Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic and EPR spectra of the species involved in $[W_{10}O_{32}]^{4-}$ photocatalysis. A Relativistic DFT Investigation

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ELECTRONIC SUPPLEMENTARY INFORMATION

1. EXPERIMENTAL SPECTRUM

The tetrabutylammonium salt (n-$Bu_4N)_4[W_{10}O_{32}]$ of the decatungstate anion was synthesized as previously described.[1] All reagents were purchased from Sigma. The experimental spectrum reported in Figure 1 was recorded from a 1×10^{-4} M acetonitrile (spectroscopic grade; Carlo Erba) solution and is in accordance with previous reports.[2,3]

2. OPTIMIZED GEOMETRIES

The following geometries were optimized at the COSMO-BP86/TZ2P (All Electron basis set) level, including the parameters of acetonitrile as solvent (ε = 37.5, radius = 2.76 Å); relativistic effects were included by means of the ZORA approximation at the Scalar Level (ZSC). Mono-reduced species (either protonated or not) have been treated using with a spin-unrestricted formalism. These structures were then employed throughout the rest of this study.

Table S1. Optimized parameters for the structures used in the study.

$[W_{10}O_{32}]^{4-}$ - D_{4h} symmetry				$[W_{10}O_{32}]^{5-}$ - D_{4h} symmetry			
1.	O	0.000000	0.000000	-6.028976	1.O	0.000000	0.000000	-6.053498
2.	O	2.871985	2.871985	-2.156078	2.O	2.879171	2.879171	-2.159553
3.	O	-2.871985	2.871985	-2.156078	3.O	-2.879171	2.879171	-2.159553
4.	O	-2.871985	-2.871985	-2.156078	4.O	-2.879171	-2.879171	-2.159553
5.	O	2.871985	-2.871985	-2.156078	5.O	2.879171	-2.879171	-2.159553
6.	O	1.326641	1.326641	-3.822796	6.O	1.326672	1.326672	-3.843888
7.	O	-1.326641	1.326641	-3.822796	7.O	-1.326672	1.326672	-3.843888
8.	O	-1.326641	-1.326641	-3.822796	8.O	-1.326672	-1.326672	-3.843888
9.	O	1.326641	-1.326641	-3.822796	9.O	1.326672	-1.326672	-3.843888
10.	O	0.000000	2.658106	-1.895747	10.O	0.000000	2.655302	-1.909187
11.	O	-2.658106	0.000000	-1.895747	11.O	-2.655302	0.000000	-1.909187
12.	O	0.000000	-2.658106	-1.895747	12.O	0.000000	-2.655302	-1.909187
13.	O	2.658106	0.000000	-1.895747	13.O	2.655302	0.000000	-1.909187
14.	O	1.633002	1.633002	0.000000	14.O	1.639134	1.639134	0.000000
15.	O	1.633002	-1.633002	0.000000	15.O	1.639134	-1.639134	0.000000
16.	O	0.000000	0.000000	-1.941740	16.O	0.000000	0.000000	-1.946391
17.	W	0.000000	0.000000	-4.282218	17.W	0.000000	0.000000	-4.295628
18.	W	1.656650	1.656650	-1.913840	18.W	1.658788	1.658788	-1.912779
19.	W	-1.656650	1.656650	-1.913840	19.W	-1.658788	1.658788	-1.912779
20.	W	-1.656650	-1.656650	-1.913840	20.W	-1.658788	-1.658788	-1.912779
21.	W	1.656650	-1.656650	-1.913840	21.W	1.658788	-1.658788	-1.912779
22.	O	0.000000	0.000000	6.028976	22.O	0.000000	0.000000	6.053498
23.	O	-2.871985	-2.871985	2.156078	23.O	-2.879171	-2.879171	2.159553
24.	O	2.871985	-2.871985	2.156078	24.O	2.879171	-2.879171	2.159553
25.	O	2.871985	2.871985	2.156078	25.O	2.879171	2.879171	2.159553
26.	O	-2.871985	2.871985	2.156078	26.O	-2.879171	2.879171	2.159553
27.	O	-1.326641	-1.326641	3.822796	27.O	-1.326672	-1.326672	3.843888
28.	O	1.326641	-1.326641	3.822796	28.O	1.326672	-1.326672	3.843888
29.	O	1.326641	1.326641	3.822796	29.O	1.326672	1.326672	3.843888
30.	O	-1.326641	1.326641	3.822796	30.O	-1.326672	1.326672	3.843888
31.	O	0.000000	-2.658106	1.895747	31.O	0.000000	-2.655302	1.909187
32.	O	2.658106	0.000000	1.895747	32.O	2.655302	0.000000	1.909187
33.	O	0.000000	2.658106	1.895747	33.O	0.000000	2.655302	1.909187
34.	O	-2.658106	0.000000	1.895747	34.O	-2.655302	0.000000	1.909187
35.	O	-1.633002	-1.633002	0.000000	35.O	-1.639134	-1.639134	0.000000
36.	O	-1.633002	1.633002	0.000000	36.O	-1.639134	1.639134	0.000000
37.	O	0.000000	0.000000	1.941740	37.O	0.000000	0.000000	1.946391
38.	W	0.000000	0.000000	4.282218	38.W	0.000000	0.000000	4.295628
39.	W	-1.656650	-1.656650	1.913840	39.W	-1.658788	-1.658788	1.912779
40.	W	1.656650	-1.656650	1.913840	40.W	1.658788	-1.658788	1.912779
41.	W	1.656650	1.656650	1.913840	41.W	1.658788	1.658788	1.912779
42.	W	-1.656650	1.656650	1.913840	42.W	-1.658788	1.658788	1.912779

