Supporting Information

Unraveling the mechanisms of O_2 activation by size-selected gold clusters: Transition from superoxo to peroxo chemisorption

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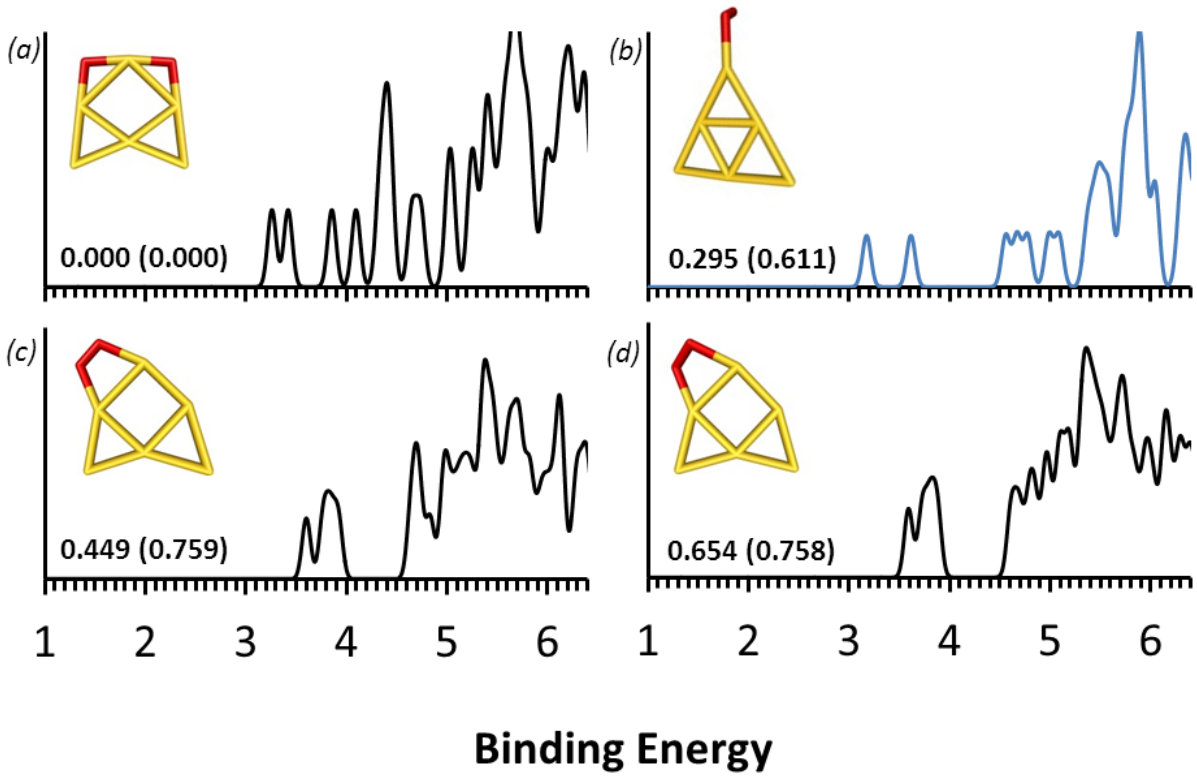


Figure S1. Computed photoelectron spectra and relative energies at the SO-PBE0 (TPSSh) level of theory for the four low-lying isomers of $O_2Au_6^-$.

