Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Structural and catalytic properties of the $Au_{25-x}Ag_x(SCH_3)_{18}$ (x = 6, 7, 8) Nanocluster

Gihan Panapitiya[†], Hong Wang[†], Yuxiang Chen[‡], Ejaz Hussain[‡], Rongchao Jin[‡*], and James P. Lewis[†]*

†Department of Physics and Astronomy, West Virginia University, Morgantown, WV, 26506-6315

‡Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA, 15213

E-mail: james.lewis@mail.wvu.edu, rongchao@andrew.cmu.edu

Structural trends of 3-Ag alloyed Au25 cluster

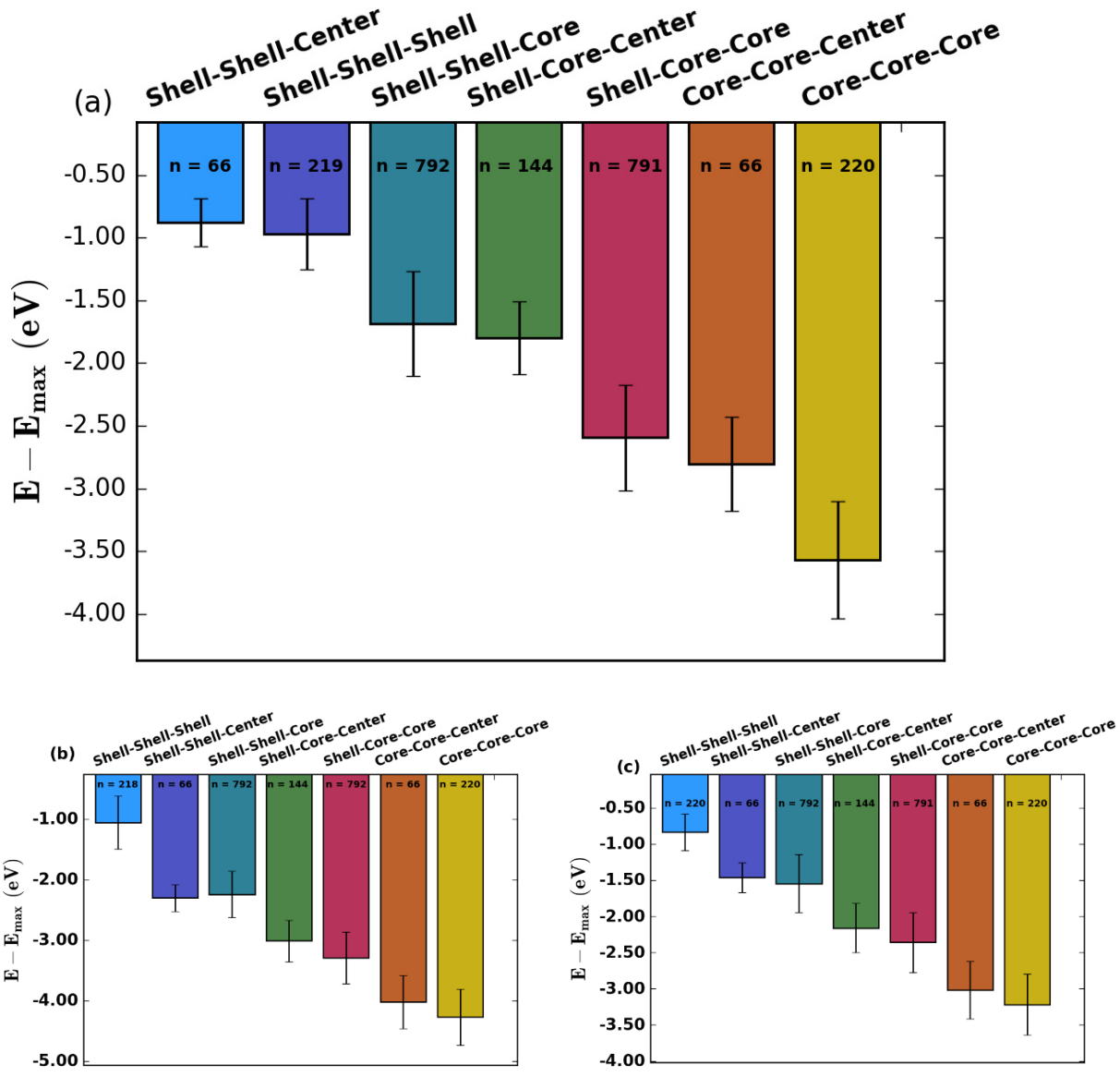


*Figure S1: Structural trends of (a) $[Au_{22}Ag_3(SCH_3)_{18}]^0$, (b) $[Au_{22}Ag_3(SH)_{18}]^0$ and (c) $[Au_{22}Ag_3(SH)_{18}]^{-1}$*

The structural trends depicted in Figure S1 agree with the those of Ref. 1.