O_1 $[HW_{10}O_{32}]^{4-}$ - C_s symmetry				O_2 $[HW_{10}O_{32}]^{4-}$ - C_s symmetry			
1.O	0.000000	-6.063745	-0.102530	1.O	6.058843	-0.035404	0.000000
2.O	-4.036591	-2.141835	0.022516	2.O	2.184863	0.018976	4.046719
3.O	0.000000	-2.270028	4.094466	3.O	2.259477	4.039391	0.000000
4.O	4.036591	-2.141835	0.022516	4.O	2.184863	0.018976	-4.046719
5.O	0.000000	-2.117218	-4.081532	5.O	2.114005	-4.114253	0.000000
6.O	-1.849565	-3.845824	0.023595	6.O	3.871367	0.005124	1.848884
7.O	0.000000	-3.957089	1.907698	7.O	3.934114	1.932086	0.000000
8.O	1.849565	-3.845824	0.023595	8.O	3.871367	0.005124	-1.848884
9.O	0.000000	-3.852649	-1.909676	9.O	3.876839	-1.948976	0.000000
10.O	-1.845784	-1.939514	1.909875	10.O	1.916292	1.908761	1.873867
11.O	1.845784	-1.939514	1.909875	11.O	1.916292	1.908761	-1.873867
12.O	1.859683	-1.916646	-1.852032	12.O	1.929510	-1.847968	-1.830010
13.O	-1.859683	-1.916646	-1.852032	13.O	1.929510	-1.847968	1.830010
14.O	-2.250403	0.000000	0.042034	14.O	0.033344	0.019784	2.247358
15.O	0.000000	0.000000	-2.285189	15.O	0.004856	-2.314209	0.000000
16.O	0.000000	-1.954425	0.066303	16.O	2.053420	0.143404	0.000000
17.W	0.000000	-4.321975	-0.084160	17.W	4.317163	-0.141557	0.000000
18.W	-2.320122	-1.907799	0.017424	18.W	1.937143	0.033036	2.332701
19.W	0.000000	-2.142761	2.358846	19.W	1.810513	2.358906	0.000000
20.W	2.320122	-1.907799	0.017424	20.W	1.937143	0.033036	-2.332701
21.W	0.000000	-1.896634	-2.366516	21.W	1.872852	-2.402934	0.000000
22.O	0.000000	6.063745	-0.102530	22.O	-6.027534	-0.028548	0.000000
23.O	4.036591	2.141835	0.022516	23.O	-2.099213	0.014950	-4.034257
24.O	0.000000	2.117218	-4.081532	24.O	-2.145622	-4.075861	0.000000
25.O	-4.036591	2.141835	0.022516	25.O	-2.099213	0.014950	4.034257
26.O	0.000000	2.270028	4.094466	26.O	-2.236097	4.107814	0.000000
27.O	1.849565	3.845824	0.023595	27.O	-3.815469	0.003402	-1.861642
28.O	0.000000	3.852649	-1.909676	28.O	-3.836795	-1.893790	0.000000
29.O	-1.849565	3.845824	0.023595	29.O	-3.815469	0.003402	1.861642
30.O	0.000000	3.957089	1.907698	30.O	-3.872119	1.889890	0.000000
31.O	1.859683	1.916646	-1.852032	31.O	-1.891269	-1.868347	-1.862551
32.O	-1.859683	1.916646	-1.852032	32.O	-1.891269	-1.868347	1.862551
33.O	-1.845784	1.939514	1.909875	33.O	-1.912283	1.899224	1.857838
34.O	1.845784	1.939514	1.909875	34.O	-1.912283	1.899224	-1.857838
35.O	2.250403	0.000000	0.042034	35.O	0.033344	0.019784	-2.247358
36.O	0.000000	0.000000	2.641737	36.O	-0.033027	2.415190	0.000000
37.O	0.000000	1.954425	0.066303	37.O	-1.934374	0.015757	0.000000
38.W	0.000000	4.321975	-0.084160	38.W	-4.283503	-0.015410	0.000000
39.W	2.320122	1.907799	0.017424	39.W	-1.882992	0.014287	-2.314383
40.W	0.000000	1.896634	-2.366516	40.W	-1.937115	-2.356013	0.000000
41.W	-2.320122	1.907799	0.017424	41.W	-1.882992	0.014287	2.314383
42.W	0.000000	2.142761	2.358846	42.W	-2.003204	2.390954	0.000000
43.H	0.000000	0.000000	3.615149	43.H	4.593138	2.636243	0.000000