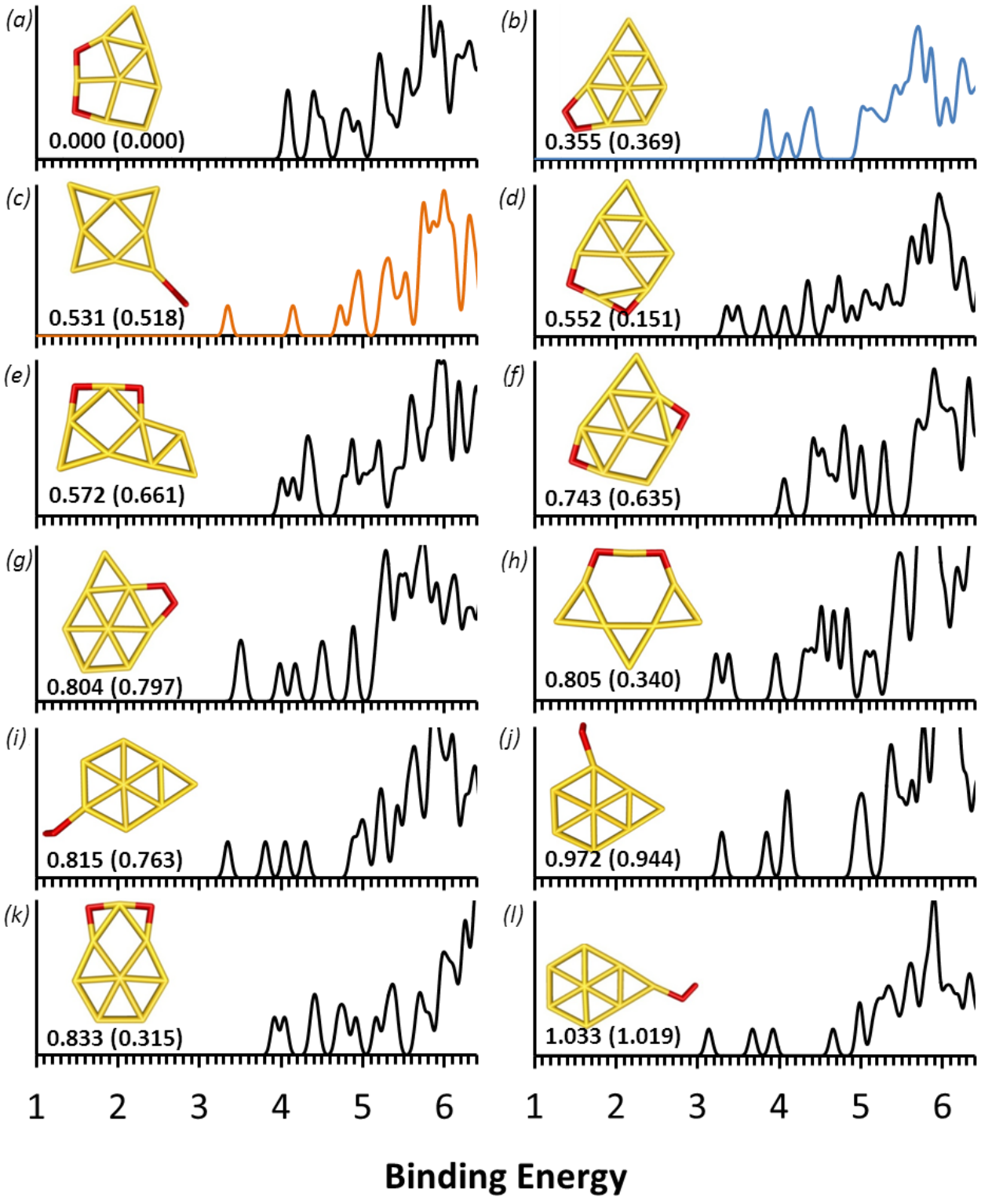


Figure S2. Computed photoelectron spectra and relative energies at the SO-PBE0 (TPSSh) level of theory for the twelve lowest-lying isomers of $O_2Au_8^-$. Colored curves are used to compare with the experimental spectra.

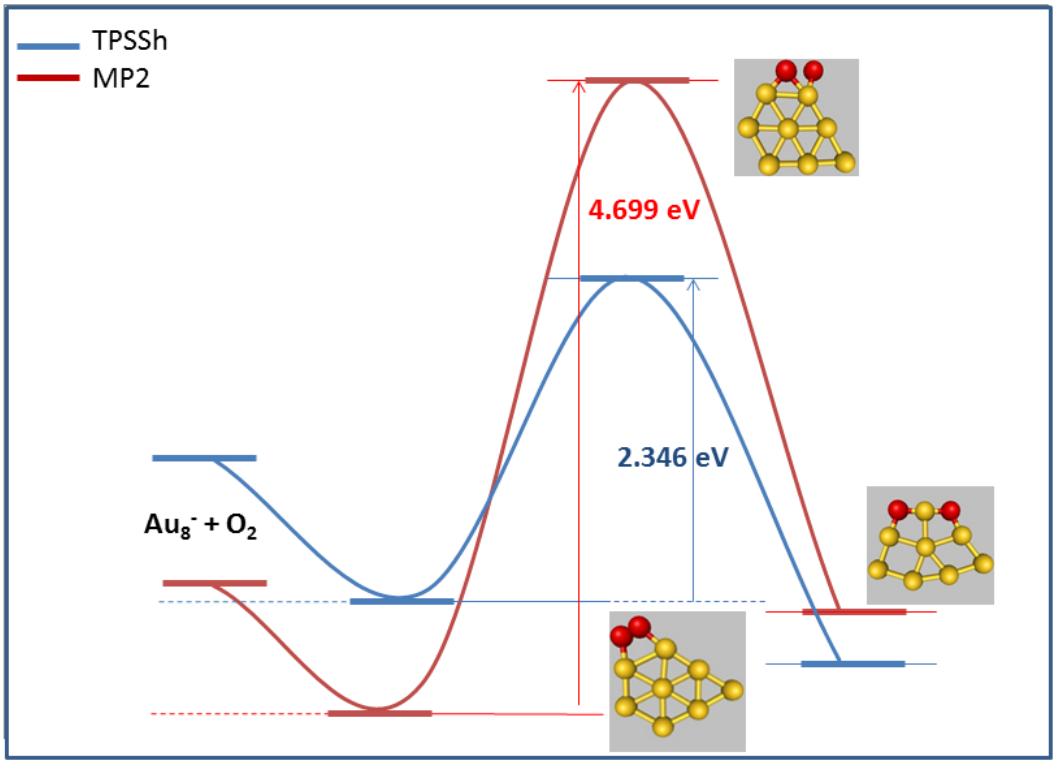


Figure S3. Theoretical reaction coordinate diagram illustrating the O_2 dissociation pathway and activation energies on Au_8^-. The reaction pathway is calculated at TPSSh (in blue) and MP2 (in red) levels of theory.