Partial DOS of 0, 3, 6, 7, 8-Ag alloyed Au25 clusters

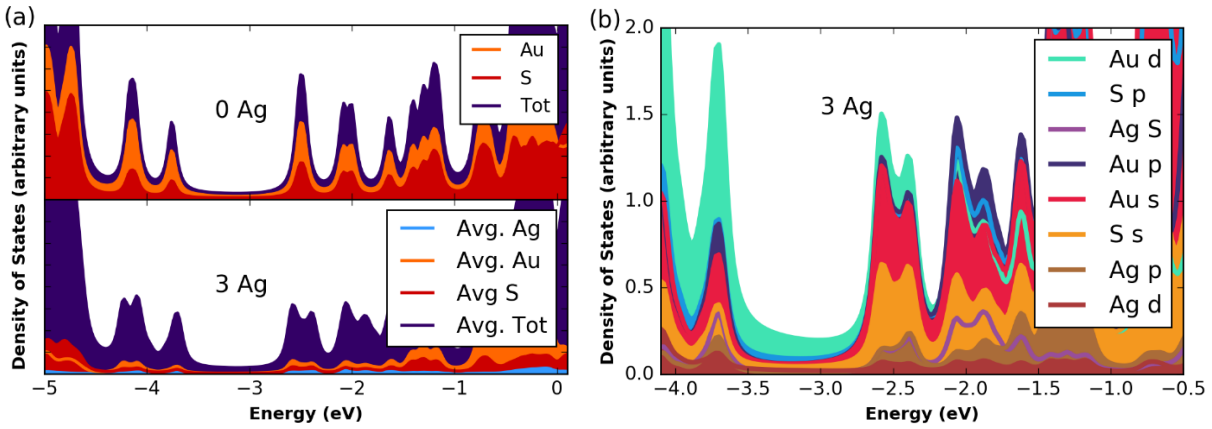


*Figure S2: (a) Partial density of states for 0 and 3 Ag alloyed $Au_{25}(SCH_3)_{18}$ and (b) orbital density of states of $Au_{22}Ag_3(SCH_3)_{18}$*

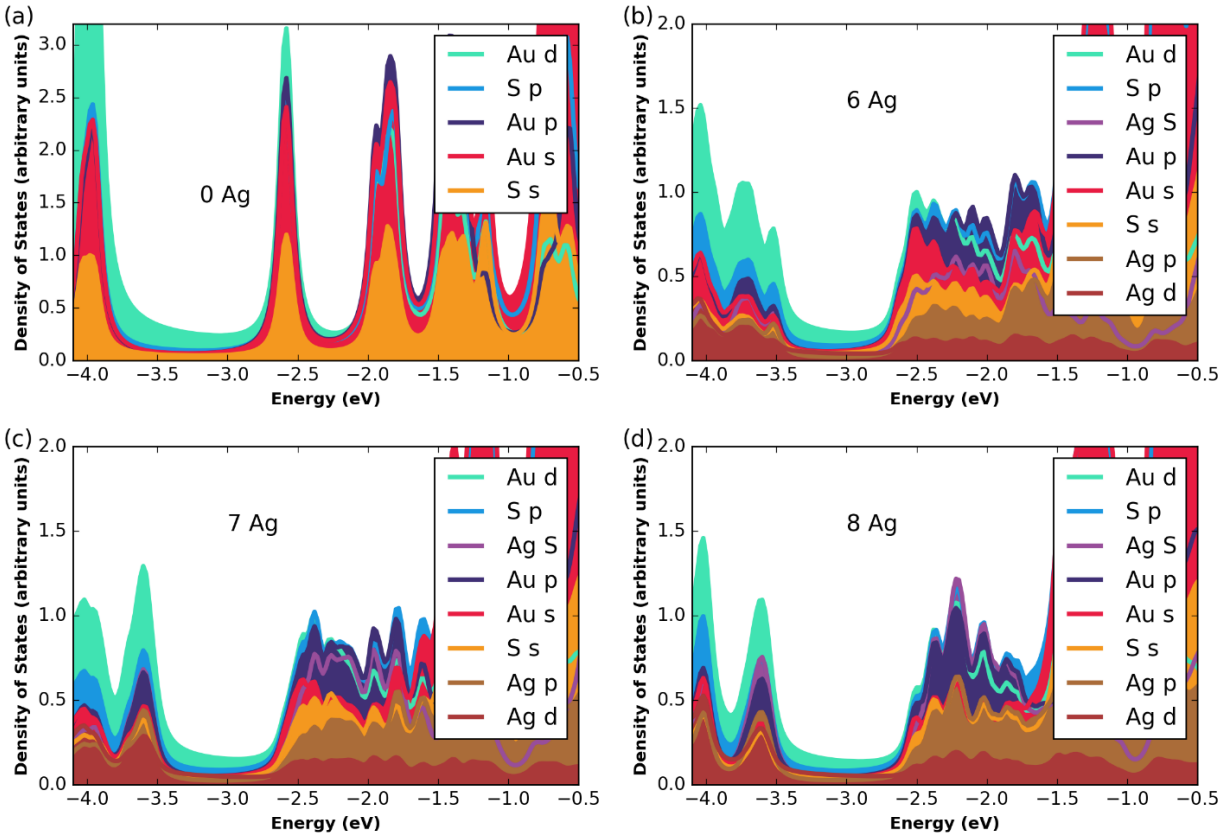


*Figure S3: Orbital density of states of (a) 0, (b) 6, (c) 7 and (d) 8 Ag alloyed Au25(SCH3)18*