O_3 'up' $[HW_{10}O_{32}]^{4-}$ - C_s symmetry			
1.O	5.995173	0.149431	0.000000
2.O	2.072115	2.806404	2.965817
3.O	2.072115	2.806404	-2.965817
4.O	2.201900	-2.914331	-2.851615
5.O	2.201900	-2.914331	2.851615
6.O	3.773026	1.440945	1.319545
7.O	3.773026	1.440945	-1.319545
8.O	3.841562	-1.226351	-1.331325
9.O	3.841562	-1.226351	1.331325
10.O	1.921276	2.826587	0.000000
11.O	1.905422	-0.019534	-2.720162
12.O	1.979928	-2.652605	0.000000
13.O	1.905422	-0.019534	2.720162
14.O	0.008776	1.630940	1.549264
15.O	0.048628	-1.624468	1.614426
16.O	1.928829	0.083180	0.000000
17.W	4.251938	0.091462	0.000000
18.W	1.857532	1.583494	1.755775
19.W	1.857532	1.583494	-1.755775
20.W	1.942270	-1.689771	-1.659975
21.W	1.942270	-1.689771	1.659975
22.O	-6.012011	-0.042753	0.000000
23.O	-2.097868	-2.857515	-2.875526
24.O	-2.097868	-2.857515	2.875526
25.O	-2.130904	2.879589	2.873507
26.O	-2.130904	2.879589	-2.873507
27.O	-3.811221	-1.319585	-1.339714
28.O	-3.811221	-1.319585	1.339714
29.O	-3.832881	1.335182	1.322082
30.O	-3.832881	1.335182	-1.322082
31.O	-1.879685	-2.634858	0.000000
32.O	-1.868696	0.023920	2.638778
33.O	-1.916109	2.677871	0.000000
34.O	-1.868696	0.023920	-2.638778
35.O	0.048628	-1.624468	-1.614426
36.O	0.008776	1.630940	-1.549264
37.O	-1.936703	0.011165	0.000000
38.W	-4.267959	-0.042214	0.000000
39.W	-1.869585	-1.647950	-1.656784
40.W	-1.869585	-1.647950	1.656784
41.W	-1.954557	1.669158	1.645364
42.W	-1.954557	1.669158	-1.645364
43.H	2.862146	3.094733	0.000000

O_3 'down' $[HW_{10}O_{32}]^{4-}$ - C_s symmetry			
1.O	5.987808	0.116687	0.000000
2.O	2.102454	2.792207	2.999731
3.O	2.102454	2.792207	-2.999731
4.O	2.181581	-2.918924	-2.844541
5.O	2.181581	-2.918924	2.844541
6.O	3.751347	1.433686	1.296601
7.O	3.751347	1.433686	-1.296601
8.O	3.852180	-1.242264	-1.347143
9.O	3.852180	-1.242264	1.347143
10.O	1.754974	2.779754	0.000000
11.O	1.915317	-0.030737	-2.725653
12.O	1.977258	-2.670188	0.000000
13.O	1.915317	-0.030737	2.725653
14.O	0.020465	1.621614	1.606692
15.O	0.028991	-1.628422	1.615781
16.O	1.938151	0.014757	0.000000
17.W	4.245646	0.031129	0.000000
18.W	1.902916	1.580803	1.778111
19.W	1.902916	1.580803	-1.778111
20.W	1.914945	-1.694726	-1.652792
21.W	1.914945	-1.694726	1.652792
22.O	-6.011646	0.024465	0.000000
23.O	-2.131920	-2.845980	-2.871941
24.O	-2.131920	-2.845980	2.871941
25.O	-2.113347	2.900350	2.872572
26.O	-2.113347	2.900350	-2.872572
27.O	-3.827862	-1.285356	-1.337885
28.O	-3.827862	-1.285356	1.337885
29.O	-3.809652	1.371011	1.316629
30.O	-3.809652	1.371011	-1.316629
31.O	-1.907473	-2.624382	0.000000
32.O	-1.882530	0.032220	2.647334
33.O	-1.848145	2.687004	0.000000
34.O	-1.882530	0.032220	-2.647334
35.O	0.028991	-1.628422	-1.615781
36.O	0.020465	1.621614	-1.606692
37.O	-1.928259	0.017883	0.000000
38.W	-4.268111	0.003775	0.000000
39.W	-1.895859	-1.635690	-1.655649
40.W	-1.895859	-1.635690	1.655649
41.W	-1.925927	1.678281	1.657130
42.W	-1.925927	1.678281	-1.657130
43.H	0.800243	3.003108	0.000000