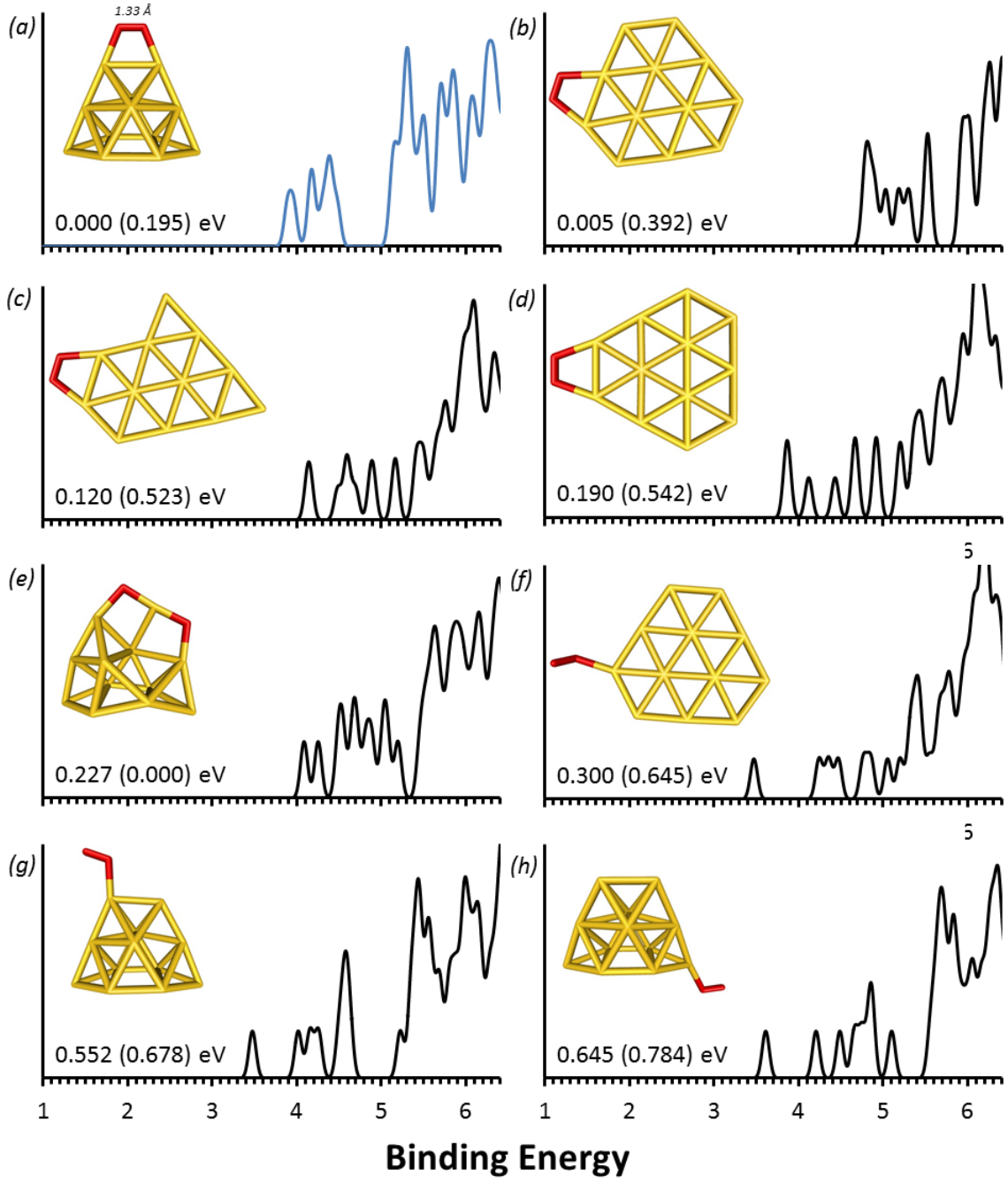


Figure S4. Computed photoelectron spectra and relative energies at the SO-PBE0 (TPSSh) level of theory for the eight low-lying isomers of $O_2Au_{12}^-$. The blue curve is used to compare with the experimental spectrum. The O-O bond length in the lowest-energy chemisorbed isomer is 1.33 Å.

