

Ultralow reaction barriers for CO oxidation in Cu-Au nanoclusters

Supporting Information

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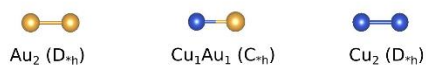
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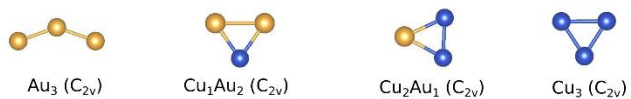
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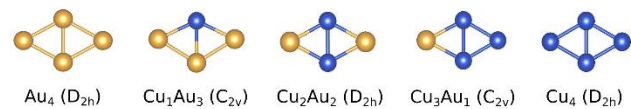
$n+m=2$



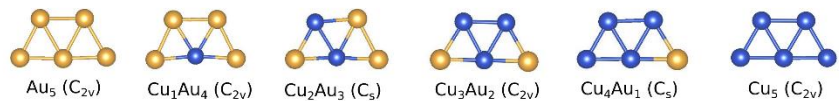
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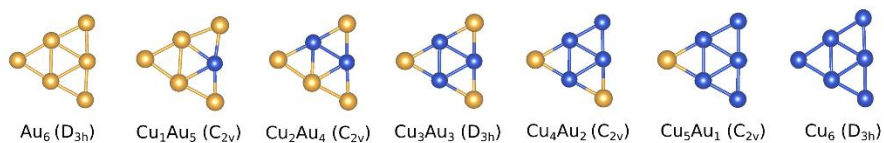
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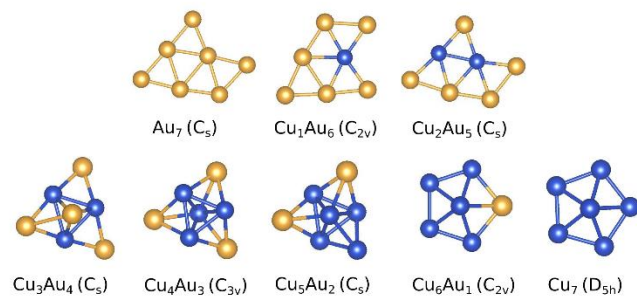
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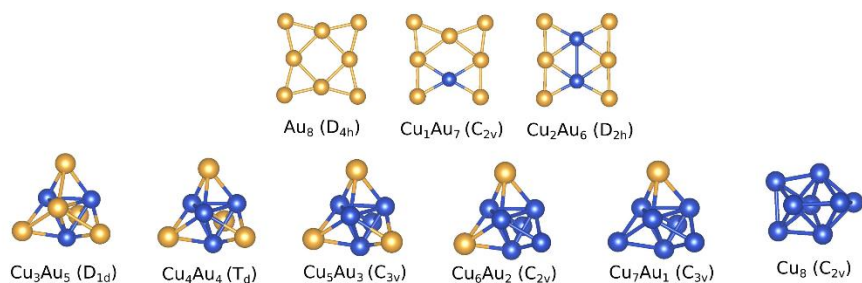
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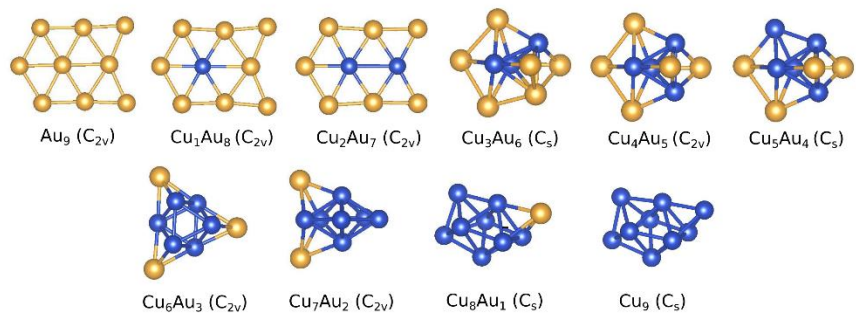
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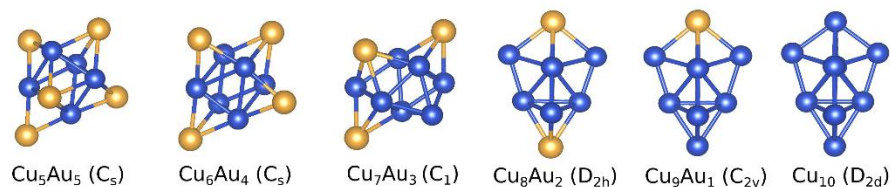
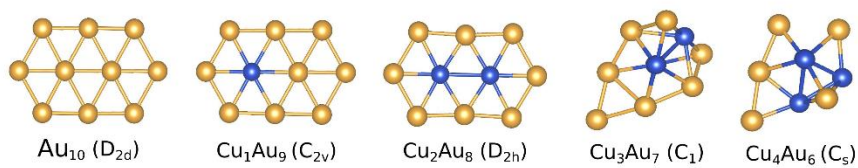
$n+m=8$