O_4 'up' $[HW_{10}O_{32}]^{4-}$ - C_s symmetry			
1.O	6.030191	-0.096207	0.000000
2.O	2.091432	-4.072612	0.000000
3.O	2.153323	0.018355	4.049079
4.O	2.268351	4.104465	0.000000
5.O	2.153323	0.018355	-4.049079
6.O	3.811344	-1.912645	0.000000
7.O	3.821775	0.007469	1.860315
8.O	3.891586	1.881179	0.000000
9.O	3.821775	0.007469	-1.860315
10.O	1.881635	-1.863441	1.867009
11.O	1.903545	1.898173	1.851577
12.O	1.903545	1.898173	-1.851577
13.O	1.881635	-1.863441	-1.867009
14.O	-0.055264	-2.324803	0.000000
15.O	-0.023368	0.006785	-2.342012
16.O	1.923247	0.020479	0.000000
17.W	4.282826	-0.077087	0.000000
18.W	1.853225	-2.354077	0.000000
19.W	1.892395	0.010676	2.332389
20.W	2.061410	2.380677	0.000000
21.W	1.892395	0.010676	-2.332389
22.O	-6.056957	0.096877	0.000000
23.O	-2.311842	4.033229	0.000000
24.O	-2.181358	-0.038925	-4.128674
25.O	-2.237281	-4.097594	0.000000
26.O	-2.181358	-0.038925	4.128674
27.O	-3.858485	1.957839	0.000000
28.O	-3.821801	0.056068	-1.866291
29.O	-3.810992	-1.769542	0.000000
30.O	-3.821801	0.056068	1.866291
31.O	-1.864756	1.872520	-1.904049
32.O	-1.930300	-1.844774	-1.854208
33.O	-1.930300	-1.844774	1.854208
34.O	-1.864756	1.872520	1.904049
35.O	0.016292	2.494075	0.000000
36.O	-0.023368	0.006785	2.342012
37.O	-1.875432	0.198645	0.000000
38.W	-4.314075	0.123736	0.000000
39.W	-1.770799	2.164199	0.000000
40.W	-1.929441	-0.003169	-2.414744
41.W	-1.968011	-2.388954	0.000000
42.W	-1.929441	-0.003169	2.414744
43.H	-3.288252	4.010015	0.000000

O_4 'down' $[HW_{10}O_{32}]^{4-}$ - C_s symmetry			
1.O	6.025281	0.006186	0.000000
2.O	2.143520	-4.038802	0.000000
3.O	2.162785	0.037871	4.062361
4.O	2.114266	4.117819	0.000000
5.O	2.162785	0.037871	-4.062361
6.O	3.834981	-1.851928	0.000000
7.O	3.821757	0.058357	1.864446
8.O	3.845022	1.937185	0.000000
9.O	3.821757	0.058357	-1.864446
10.O	1.907458	-1.839329	1.869887
11.O	1.874732	1.912051	1.863873
12.O	1.874732	1.912051	-1.863873
13.O	1.907458	-1.839329	-1.869887
14.O	-0.025641	-2.311817	0.000000
15.O	-0.021371	-0.002289	-2.362630
16.O	1.921681	0.045033	0.000000
17.W	4.278122	-0.003377	0.000000
18.W	1.890235	-2.322642	0.000000
19.W	1.899270	0.031015	2.346483
20.W	1.988170	2.381284	0.000000
21.W	1.899270	0.031015	-2.346483
22.O	-6.043214	0.041086	0.000000
23.O	-2.139230	4.072420	0.000000
24.O	-2.188214	-0.061826	-4.134546
25.O	-2.184855	-4.098036	0.000000
26.O	-2.188214	-0.061826	4.134546
27.O	-3.828350	1.941887	0.000000
28.O	-3.821578	0.031145	-1.862650
29.O	-3.808301	-1.805419	0.000000
30.O	-3.821578	0.031145	1.862650
31.O	-1.890516	1.843552	-1.907074
32.O	-1.921547	-1.866878	-1.863577
33.O	-1.921547	-1.866878	1.863577
34.O	-1.890516	1.843552	1.907074
35.O	-0.020339	2.376009	0.000000
36.O	-0.021371	-0.002289	2.362630
37.O	-1.869716	0.135290	0.000000
38.W	-4.301100	0.065223	0.000000
39.W	-1.846793	2.132058	0.000000
40.W	-1.922341	-0.026924	-2.422562
41.W	-1.929457	-2.387444	0.000000
42.W	-1.922341	-0.026924	2.422562
43.H	-1.270857	4.513694	0.000000