HOMO and LUMO molecular orbitals and electron densities of non-alloyed and alloyed Au25 cluster

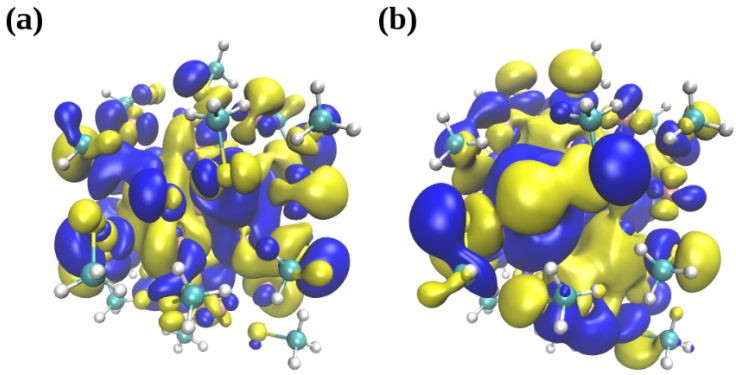


*Figure S4: (a) HOMO and (b) LUMO orbitals of $Au_{25}(SCH_3)_{18}$ (isovalue = 0.0002)*

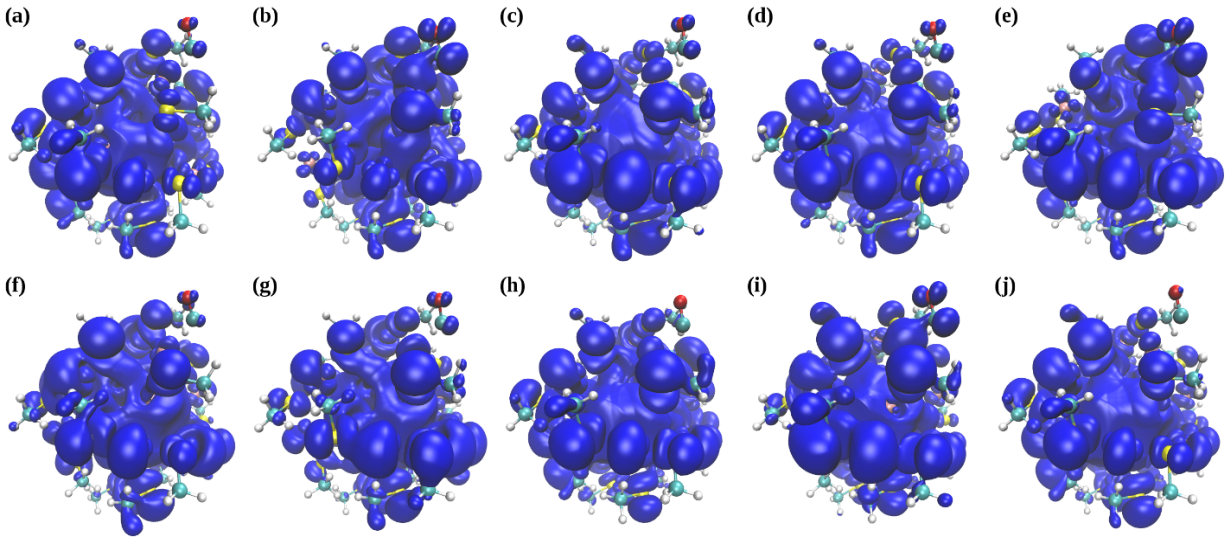


*Figure S5: (a)-(j) HOMO electron densities of 6-Ag alloyed nanoclusters in the order of increasing energy (isovalue = 0.0002).*