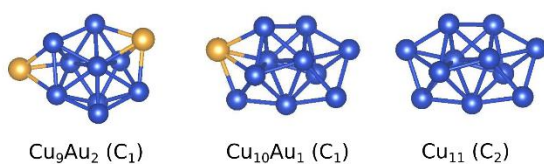
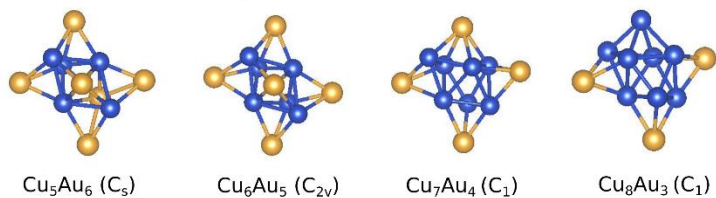
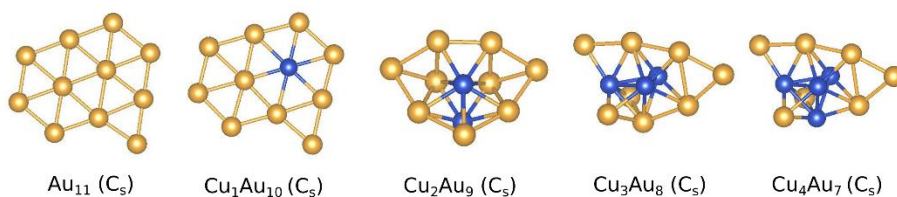
$n+m=9$



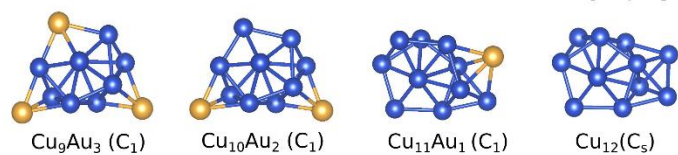
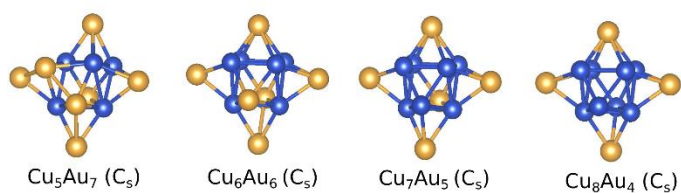
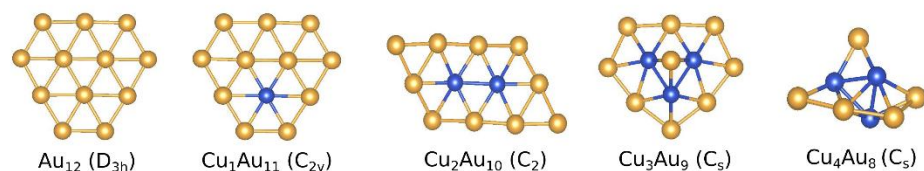
$n+m=10$