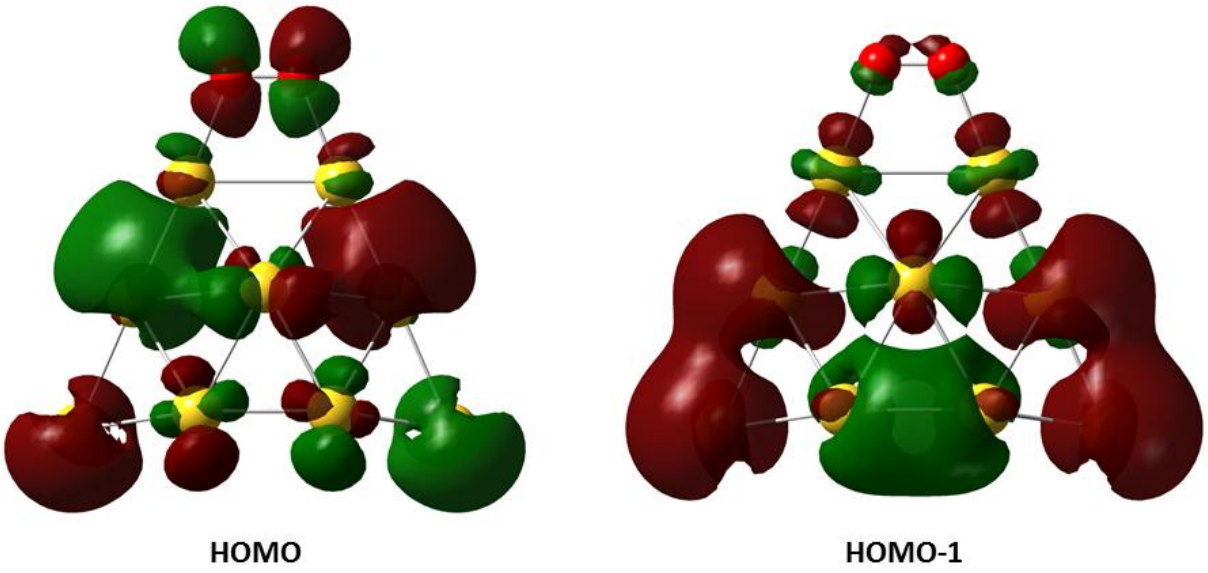


Figure S5. The HOMO and HOMO-1 of the lowest-energy molecularly chemisorbed isomer of $O_2Au_{12}^-$, showing major contributions from the Au skeleton for the two orbitals.

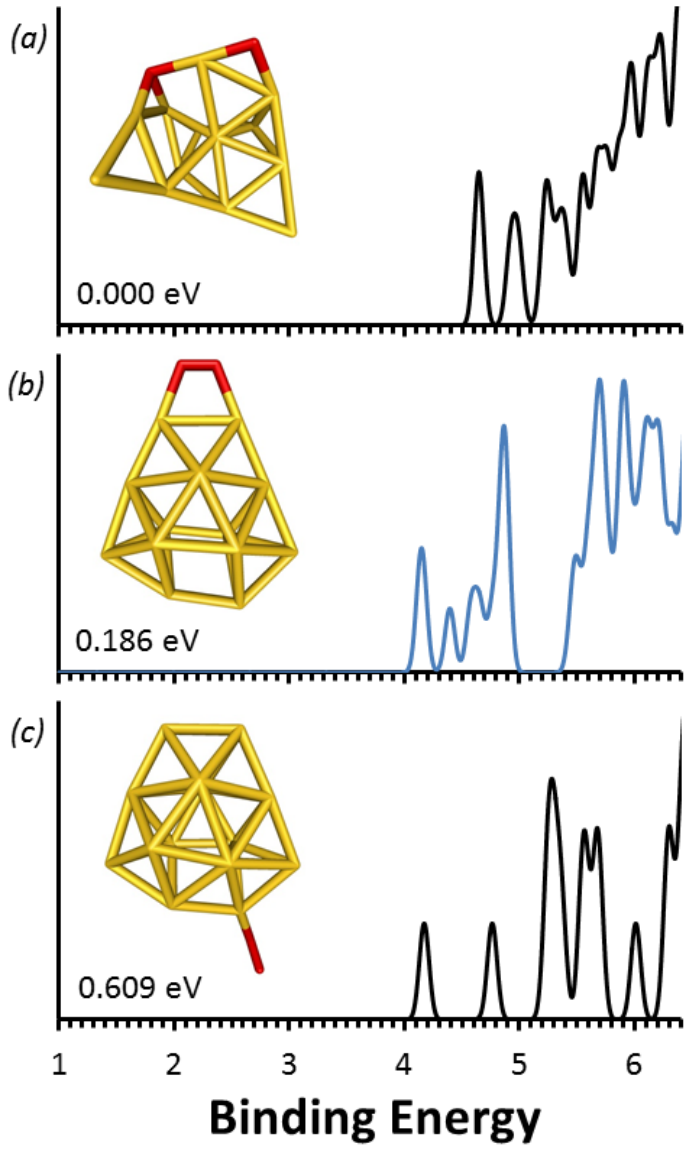


Figure S6. Computed photoelectron spectra and relative energies at the SO-PBE0 level of theory for the three low-lying isomers of $O_2Au_{14}^-$. The blue curve is used to compare with the experimental PES spectrum.