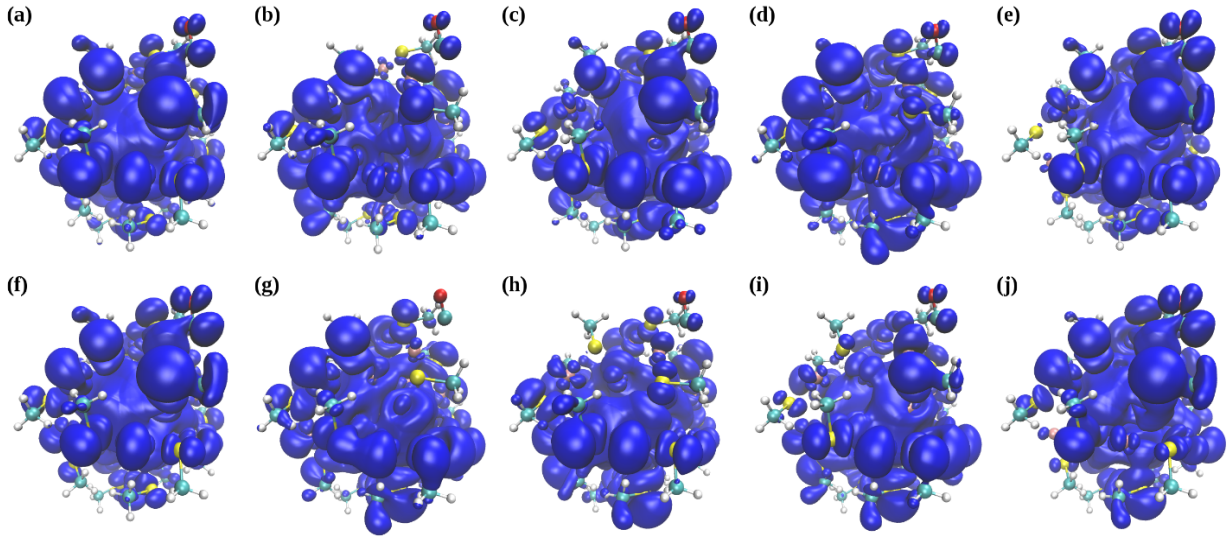


*Figure S6: (a)-(j) HOMO electron densities of 7-Ag alloyed nanoclusters in the order of increasing energy (isovalue = 0.0002).*

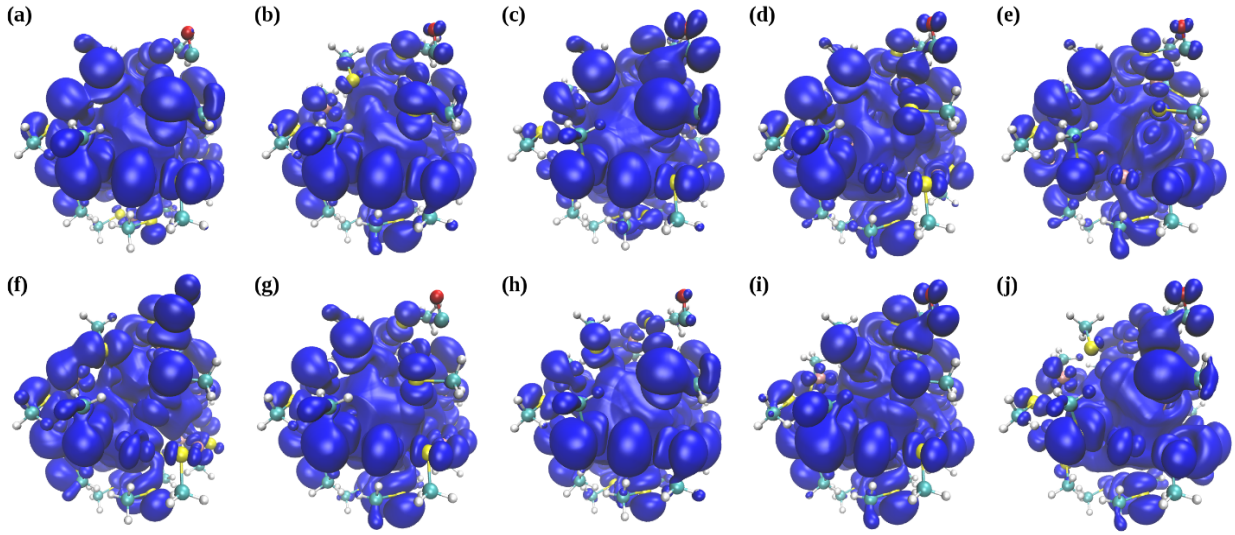


*Figure S7: (a)-(j) HOMO electron densities of 8-Ag alloyed nanoclusters in the order of increasing energy (isovalue = 0.0002).*