$n+m=11$



$n+m=12$



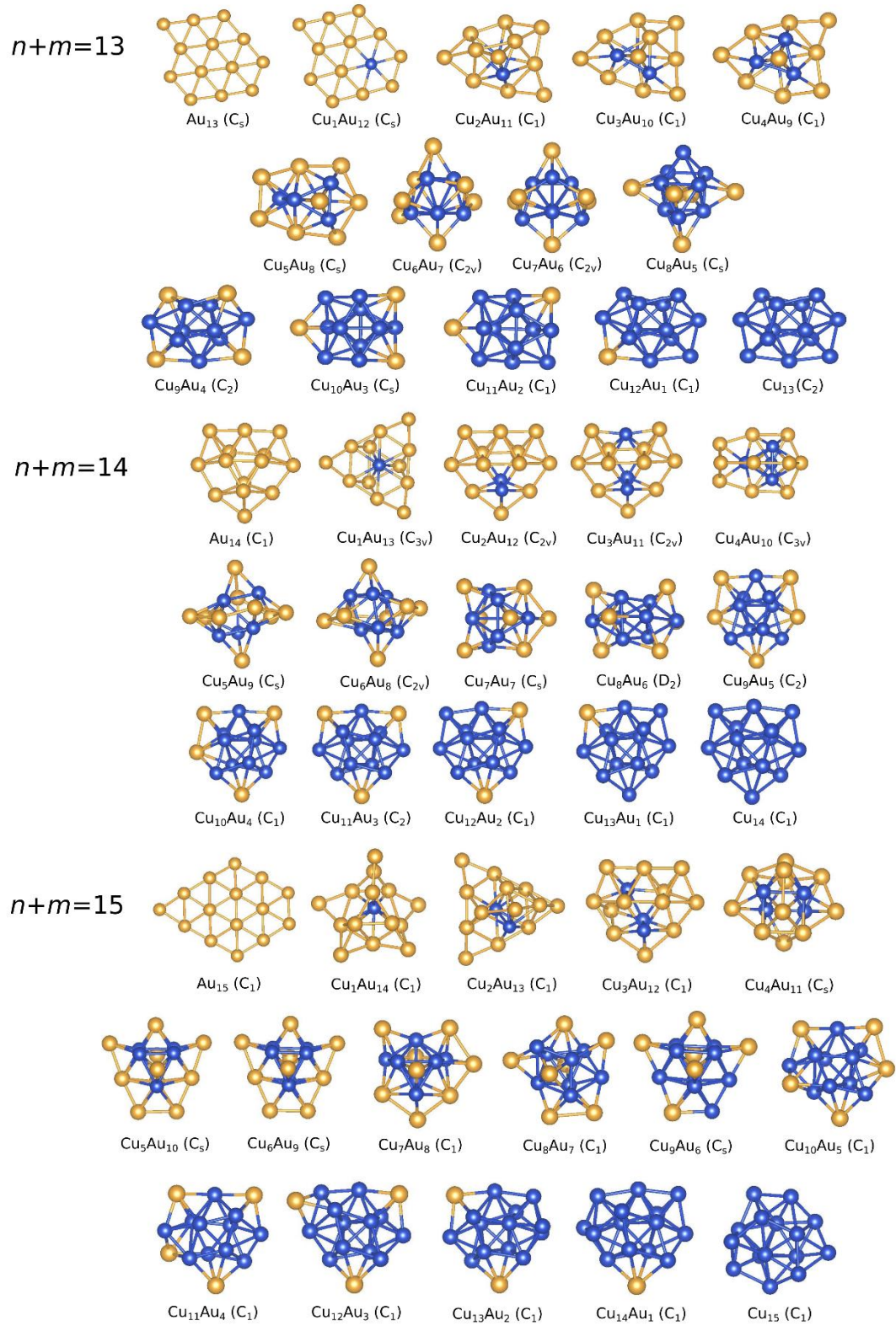


Figure S1. Ground-state structures of Cu_nAu_m clusters ($m + n \leq 15$).