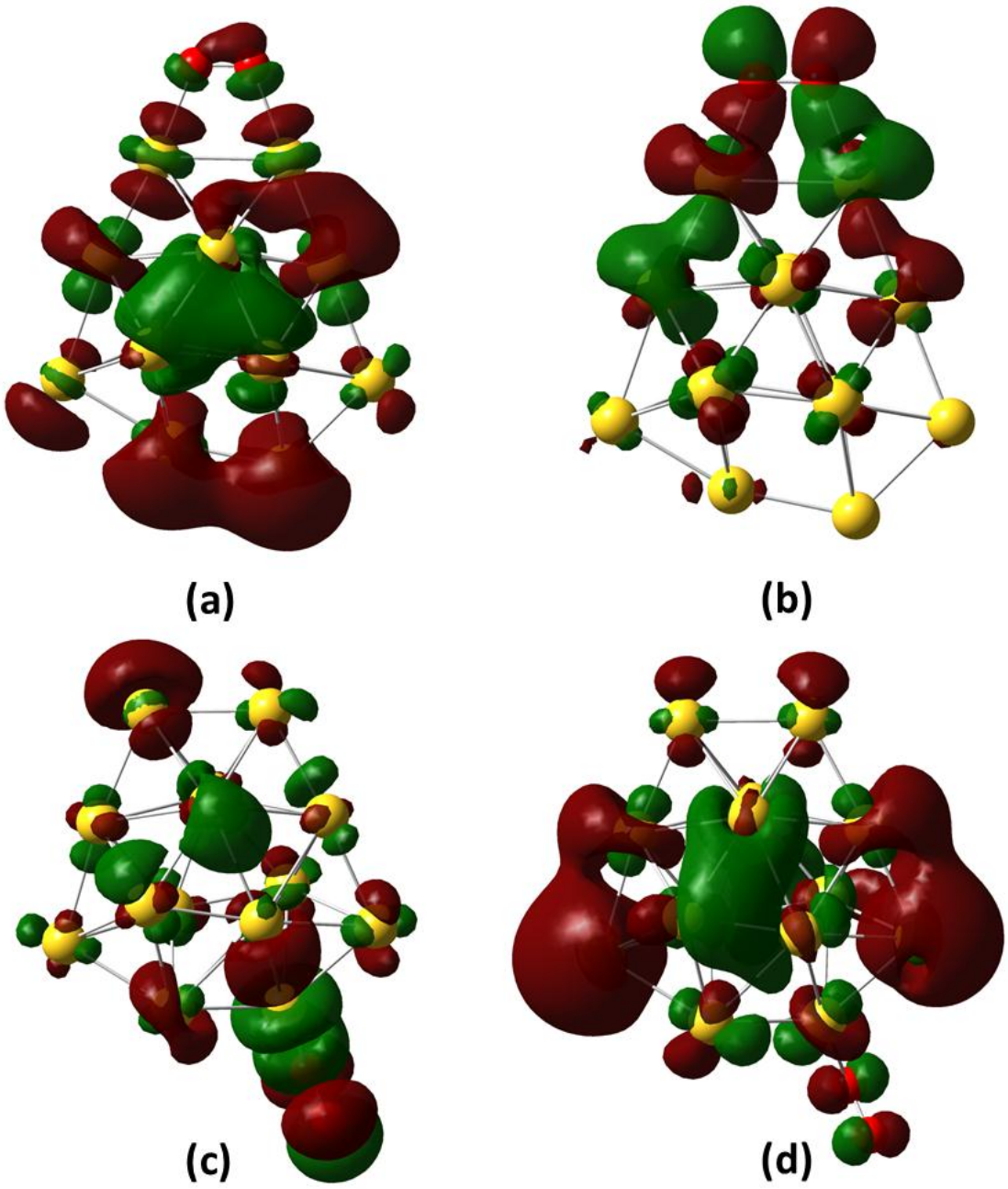


Figure S7. The HOMO and HOMO-1 of the peroxo [(a) and (b)] and superoxo [(c) and (d)] isomers of $O_2Au_{14}^-$. Note the HOMO of the superoxo isomer (c) is mainly from the π^* orbital of the superoxo unit.