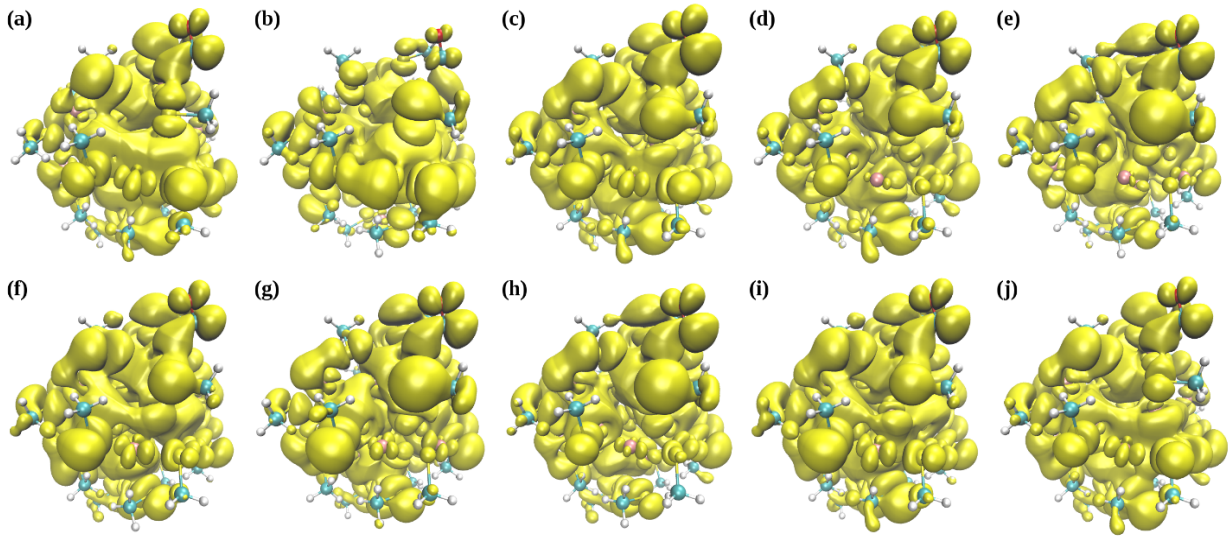


*Figure S8: (a)-(j) LUMO electron densities of 6-Ag alloyed nanoclusters in the order of increasing energy (isovalue = 0.0002).*

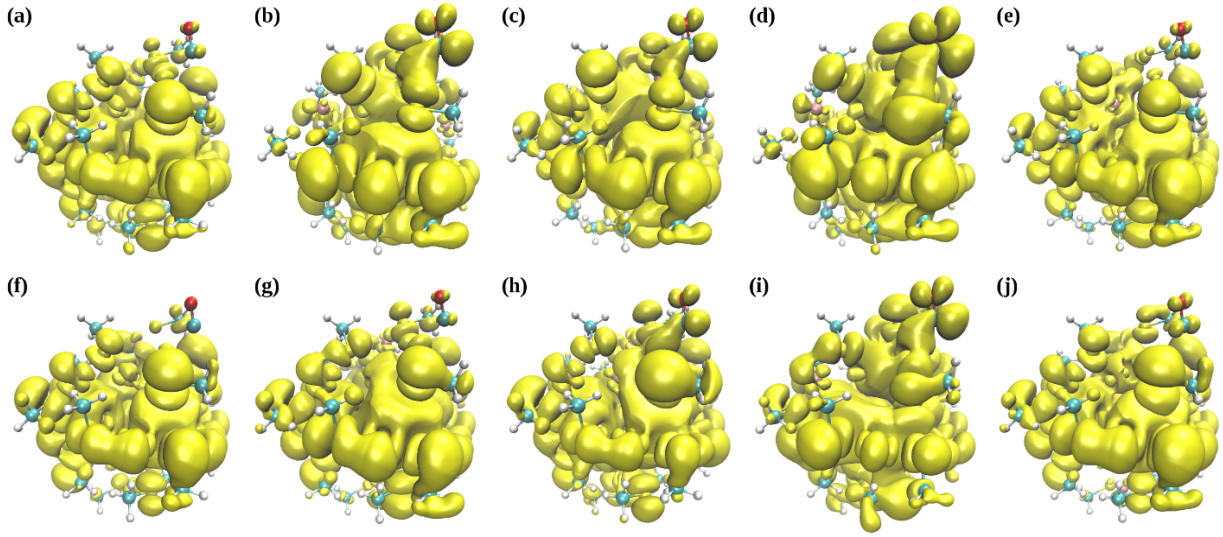


*Figure S9: (a)-(j) LUMO electron densities of 7-Ag alloyed nanoclusters in the order of increasing energy (isovalue = 0.0002).*

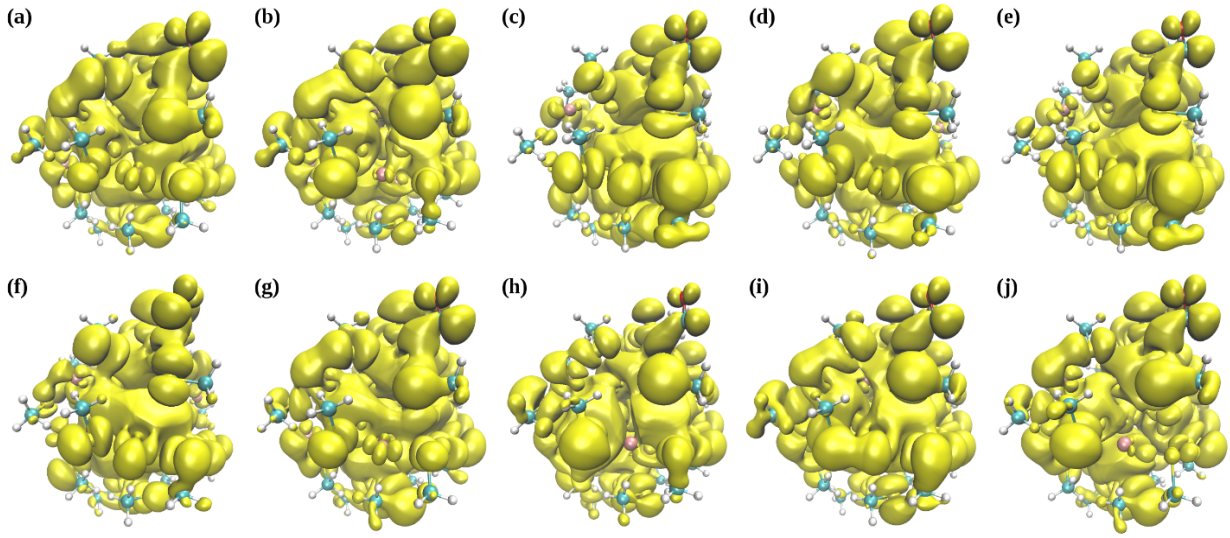


*Figure S10: (a)-(j) LUMO electron densities of 8-Ag alloyed nanoclusters in the order of increasing energy (isovalue = 0.0002).*

CO adsorbed isomers considered in this work. The first number next to the label is the relative energy and the second number is the Boltzmann weight calculated based on the relative energy per atom.