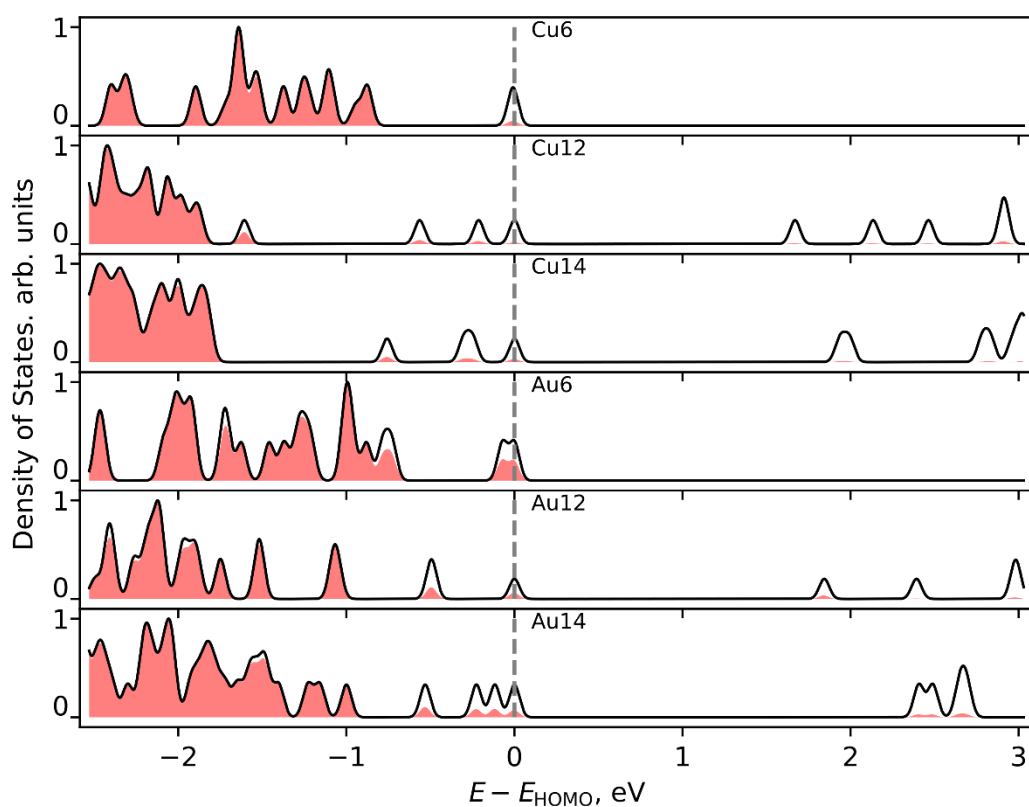
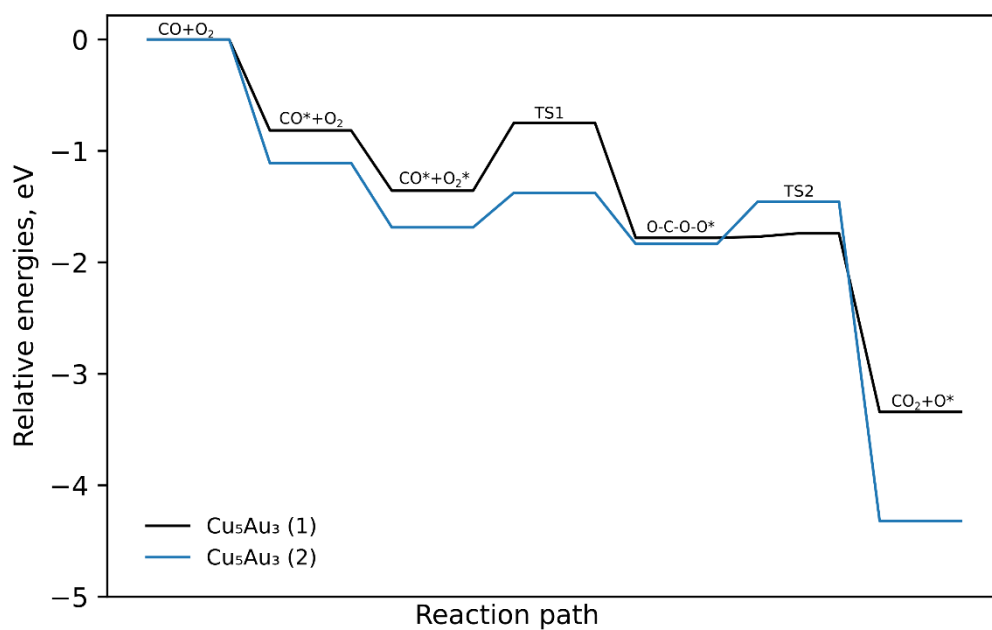
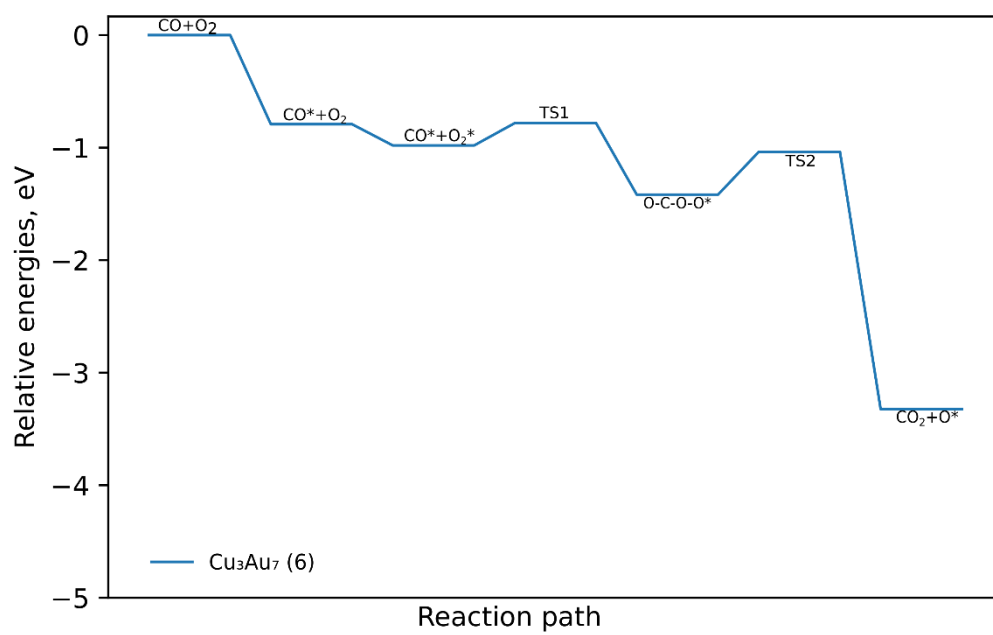
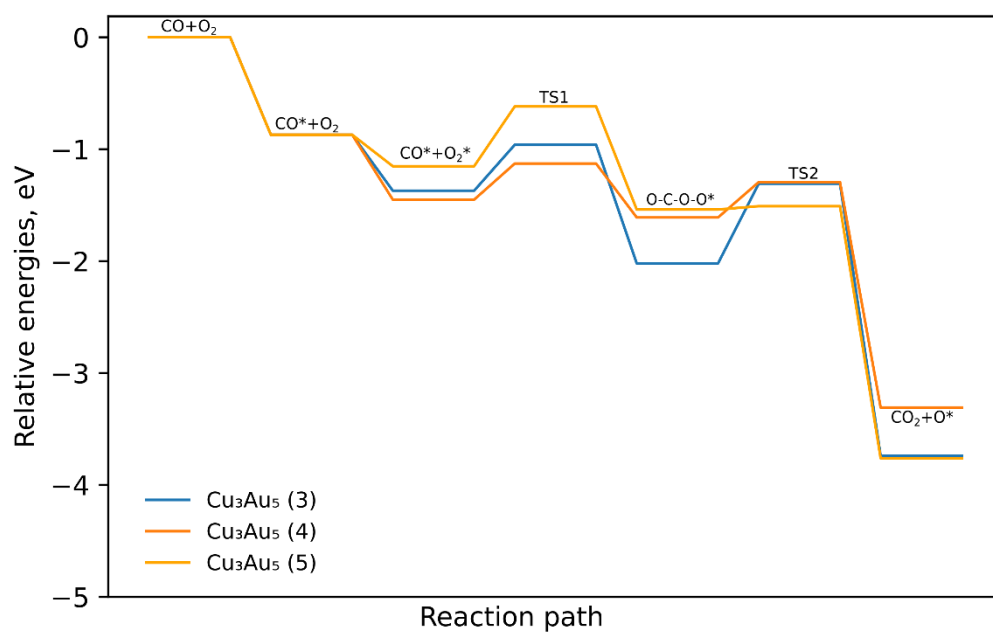