O_5 $[HW_{10}O_{32}]^{4-}$ - C_s symmetry

1.O	-4.256471	4.259036	0.000000
2.O	1.362631	4.392678	0.000000
3.O	-1.506976	1.505856	4.064593
4.O	-4.399662	-1.359485	0.000000
5.O	-1.506976	1.505856	-4.064593
6.O	-1.376345	4.036580	0.000000
7.O	-2.703490	2.703641	1.877149
8.O	-4.037876	1.378921	0.000000
9.O	-2.703490	2.703641	-1.877149
10.O	-0.011052	2.661254	1.871907
11.O	-2.664298	0.010908	1.871449
12.O	-2.664298	0.010908	-1.871449
13.O	-0.011052	2.661254	-1.871907
14.O	1.662320	1.631489	0.000000
15.O	0.015488	-0.017851	-2.308410
16.O	-1.365314	1.363886	0.000000
17.W	-3.020941	3.022228	0.000000
18.W	0.304914	3.015728	0.000000
19.W	-1.350503	1.349057	2.342170
20.W	-3.021142	-0.303917	0.000000
21.W	-1.350503	1.349057	-2.342170
22.O	4.417086	-4.314021	0.000000
23.O	-1.314923	-4.439099	0.000000
24.O	1.548427	-1.546020	-4.076535
25.O	4.439572	1.321286	0.000000
26.O	1.548427	-1.546020	4.076535
27.O	1.441055	-4.049692	0.000000
28.O	2.729959	-2.728879	-1.858949
29.O	4.044735	-1.427429	0.000000
30.O	2.729959	-2.728879	1.858949
31.O	0.042037	-2.686167	-1.866304
32.O	2.684828	-0.040172	-1.867159
33.O	2.684828	-0.040172	1.867159
34.O	0.042037	-2.686167	1.866304
35.O	-1.638653	-1.666117	0.000000
36.O	0.015488	-0.017851	2.308410
37.O	1.448250	-1.451485	0.000000
38.W	2.990373	-2.997529	0.000000
39.W	-0.330136	-3.011173	0.000000
40.W	1.350349	-1.348970	-2.364270
41.W	3.017540	0.327983	0.000000
42.W	1.350349	-1.348970	2.364270
43.H	5.309885	-3.931481	0.000000

$[W_{10}O_{32}]^{6-}$ - D_{4h} symmetry

1.O	0.000000	0.000000	-6.071529
2.O	2.888297	2.888297	-2.164991
3.O	-2.888297	2.888297	-2.164991
4.O	-2.888297	-2.888297	-2.164991
5.O	2.888297	-2.888297	-2.164991
6.O	1.327691	1.327691	-3.863289
7.O	-1.327691	1.327691	-3.863289
8.O	-1.327691	-1.327691	-3.863289
9.O	1.327691	-1.327691	-3.863289
10.O	0.000000	2.651337	-1.915879
11.O	-2.651337	0.000000	-1.915879
12.O	0.000000	-2.651337	-1.915879
13.O	2.651337	0.000000	-1.915879
14.O	1.649356	1.649356	0.000000
15.O	1.649356	-1.649356	0.000000
16.O	0.000000	0.000000	-1.953097
17.W	0.000000	0.000000	-4.301847
18.W	1.662620	1.662620	-1.911742
19.W	-1.662620	1.662620	-1.911742
20.W	-1.662620	-1.662620	-1.911742
21.W	1.662620	-1.662620	-1.911742
22.O	0.000000	0.000000	6.071529
23.O	-2.888297	-2.888297	2.164991
24.O	2.888297	-2.888297	2.164991
25.O	2.888297	2.888297	2.164991
26.O	-2.888297	2.888297	2.164991
27.O	-1.327691	-1.327691	3.863289
28.O	1.327691	-1.327691	3.863289
29.O	1.327691	1.327691	3.863289
30.O	-1.327691	1.327691	3.863289
31.O	0.000000	-2.651337	1.915879
32.O	2.651337	0.000000	1.915879
33.O	0.000000	2.651337	1.915879
34.O	-2.651337	0.000000	1.915879
35.O	-1.649356	-1.649356	0.000000
36.O	-1.649356	1.649356	0.000000
37.O	0.000000	0.000000	1.953097
38.W	0.000000	0.000000	4.301847
39.W	-1.662620	-1.662620	1.911742
40.W	1.662620	-1.662620	1.911742
41.W	1.662620	1.662620	1.911742
42.W	-1.662620	1.662620	1.911742

3. CALCULATED SPECTRA

All calculations have been carried out at the PBE0/TZP (Frozen Core basis set) level, including the solvation effects (COSMO model, solvent acetonitrile) and the solvent response (CSMRSP option). Relativistic effects were included by means of the ZORA approximation at the Scalar Level (ZSC). Mono-reduced species (either protonated or not) have been treated using the spin-unrestricted formalism. The calculations were carried out only on the allowed transitions, using the Davidson algorithm. The output provided the energy of the transition (E) in eV and oscillator strengths (f). The first parameter was then converted to wavelength by means of the relationship λ [nm] = 1240.82/E [eV].

The given f values have been multiplied by the degree of degeneracy of the irreducible representation to which the transition belongs, as recommended in the ADF documentation.[4]

3.1 CALCULATED SPECTRUM OF $[W_{10}O_{32}]^{4-}$

Table S2. $[W_{10}O_{32}]^{4-}$ 30 lowest allowed transitions (ZSC-COSMO-PBE0/TZP-FC level).