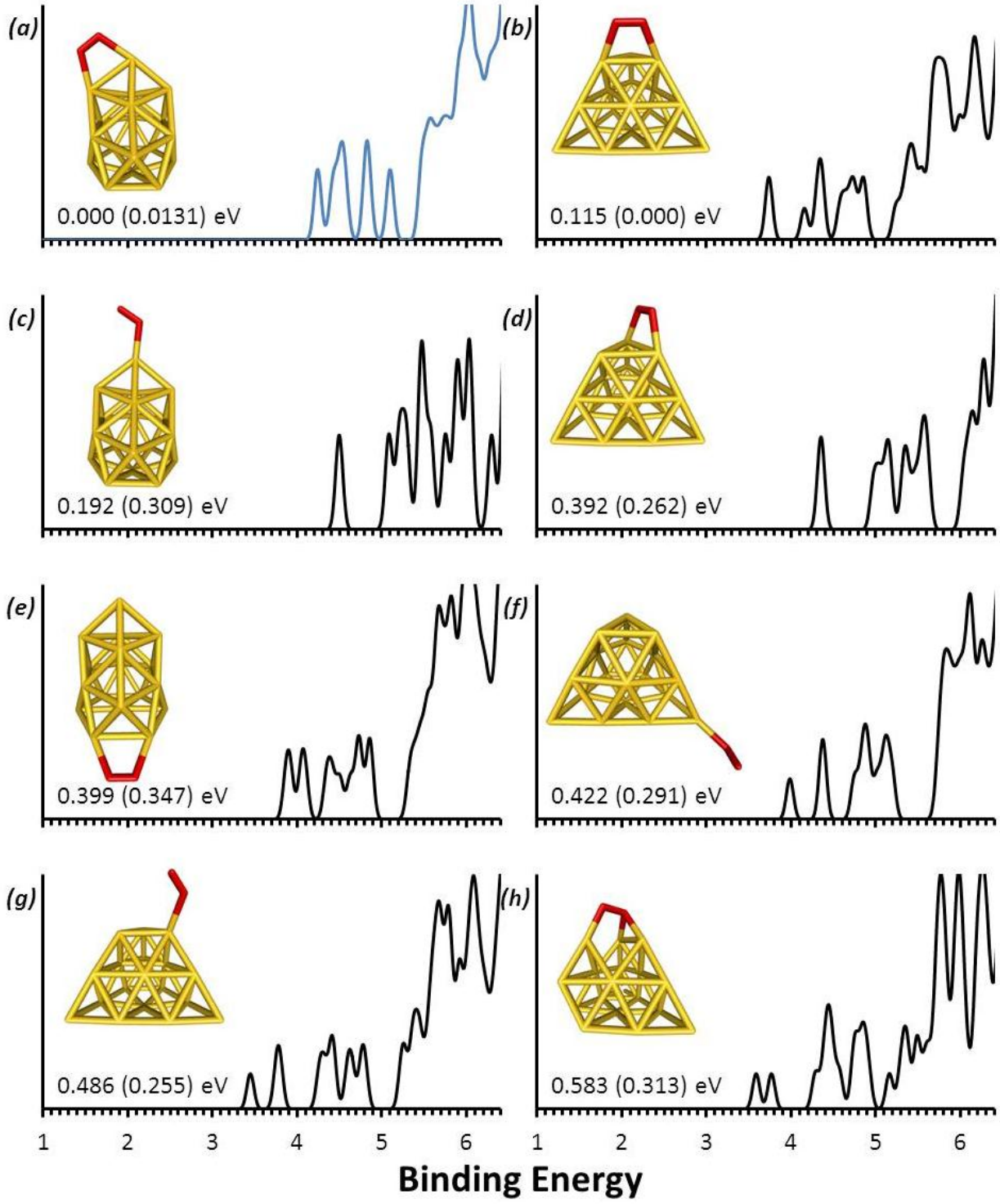


Figure S8. Computed photoelectron spectra and relative energies at the SO-PBE0 (TPSSh) level of theory for the three low-lying isomers of $O_2Au_{18}^-$. The blue curve is used to compare with the experimental PES spectrum.