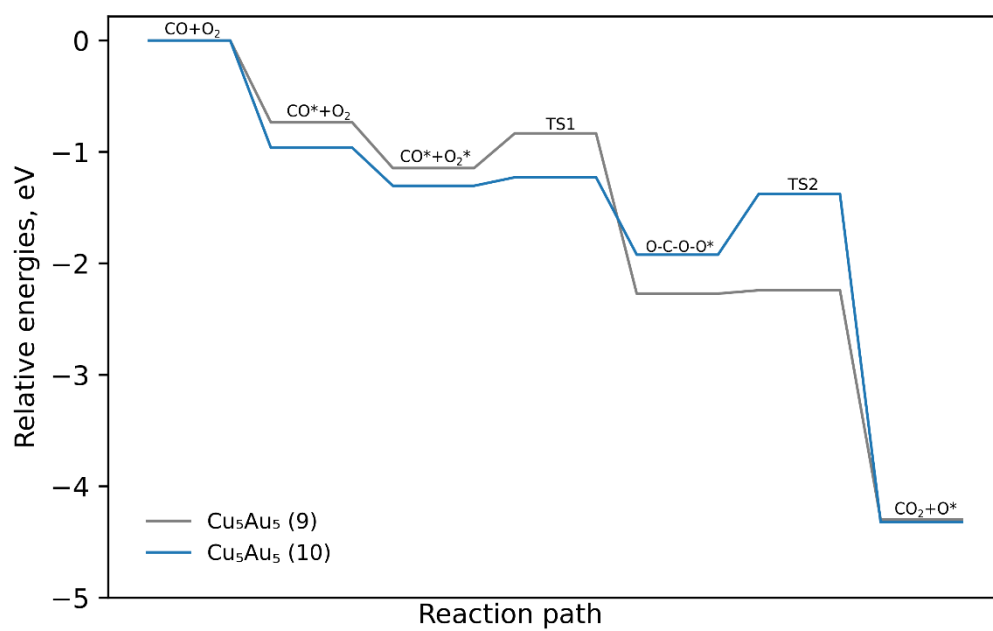
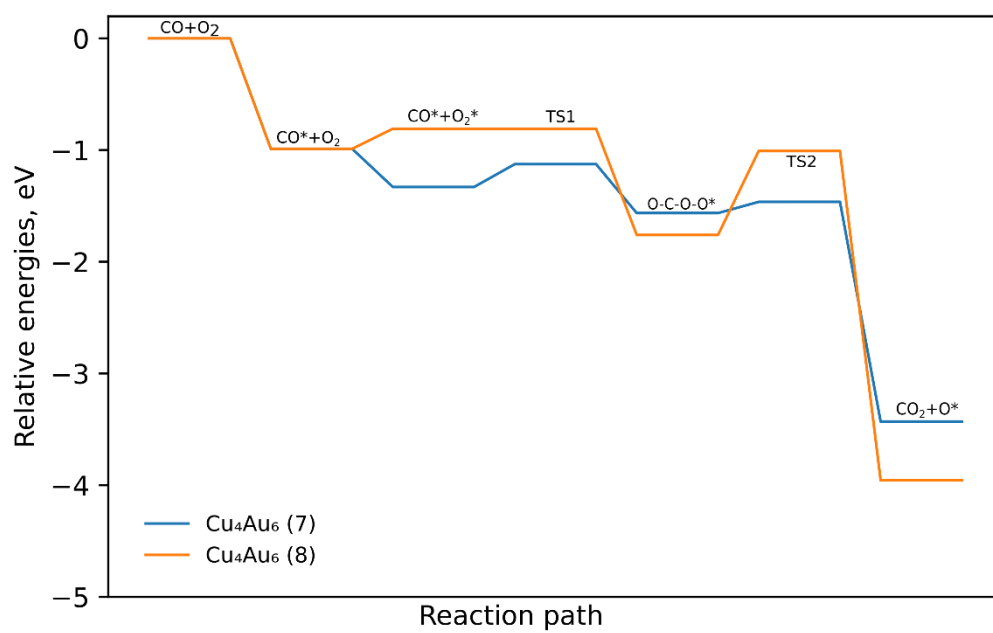
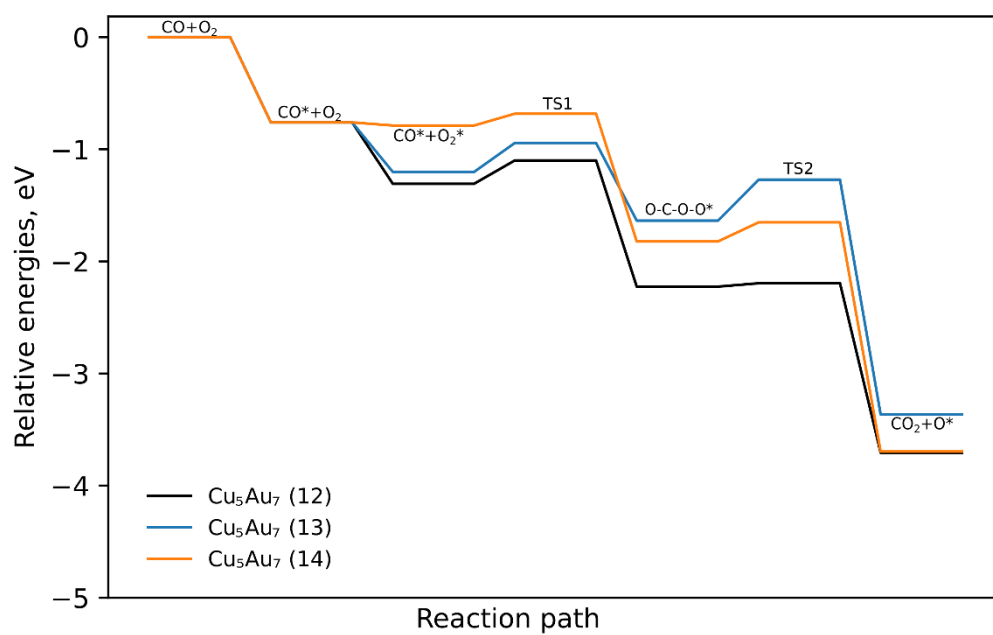
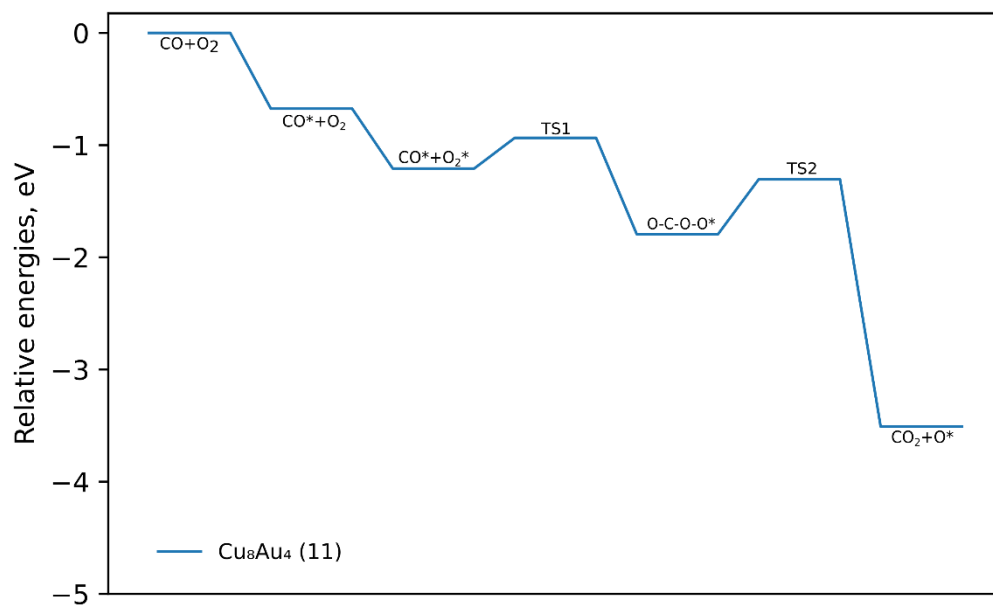