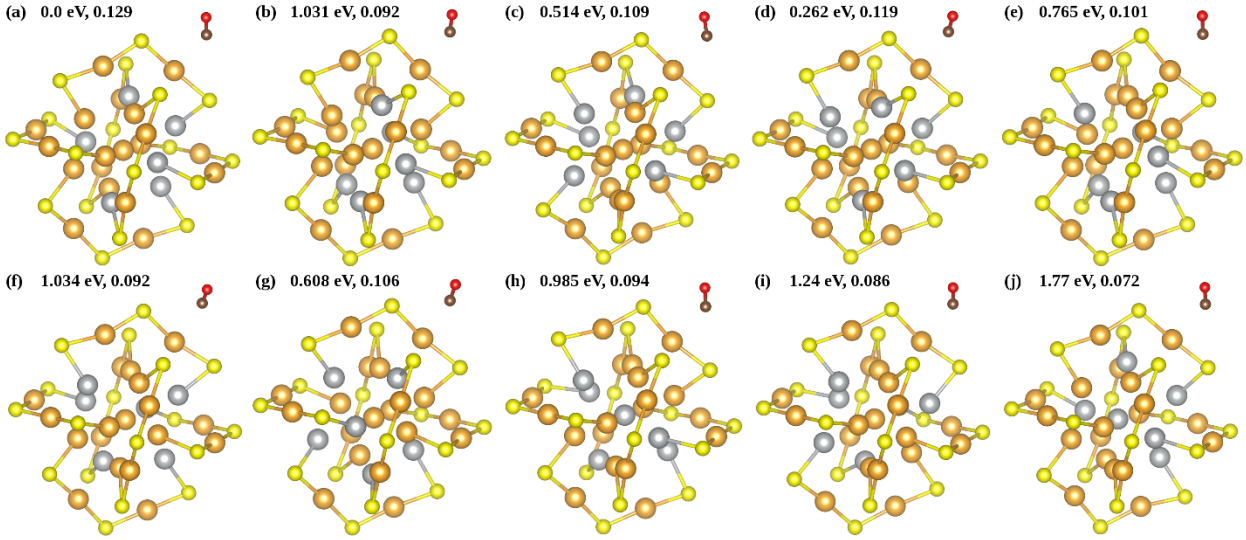


*Figure S11: CO adsorbed 6-Ag alloyed isomers.*

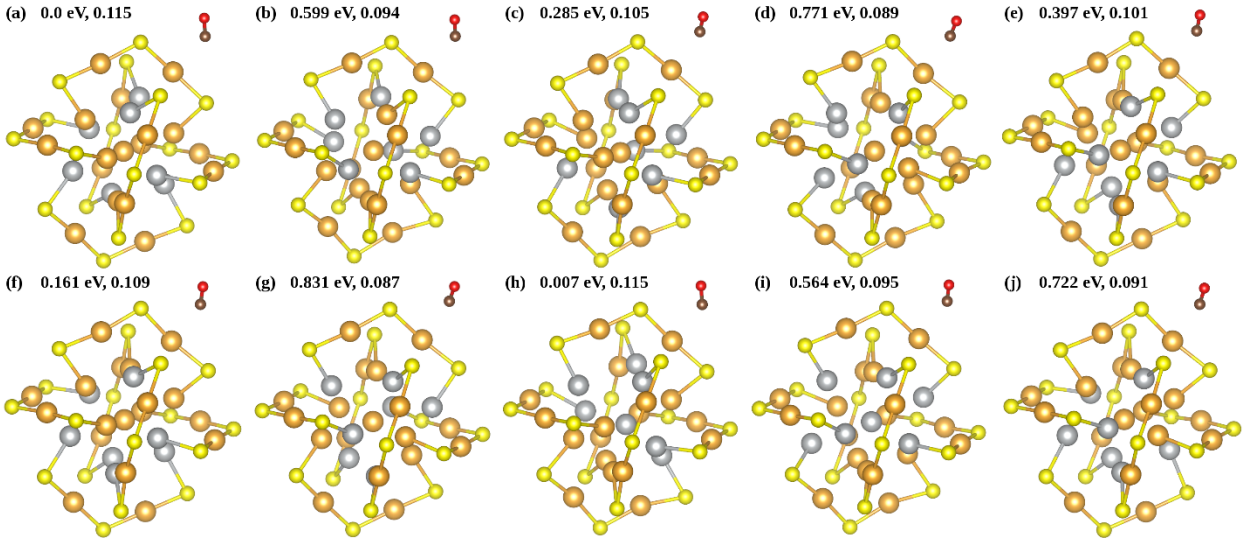


*Figure S12: CO adsorbed lowest energy 7-Ag alloyed isomers.*

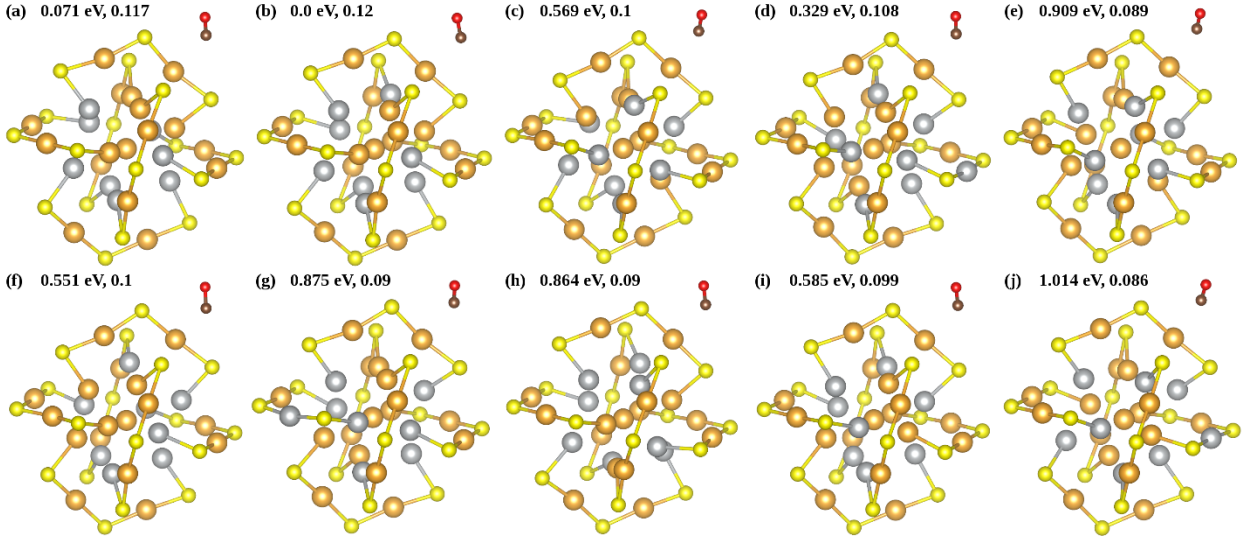


*Figure S13: CO adsorbed 8-Ag alloyed isomers.*