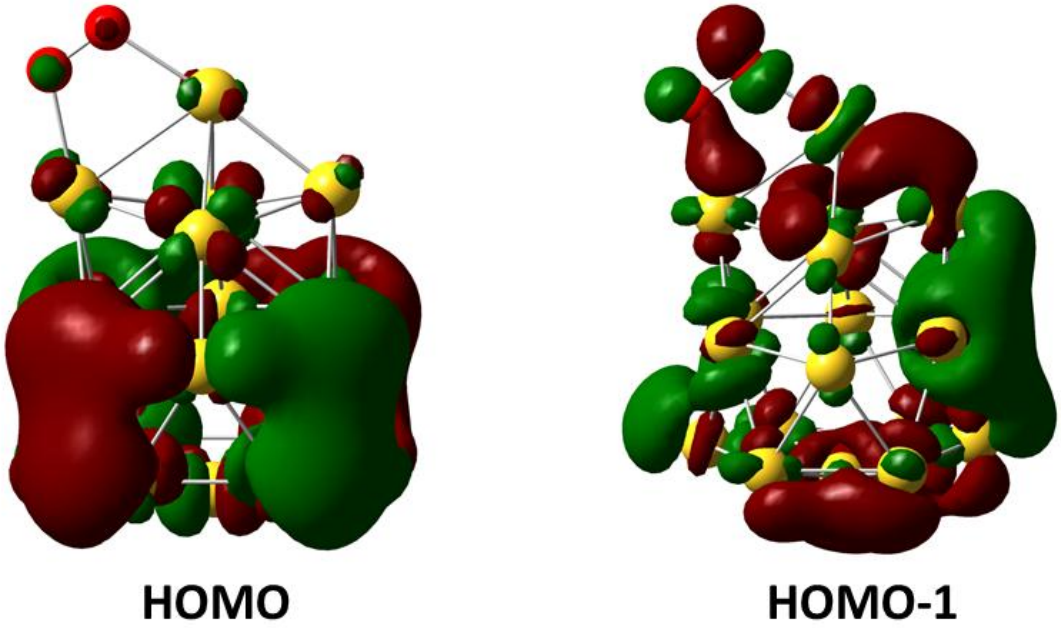


Figure S9. The HOMO and HOMO-1 of the peroxo cage isomer (a) of $O_2Au_{18}^-$ showing almost no contributions from the O-O π^* orbital in the HOMO and only a small contribution of the π^* in HOMO-1.

Table S1. Vibrational frequencies for isomers (**a**)-(**l**) of $O_2Au_8^-$ (see Figure S2). The **O-O** and **O-Au-O** stretching frequencies are highlighted in red and green, respectively.

Isomer (a)	Isomer (b)	Isomer (c)	Isomer (d)	Isomer (e)	Isomer (f)	Isomer (g)	Isomer (h)	Isomer (i)	Isomer (j)	Isomer (k)	Isomer (l)
13.7566	13.3986	8.2164	8.8577	16.0233	12.9425	13.5012	6.827	14.7232	11.1834	9.3599	0.4887
16.0383	21.0844	8.542	12.4529	17.4846	22.793	22.6358	19.6787	34.0418	24.9492	13.9218	12.2923
21.8715	33.579	26.4558	27.6626	25.319	30.4578	29.7479	26.2178	50.7856	50.3178	21.0619	22.991
25.2351	35.6433	26.8702	32.3064	32.8273	32.3698	32.5111	29.9262	59.0926	62.3257	32.9115	23.6692
42.7751	42.8079	34.0186	34.801	46.16	37.4215	39.1998	31.3663	78.1909	78.3786	46.658	28.7234
50.4041	53.4265	38.9026	46.217	49.3806	45.7208	40.7382	44.7016	108.175	110.2302	47.7731	34.6366
50.6852	55.9197	43.159	48.0569	52.2357	50.4099	50.4293	45.8425	150.889	157.1774	54.6721	37.6038
65.8863	58.9165	53.5145	58.472	56.0648	60.3089	56.3691	53.6368	203.1162	191.245	57.0307	47.8532
70.9582	66.9904	60.0242	69.851	65.4727	67.2976	64.3855	57.7564	17.4669	21.8297	63.2615	55.6371
77.1748	76.0905	63.3492	80.6226	69.7603	76.8403	74.0561	77.6019	35.1195	33.2132	77.5252	63.2006
91.0456	76.6702	65.0803	93.2687	87.7634	93.9522	82.9748	84.2239	54.286	54.0314	101.2232	68.4778
109.0887	83.7423	69.7224	94.0875	102.9637	106.6467	90.5952	93.5181	65.783	65.9758	103.4084	69.6807
117.3263	95.5829	81.5167	105.0842	107.1832	122.6658	94.4092	100.9382	88.4149	88.0039	109.1122	81.5395
125.6027	108.1378	98.1908	107.8577	111.9065	133.2123	105.1166	121.0895	115.1748	125.2654	114.3696	84.464
138.5486	130.2856	105.1462	131.4449	131.2315	139.0147	123.3945	132.4617	176.8977	168.4086	138.9757	98.6558
139.7359	135.7271	109.2651	142.8069	149.6849	142.8763	124.2909	143.8205	382.6158	353.6946	141.6699	112.075
147.8361	152.9705	127.5685	155.0766	155.1967	145.6895	147.701	156.3993	23.1842	24.7226	146.7484	119.003
169.7281	164.5744	129.0312	164.2661	163.1157	147.9061	149.7007	171.4613	40.8867	41.5097	148.4264	129.92
182.0717	172.5535	174.0216	175.6105	179.9421	164.9736	167.6522	188.0524	56.0472	57.9597	173.9251	141.5174
190.6472	175.2303	175.1392	180.6386	185.8413	180.6866	174.1814	195.9473	72.5926	73.4424	182.1437	155.8455
413.5335	193.4654	193.8621	407.3616	424.6764	386.0243	187.4934	448.3408	102.8654	95.6234	326.1275	173.5597
458.298	293.6722	211.1585	489.9894	468.6138	428.3078	284.4607	478.9888	144.1606	128.7868	385.9124	186.1662
568.5596	420.0972	385.0082	515.2042	554.8259	465.7048	412.7679	613.93	184.3504	172.5361	575.1694	313.0571
609.2964	1119.119	1157.4806	568.5103	590.4278	532.4027	1125.8953	633.8327	1165.4939	1106.5265	592.3881	1179.4434

Table S1. Cartesian Coordinates of major isomers of $O_2Au_n^-$ (n = 6-18).