Figure S2. Density of electronic states — total (black line) and projected on d-orbitals (red fill) in 6 characteristic clusters: Cu₆ (planar), Cu₁₂ (non-planar), Cu₁₄ (non-planar), Au₆ (planar), Au₁₂ (planar), Au₁₄ (non-planar).









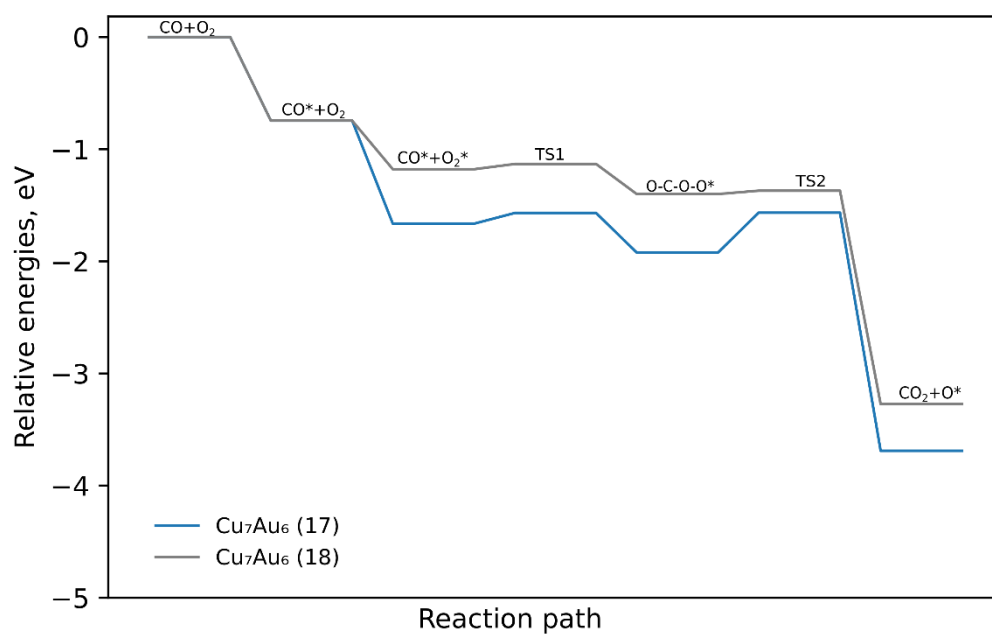
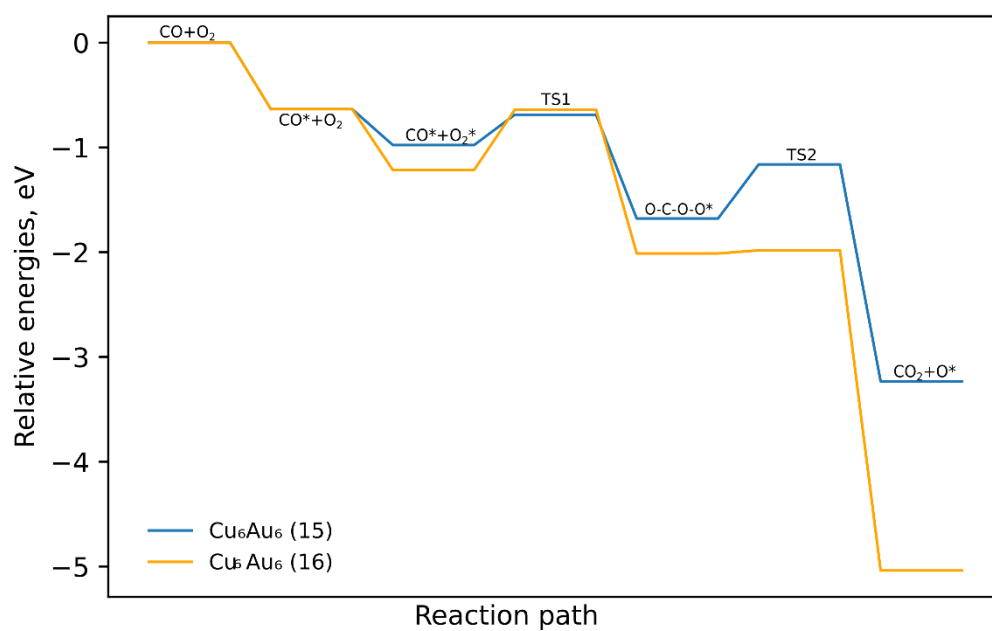