Bond lengths of $Au_{25}(SCH_3)_{18}$ obtained with BLYP

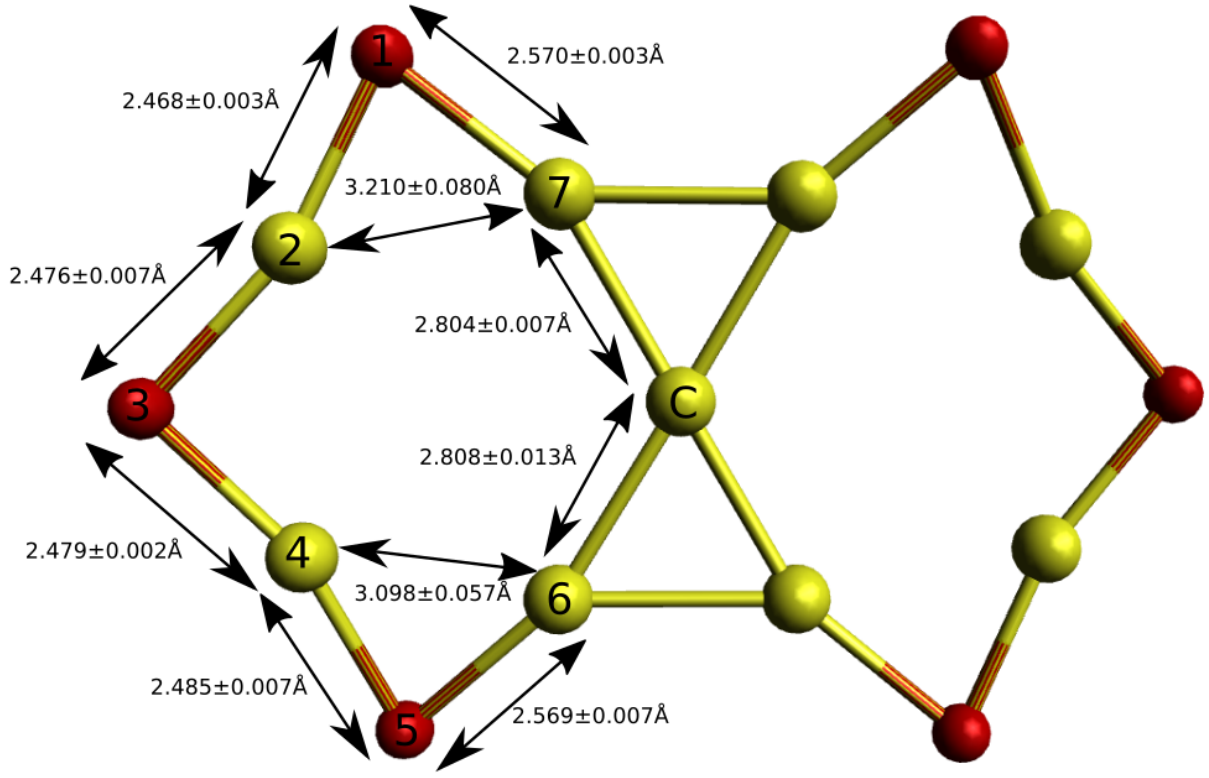


*Figure S14: Bond lengths obtained with BLYP functional.*

The bond lengths in **Error! Reference source not found.** agree quite well the experimental values given in Ref. 2