$O_2Au_6^-$

O	-0.03429163	-5.02279637	-0.08128920
O	-0.03188211	-5.64185166	1.05968745
Au	2.68570978	1.73013730	-0.06914207
Au	1.36213966	-0.63194380	-0.03237147
Au	0.04103184	1.83365945	-0.00696659
Au	-0.01384094	-2.92454343	-0.00088130
Au	-1.33638589	-0.60119940	0.03179944
Au	-2.60590036	1.79015670	0.05511733

$O_2Au_8^-$

Peroxo

O	-3.07130195	-3.57136892	0.02234983
O	-3.82227959	-2.50587944	0.02821332
Au	2.80811244	-0.19078863	0.00162232
Au	1.32226462	2.01803370	-0.00252170
Au	1.65168730	-2.80679739	-0.00747752
Au	0.11941554	-0.54236575	0.00537364
Au	-2.61083615	-0.66320488	0.01919906
Au	-0.95608047	-3.14555098	0.00792245
Au	-1.43959851	1.69844536	0.00537739
Au	-0.30906952	4.14808228	-0.00916940

Superoxo

O	0.01586781	-6.32039106	0.66882825
O	-0.03902081	-5.63777502	-0.41549883
Au	-0.01652093	-3.54511033	-0.22239882
Au	3.65198196	0.09403545	-0.05723699
Au	1.38936323	1.47719710	0.02775185
Au	-1.34625342	-1.24840155	-0.09300644
Au	-1.35149417	1.49462462	0.04457484
Au	1.34450220	-1.26588543	-0.10988731
Au	-3.63407945	0.14285646	-0.01367760
Au	0.03401688	3.76144925	0.15332561

$O_2Au_{12}^-$

O	5.01206656	-0.64631172	0.00202571
O	5.01013358	0.66273170	0.02275189
Au	3.00257979	-1.49196991	0.00244342
Au	0.89638340	-0.00527850	1.37690719
Au	0.62857622	2.58118220	0.02183283
Au	0.92614696	0.00729383	-1.38540512
Au	0.63592933	-2.57906940	0.00556533
Au	2.99827655	1.50181053	0.02961871
Au	-1.88007440	3.65827043	-0.00329357
Au	-1.50627505	1.33785949	-1.44571830
Au	-1.54342467	1.32188834	1.42057196
Au	-1.53834934	-1.34057979	1.42836568
Au	-1.86971062	-3.66315221	-0.01825296
Au	-1.50605860	-1.32627669	-1.43723918

$O_2Au_{14}^-$

O	1.44759914	-5.46087144	-0.02993278
O	0.16093026	-5.63165260	-0.09258965
Au	-0.93102216	-3.69923013	-0.03326087
Au	2.65177746	-0.73023980	0.06038670
Au	-1.51006710	0.58453344	-1.61196588
Au	0.19934345	-1.43366395	1.37932681
Au	1.97725958	-3.28932320	0.05030885
Au	1.08491583	1.17812196	-1.46069949
Au	3.31670599	1.95085424	0.01800037
Au	1.02274405	1.21787929	1.43135508
Au	0.25662969	-1.45498830	-1.38600939
Au	-1.56302726	0.61366552	1.62909378
Au	-1.53499109	2.87340293	-0.01664728
Au	-3.71793386	1.03742733	-0.03372483
Au	-2.42605194	-1.51258298	0.01439519
Au	1.03466099	3.61631323	-0.04147902

$O_2Au_{18}^-$

O	0.01140492	5.06265434	2.45734713
O	0.02717107	5.74257925	1.35488949
Au	0.01906213	4.39970803	-0.39784743
Au	-0.01935052	2.82001416	2.22155664
Au	-1.47968365	2.08352831	-0.14075738
Au	0.03329958	2.53594785	-2.40938412
Au	1.48983920	2.07221480	-0.10495161
Au	-0.00700238	-2.87564060	0.15656069
Au	-3.17768010	0.00688074	-0.09224514
Au	-0.03822150	-1.88199436	2.85366927
Au	-2.34012677	-2.35022736	-1.28463911
Au	-1.39383504	0.14825037	-2.26346050
Au	-1.41756278	0.42716780	2.07599235
Au	1.37236394	0.41905765	2.11214030
Au	2.36278131	-2.35899425	-1.22732151
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Au	3.18145728	-0.00718930	-0.01399416
Au	-2.37323160	-2.12841100	1.47815859
Au	1.44953335	0.14259855	-2.22859514