Figure S3. Computed reaction pathways of $\text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}^*$ on both stable and catalytically active Cu_nAu_m clusters. Here, * denotes the species adsorbed on a cluster.

Table S1. Computed relative energy (eV), with respect to the reactant in the gas phase ($\text{CO} + \text{O}_2$) of the co-adsorption states, first transition state (TS1), intermediate states (O-O-C-O^*), second transition state (TS2), and the final state ($\text{CO}_2 + \text{O}^*$) for $\text{CO} + \text{O}^* \rightarrow \text{CO}_2$ during CO oxidation on the clusters that are both stable and catalytically active. N – number of the pathway.

N	Cluster	$\text{CO} + \text{O}_2$	$\text{CO}^* + \text{O}_2$	$\text{CO} + \text{O}^*_2$	TS1	O-C-O-O^*	TS2	$\text{CO}_2 + \text{O}^*$
1	Cu_5Au_3	0	-0.82	-1.36	-0.75	-1.78	-1.77	-3.34
2	Cu_5Au_3	0	-1.11	-1.69	-1.38	-1.83	-1.46	-4.32
3	Cu_3Au_5	0	-0.87	-1.37	-0.96	-2.02	-1.31	-3.74
4	Cu_3Au_5	0	-0.87	-1.45	-1.13	-1.61	-1.29	-3.31
5	Cu_3Au_5	0	-0.87	-1.15	-0.62	-1.54	-1.51	-3.76
6	Cu_3Au_7	0	-0.79	-0.98	-0.78	-1.42	-1.04	-3.32
7	Cu_4Au_6	0	-0.99	-1.33	-1.13	-1.56	-1.46	-3.43
8	Cu_4Au_6	0	-0.99	-0.81	-0.81	-1.76	-1.01	-3.96
9	Cu_5Au_5	0	-0.73	-1.14	-0.83	-2.27	-2.24	-4.30
10	Cu_5Au_5	0	-0.96	-1.30	-1.23	-1.92	-1.38	-4.32
11	Cu_8Au_4	0	-0.68	-1.21	-0.94	-1.79	-1.31	-3.51
12	Cu_5Au_7	0	-0.76	-1.31	-1.10	-2.22	-2.19	-3.71
13	Cu_5Au_7	0	-0.76	-1.20	-0.94	-1.64	-1.27	-3.36
14	Cu_5Au_7	0	-0.76	-0.79	-0.68	-1.82	-1.65	-3.70
15	Cu_6Au_6	0	-0.63	-0.98	-0.69	-1.68	-1.16	-3.23
16	Cu_6Au_6	0	-0.63	-1.21	-0.64	-2.01	-1.98	-5.04
17	Cu_7Au_6	0	-0.75	-1.66	-1.57	-1.92	-1.57	-3.69
18	Cu_7Au_6	0	-0.75	-1.18	-1.13	-1.40	-1.37	-3.27