Transition	Transition energy [eV]	Transition energy [nm]	Calculated *f*	Symmetry block	Real *f*
1	3.60655	344.047	2.07E-03	E_u	4.13E-03
2	3.77609	328.600	3.62E-01	A_{2u}	3.62E-01
3	3.84213	322.952	1.74E-02	E_u	3.48E-02
4	4.29935	288.607	2.10E-03	E_u	4.20E-03
5	4.50484	275.442	1.09E-03	E_u	2.19E-03
6	4.56309	271.926	6.92E-02	A_{2u}	6.92E-02
7	4.59525	270.023	2.74E-02	E_u	5.49E-02
8	4.73783	261.897	2.05E-02	A_{2u}	2.05E-02
9	4.86261	255.177	3.45E-02	E_u	6.91E-02
10	4.91589	252.411	2.22E-02	E_u	4.43E-02
11	4.96919	249.703	8.65E-04	A_{2u}	8.65E-04
12	5.06823	244.824	1.80E-03	A_{2u}	1.80E-03
13	5.08116	244.201	3.13E-05	E_u	6.26E-05
14	5.17402	239.818	1.23E-01	A_{2u}	1.23E-01
15	5.18692	239.222	5.00E-05	E_u	9.99E-05
16	5.19660	238.776	1.48E-02	E_u	2.96E-02
17	5.21788	237.802	4.09E-04	E_u	8.17E-04
18	5.23655	236.954	6.43E-03	E_u	1.29E-02
19	5.24877	236.403	1.51E-05	A_{2u}	1.51E-05
20	5.27270	235.330	8.22E-04	E_u	1.64E-03
21	5.29120	234.507	1.47E-02	E_u	2.94E-02
22	5.30384	233.948	1.03E-02	A_{2u}	1.03E-02
23	5.33046	232.780	7.11E-03	E_u	1.42E-02
24	5.33781	232.459	9.34E-04	E_u	1.87E-03
25	5.34572	232.115	5.42E-04	A_{2u}	5.42E-04
26	5.35634	231.655	1.25E-02	A_{2u}	1.25E-02
27	5.36740	231.178	3.63E-03	E_u	7.26E-03
28	5.48596	226.182	3.12E-02	A_{2u}	3.12E-02
29	5.51801	224.868	1.31E-01	A_{2u}	1.31E-01
30	5.68307	218.337	4.76E-01	A_{2u}	4.76E-01

3.2 CALCULATED SPECTRUM OF $[W_{10}O_{32}]^{5-}$

Table S3. $[W_{10}O_{32}]^{5-}$ 30 lowest allowed transitions (ZSC-COSMO-PBE0/TZP-FC level).

Transition	Transition energy [eV]	Transition energy [nm]	Calculated *f*	Symmetry block	Real *f*
1	0.93366	1328.989	3.07E-02	E_u	6.15E-02
2	1.65156	751.304	7.37E-04	E_u	1.47E-03
3	1.66474	745.356	1.47E-01	A_{2u}	1.47E-01
4	1.88440	658.472	1.21E-02	A_{2u}	1.21E-02
5	2.72045	456.110	9.06E-06	E_u	1.81E-05
6	3.12491	397.075	2.17E-04	E_u	4.34E-04
7	3.47884	356.678	8.82E-02	A_{2u}	8.82E-02
8	3.57581	347.005	5.80E-04	E_u	1.16E-03
9	3.90855	317.464	5.95E-05	E_u	1.19E-04
10	3.93108	315.645	9.73E-03	A_{2u}	9.73E-03
11	4.15767	298.442	1.23E-02	E_u	2.46E-02
12	4.23495	292.996	1.50E-03	E_u	3.00E-03
13	4.28962	289.262	4.23E-02	A_{2u}	4.23E-02
14	4.45728	278.381	1.70E-04	E_u	3.40E-04
15	4.47587	277.225	3.86E-03	A_{2u}	3.86E-03
16	4.63119	267.928	2.81E-03	E_u	5.61E-03
17	4.63687	267.599	1.43E-02	E_u	2.85E-02
18	4.64415	267.180	1.25E-03	E_u	2.50E-03
19	4.66879	265.770	1.41E-03	A_{2u}	1.41E-03
20	4.66879	265.770	1.17E-02	E_u	2.34E-02
21	4.68531	264.833	8.13E-05	E_u	1.63E-04
22	4.71879	262.954	4.08E-03	A_{2u}	4.08E-03
23	4.78426	259.355	3.32E-02	A_{2u}	3.32E-02
24	4.82136	257.360	3.31E-02	A_{2u}	3.31E-02
25	4.94655	250.846	4.50E-03	A_{2u}	4.50E-03
26	5.06315	245.070	2.58E-03	A_{2u}	2.58E-03
27	5.09567	243.506	3.17E-04	A_{2u}	3.17E-04
28	5.10338	243.138	5.87E-04	A_{2u}	5.87E-04
29	5.12493	242.115	4.82E-02	A_{2u}	4.82E-02
30	5.14314	241.258	7.89E-03	A_{2u}	7.89E-03

3.3 CALCULATED SPECTRUM OF O_2 $[HW_{10}O_{32}]^{4-}$

Table S4. O_2 $[HW_{10}O_{32}]^{4-}$ 30 lowest allowed transitions (ZSC-COSMO-PBE0/TZP-FC level).

