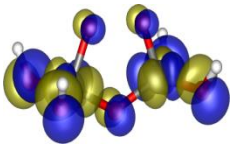

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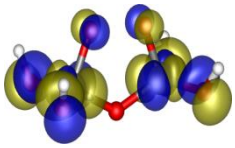

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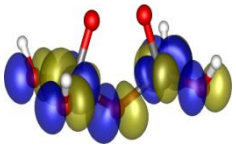

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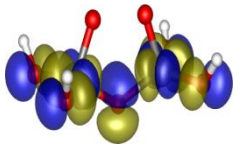

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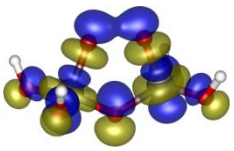

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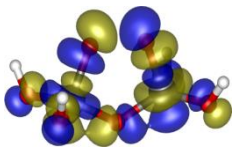

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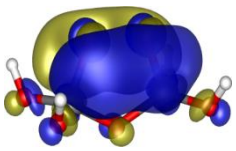

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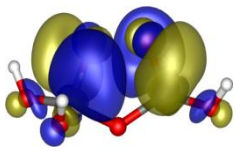

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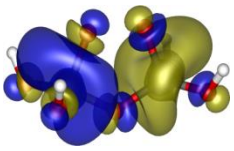

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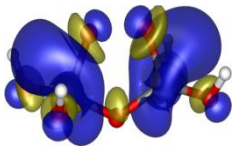

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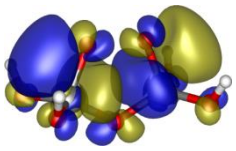

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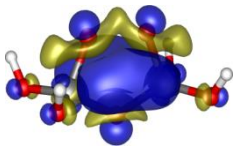

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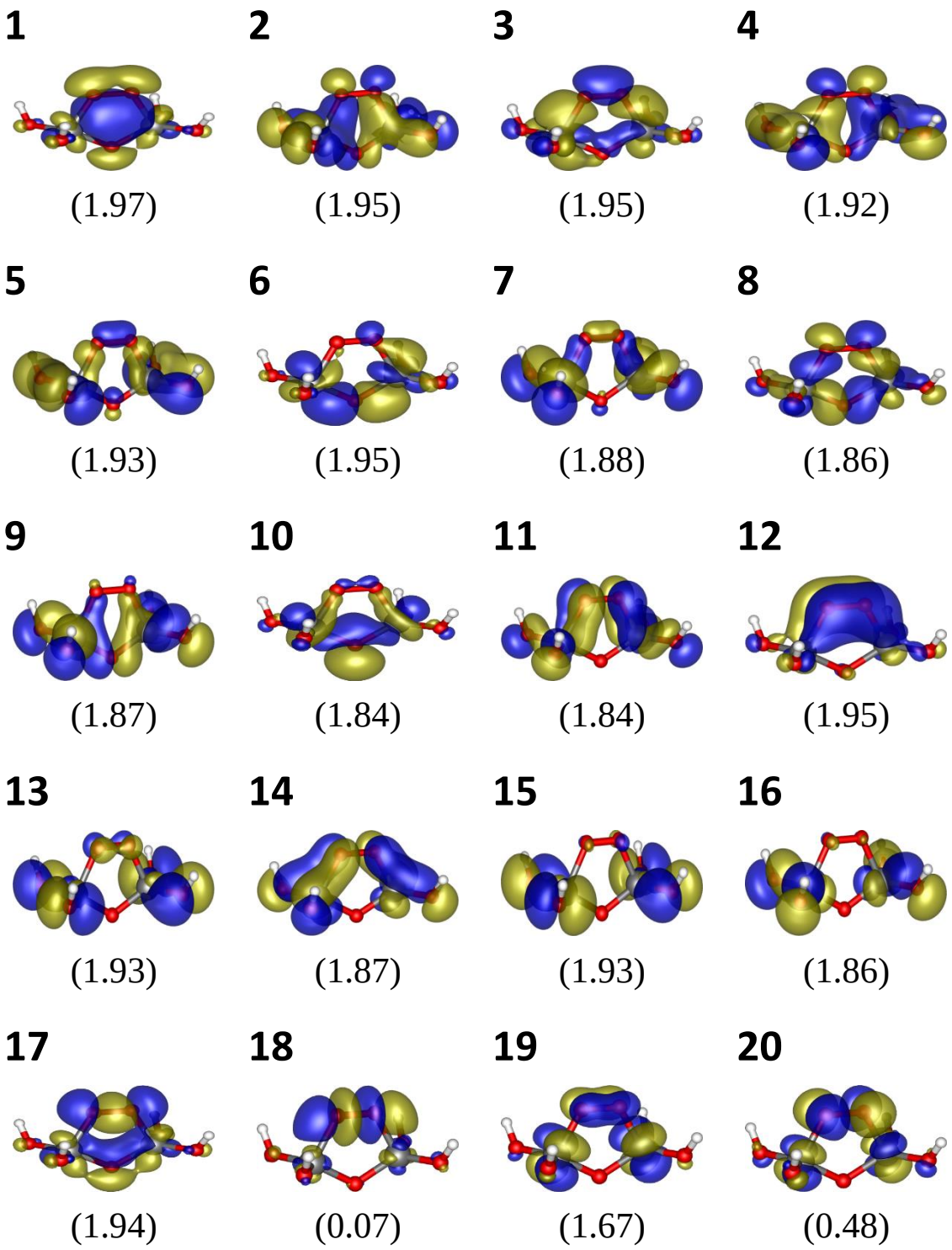
Fig. S6. Natural orbitals and occupation numbers obtained by DMRG-CASSCF(36e,32o) for **P** (product: O-O = 1.347 Å)



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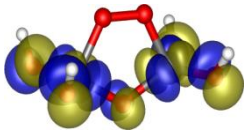

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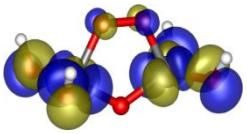

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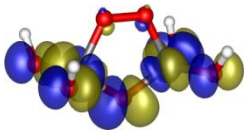

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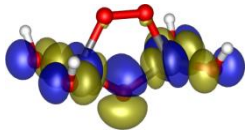

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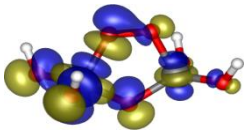

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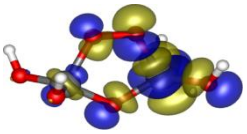

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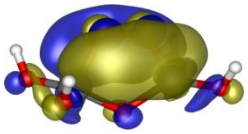

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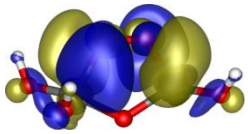

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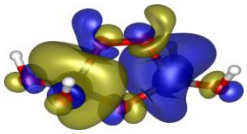

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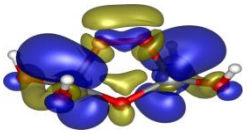

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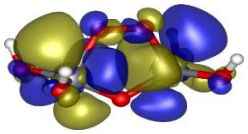

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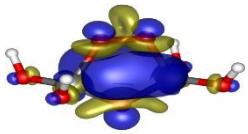

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