Cartesian coordinates of Cu-Au clusters in XYZ format for which catalytic pathways were calculated:

Cu_5Au_3 geometry:

8

Pathways 1,2

Cu 7.197208 8.673366 10.915418

Cu 8.468375 9.293315 8.833409

Cu 8.592681 10.696669 10.915982

Cu 8.491272 9.272569 12.842942

Cu	9.648013	8.476955	10.900263
Au	8.276440	6.852052	9.499282
Au	6.456423	10.675735	9.528124
Au	10.682365	10.338260	9.503748

Cu₃Au₅ geometry:

8

Pathways 3,4,5

Cu	8.999017	10.333368	10.964516
Cu	11.359471	9.435642	10.987507
Cu	10.960772	11.929852	10.958216
Au	10.425974	10.590397	13.051293
Au	9.530579	8.149871	9.773382
Au	10.451820	10.545249	8.773004
Au	12.987829	10.961136	9.766040
Au	8.821560	12.549268	9.728981

Cu₃Au₇ geometry:

10

Pathway 6

Cu	7.449156	9.500144	9.399808
Cu	9.375749	10.322219	10.763555
Cu	9.712491	8.897240	8.585683
Au	9.042982	7.785726	10.825448
Au	11.477917	8.867152	10.701760
Au	7.230929	11.713582	10.479370
Au	7.743986	7.258765	8.406140
Au	13.790739	9.596129	9.623106
Au	9.107291	11.423903	8.450741
Au	11.607561	10.582107	8.483863

Cu₄Au₆ geometry:

10

Pathways 7,8

Cu	8.901541	9.874707	9.278243
Cu	8.887437	9.860318	11.781206
Cu	10.927447	8.726392	10.524256
Cu	8.584562	7.769845	10.523521
Au	9.928136	7.790158	8.364651
Au	6.637399	9.400852	10.504392
Au	8.183103	11.966672	10.546169
Au	10.755421	11.315972	10.540543
Au	9.932855	7.781784	12.682539
Au	13.053805	10.087239	10.501776

Cu₅Au₅ geometry:

10

Pathways 9,10

Cu	12.362270	10.853913	9.012159
Cu	12.669001	12.110713	11.093676
Cu	12.682495	9.624665	11.108923
Cu	10.355625	9.643573	10.174116
Cu	10.343492	12.057909	10.158858
Au	12.077502	13.366481	8.948160
Au	14.710840	10.875144	10.282789
Au	8.207919	10.838989	9.914249
Au	12.101729	8.338298	8.977829
Au	10.912596	10.867397	12.450085

Cu₈Au₄ geometry:

12

Pathway 11

Cu	10.837189	8.848364	7.032205
Cu	8.489419	8.798409	7.020088
Cu	10.902914	8.268045	9.410787
Cu	8.405464	10.585164	8.817149
Cu	10.847545	10.634344	8.818753
Cu	9.620982	10.895936	6.704649

Cu	8.504295	8.215498	9.396724
Cu	9.650123	9.822588	10.788026
Au	12.967480	9.316016	8.367121
Au	9.735823	6.568689	7.878648
Au	6.354845	9.140097	8.394926
Au	9.579647	12.802052	8.408486

Cu₅Au₇ geometry:

12

Pathways 12,13,14

Cu	10.021946	8.810354	7.261742
Cu	10.712672	8.808838	9.613411
Cu	8.984284	10.492299	9.056752
Cu	7.081154	8.898709	8.902060
Cu	8.883896	7.216890	9.147822
Au	11.192307	6.733032	8.240695
Au	8.620648	8.916613	11.063396
Au	11.341668	10.812068	8.198593
Au	7.940286	10.172791	6.701193
Au	6.602716	11.400415	8.744617
Au	6.465100	6.424886	8.820760
Au	7.910276	7.484797	6.759278

Cu₆Au₆ geometry:

12

Pathways 15,16

Cu	10.885031	10.585234	10.689522
Cu	8.448554	10.680287	10.690435
Cu	10.854040	10.141362	8.300576
Cu	8.454070	10.234855	8.300948
Cu	10.809219	8.190284	10.005540
Cu	8.333023	8.288600	10.003496
Au	12.934598	9.535514	9.644513
Au	9.571027	8.057823	7.694084

Au	9.734050	12.347363	9.227390
Au	9.603636	8.997537	12.201345
Au	9.482638	6.049736	9.673035
Au	6.325157	9.801803	9.635475

Cu₇Au₆ geometry:

13

Pathways 17,18

Cu	7.752647	11.088600	8.665852
Cu	8.465788	9.222525	10.102645
Cu	9.745659	7.724696	8.626601
Cu	9.716795	9.992165	7.886233
Cu	10.978740	9.242754	10.103073
Cu	11.654446	11.133562	8.684393
Cu	9.697149	11.403913	10.145321
Au	7.349589	11.267296	11.142153
Au	7.511545	8.683134	7.686048
Au	9.736678	7.252252	11.101604
Au	11.952037	8.748900	7.674909
Au	12.039092	11.299989	11.166469
Au	9.691694	12.559949	7.742119