Transition	Transition energy [eV]	Transition energy [nm]	Calculated *f*	Symmetry block	Real *f*
1	0.99545	1246.496	3.36E-02	*A″*	3.36E-02
2	1.04227	1190.501	3.26E-02	*A′*	3.26E-02
3	1.56434	793.193	7.30E-02	*A′*	7.30E-02
4	1.69213	733.291	4.24E-02	*A′*	4.24E-02
5	1.75891	705.451	1.32E-03	*A″*	1.32E-03
6	1.83450	676.383	3.11E-02	*A′*	3.11E-02
7	1.91054	649.462	2.60E-03	*A′*	2.60E-03
8	1.92632	644.142	1.49E-04	*A″*	1.49E-04
9	2.02524	612.680	1.62E-02	*A′*	1.62E-02
10	2.16205	573.911	1.17E-03	*A′*	1.17E-03
11	2.16848	572.209	1.16E-05	*A″*	1.16E-05
12	2.27638	545.086	3.98E-05	*A″*	3.98E-05
13	2.33570	531.243	8.94E-04	*A′*	8.94E-04
14	2.49806	496.715	2.30E-04	*A″*	2.30E-04
15	2.69586	460.270	7.38E-05	*A′*	7.38E-05
16	2.70505	458.706	3.82E-05	*A″*	3.82E-05
17	2.75466	450.445	1.38E-07	*A″*	1.38E-07
18	2.83464	437.736	1.35E-04	*A″*	1.35E-04
19	2.85278	434.953	3.46E-06	*A′*	3.46E-06
20	2.88584	429.970	1.78E-04	*A′*	1.78E-04
21	2.90421	427.250	4.78E-04	*A″*	4.78E-04
22	2.95762	419.535	4.07E-05	*A″*	4.07E-05
23	3.05353	406.357	2.09E-05	*A′*	2.09E-05
24	3.32460	373.225	3.63E-05	*A″*	3.63E-05
25	3.38081	367.020	2.81E-05	*A′*	2.81E-05
26	3.50008	354.513	2.45E-04	*A″*	2.45E-04
27	3.51480	353.028	2.00E-04	*A′*	2.00E-04
28	3.52985	351.523	7.98E-07	*A″*	7.98E-07
29	3.57293	347.285	2.10E-02	*A′*	2.10E-02
30	3.60521	344.175	5.02E-02	*A′*	5.02E-02

3.4 CALCULATED SPECTRUM OF O_4 'UP' $[HW_{10}O_{32}]^{4-}$

Table S5. O_4 'up' $[HW_{10}O_{32}]^{4-}$ 30 lowest allowed transitions (ZSC-COSMO-PBE0/TZP-FC level).

Transition	Transition energy [eV]	Transition energy [nm]	Calculated *f*	Symmetry block	Real *f*
1	0.83607	1484.115	2.23E-02	*A″*	2.23E-02
2	0.95340	1301.473	2.85E-02	*A′*	2.85E-02
3	1.00656	1232.737	1.80E-03	*A′*	1.80E-03
4	1.03306	1201.115	8.82E-03	*A″*	8.82E-03
5	1.47566	840.860	6.06E-03	*A′*	6.06E-03
6	1.59938	775.816	1.03E-01	*A′*	1.03E-01
7	1.65490	749.788	4.43E-02	*A′*	4.43E-02
8	1.74801	709.849	5.25E-03	*A′*	5.25E-03
9	1.89077	656.253	3.16E-04	*A″*	3.16E-04
10	1.99711	621.310	2.35E-04	*A′*	2.35E-04
11	2.03520	609.682	1.58E-06	*A″*	1.58E-06
12	2.13405	581.441	2.48E-03	*A′*	2.48E-03
13	2.16634	572.774	1.38E-06	*A″*	1.38E-06
14	2.28645	542.686	1.23E-03	*A′*	1.23E-03
15	2.41271	514.286	8.29E-06	*A″*	8.29E-06
16	2.52507	491.402	1.91E-05	*A″*	1.91E-05
17	2.56814	483.161	6.09E-05	*A′*	6.09E-05
18	2.68985	461.299	4.97E-05	*A″*	4.97E-05
19	2.78541	445.473	5.65E-04	*A′*	5.65E-04
20	2.79179	444.455	1.93E-05	*A″*	1.93E-05
21	2.82915	438.585	3.98E-06	*A″*	3.98E-06
22	2.90322	427.396	1.25E-04	*A′*	1.25E-04
23	3.12765	396.727	2.09E-04	*A″*	2.09E-04
24	3.26139	380.459	1.07E-04	*A″*	1.07E-04
25	3.30337	375.624	2.12E-04	*A′*	2.12E-04
26	3.42445	362.343	1.05E-04	*A″*	1.05E-04
27	3.43579	361.147	3.08E-05	*A′*	3.08E-05
28	3.45278	359.370	9.57E-04	*A′*	9.57E-04
29	3.54448	350.072	7.50E-02	*A′*	7.50E-02
30	3.61603	343.145	9.21E-05	*A″*	9.21E-05

3.5 CALCULATED SPECTRUM OF O_5 $[HW_{10}O_{32}]^{4-}$

Table S6. O_5 $[HW_{10}O_{32}]^{4-}$ 30 lowest allowed transitions (ZSC-COSMO-PBE0/TZP-FC level).

Transition	Transition energy [eV]	Transition energy [nm]	Calculated *f*	Symmetry block	Real *f*
1	0.91334	1358.556	2.38E-02	A″	2.38E-02
2	0.95110	1304.620	2.93E-02	A′	2.93E-02
3	1.22803	1010.418	8.51E-03	A″	8.51E-03
4	1.42017	873.715	3.09E-03	A′	3.09E-03
5	1.56655	792.074	3.76E-04	A′	3.76E-04
6	1.69401	732.477	1.41E-01	A′	1.41E-01
7	1.71564	723.243	3.73E-03	A′	3.73E-03
8	1.95950	633.235	1.08E-04	A″	1.08E-04
9	1.96698	630.827	1.21E-02	A′	1.21E-02
10	1.98541	624.971	1.67E-04	A″	1.67E-04
11	2.06494	600.901	1.26E-06	A″	1.26E-06
12	2.07226	598.778	1.43E-04	A′	1.43E-04
13	2.08662	594.657	8.24E-04	A′	8.24E-04
14	2.26789	547.127	4.66E-06	A″	4.66E-06
15	2.27066	546.460	1.43E-05	A′	1.43E-05
16	2.69759	459.975	2.80E-07	A″	2.80E-07
17	2.74368	452.248	2.01E-08	A″	2.01E-08
18	2.76156	449.320	2.64E-06	A″	2.64E-06
19	2.77264	447.524	4.28E-08	A′	4.28E-08
20	2.83794	437.227	1.11E-05	A′	1.11E-05
21	2.89587	428.481	9.74E-05	A″	9.74E-05
22	2.90723	426.806	4.39E-05	A′	4.39E-05
23	2.95498	419.909	9.46E-05	A″	9.46E-05
24	2.99708	414.011	1.01E-04	A′	1.01E-04
25	3.32587	373.083	3.98E-05	A″	3.98E-05
26	3.35440	369.909	5.21E-05	A′	5.21E-05
27	3.37924	367.190	1.27E-05	A″	1.27E-05
28	3.52827	351.681	1.36E-03	A′	1.36E-03
29	3.53606	350.906	3.49E-04	A″	3.49E-04
30	3.54354	350.165	8.20E-02	A′	8.20E-02

3.6 CALCULATED SPECTRUM OF $[W_{10}O_{32}]^{6-}$

Table S7. $[W_{10}O_{32}]^{6-}$ 30 lowest allowed transitions (ZSC-COSMO-PBE0/TZP-FC level).

Transition	Transition energy [eV]	Transition energy [nm]	Calculated *f*	Symmetry block	Real *f*
1	1.24285	998.370	5.64E-02	E_u	1.13E-01
2	1.50045	826.968	1.13E-02	E_u	2.27E-02
3	1.71372	724.053	4.62E-03	A_{2u}	4.62E-03
4	2.12323	584.404	4.15E-01	A_{2u}	4.15E-01
5	2.57055	482.708	1.95E-04	E_u	3.90E-04
6	2.86865	432.546	4.92E-04	E_u	9.85E-04
7	3.96172	313.203	5.26E-04	E_u	1.05E-03
8	4.36559	284.228	2.70E-03	E_u	5.40E-03
9	4.50450	275.463	4.52E-02	A_{2u}	4.52E-02
10	4.61419	268.915	6.22E-02	A_{2u}	6.22E-02
11	4.71395	263.224	5.97E-02	E_u	1.19E-01
12	4.86651	254.972	2.67E-03	E_u	5.34E-03
13	4.97359	249.483	4.20E-03	A_{2u}	4.20E-03
14	4.99124	248.600	2.69E-03	E_u	5.38E-03
15	5.01930	247.211	3.20E-04	E_u	6.39E-04
16	5.05158	245.631	4.36E-02	A_{2u}	4.36E-02
17	5.07602	244.448	1.12E-02	E_u	2.24E-02
18	5.09174	243.694	1.63E-02	A_{2u}	1.63E-02
19	5.11958	242.368	1.78E-03	E_u	3.56E-03
20	5.18113	239.489	3.11E-02	E_u	6.21E-02
21	5.19001	239.079	4.85E-02	A_{2u}	4.85E-02
22	5.19498	238.851	1.98E-02	E_u	3.96E-02
23	5.26123	235.843	4.65E-02	A_{2u}	4.65E-02
24	5.26346	235.743	7.18E-03	E_u	1.44E-02
25	5.26779	235.549	6.78E-03	E_u	1.36E-02
26	5.29051	234.538	3.44E-02	E_u	6.88E-02
27	5.29592	234.298	7.83E-03	A_{2u}	7.83E-03
28	5.42068	228.906	8.15E-03	A_{2u}	8.15E-03
29	5.42487	228.729	2.91E-01	A_{2u}	2.91E-01
30	5.60551	221.358	2.44E-01	A_{2u}	2.44E-01

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