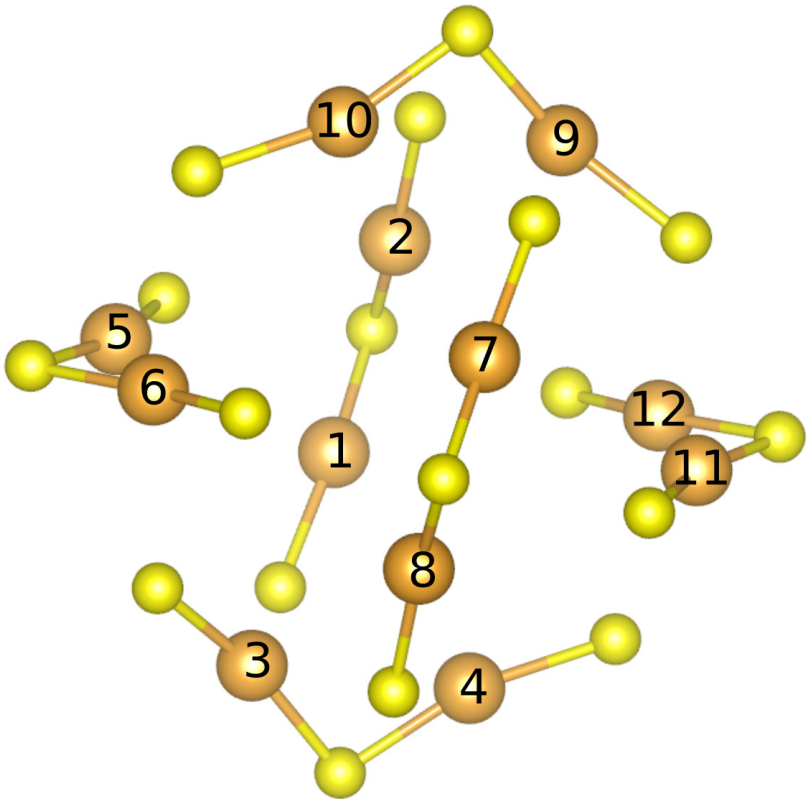


*Figure S15: Different Ag/Au sites considered for CO adsorption.*

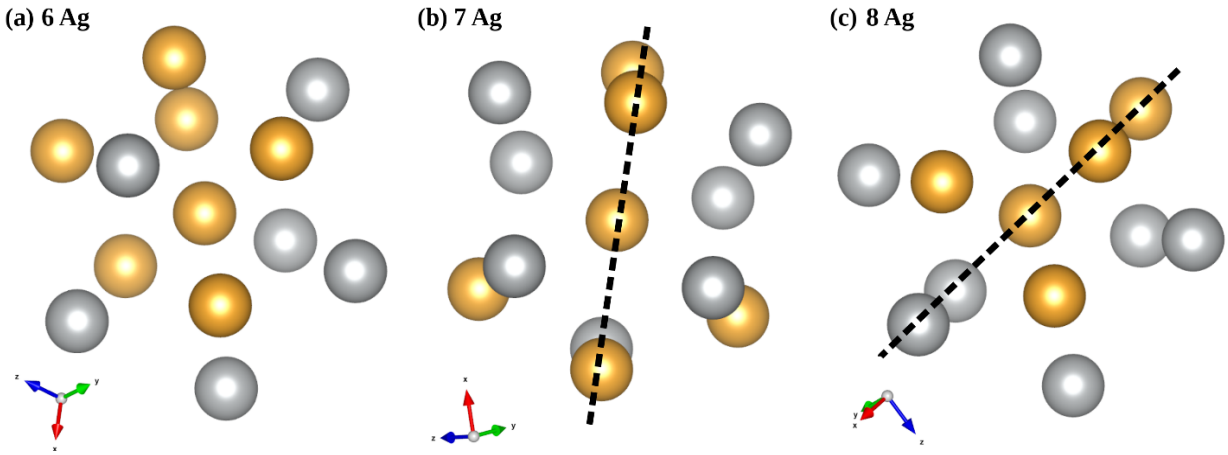


*Figure S16: Symmetries displayed by the lowest energy (a) 6- , (b)7- and (c)8-Ag alloyed isomers*

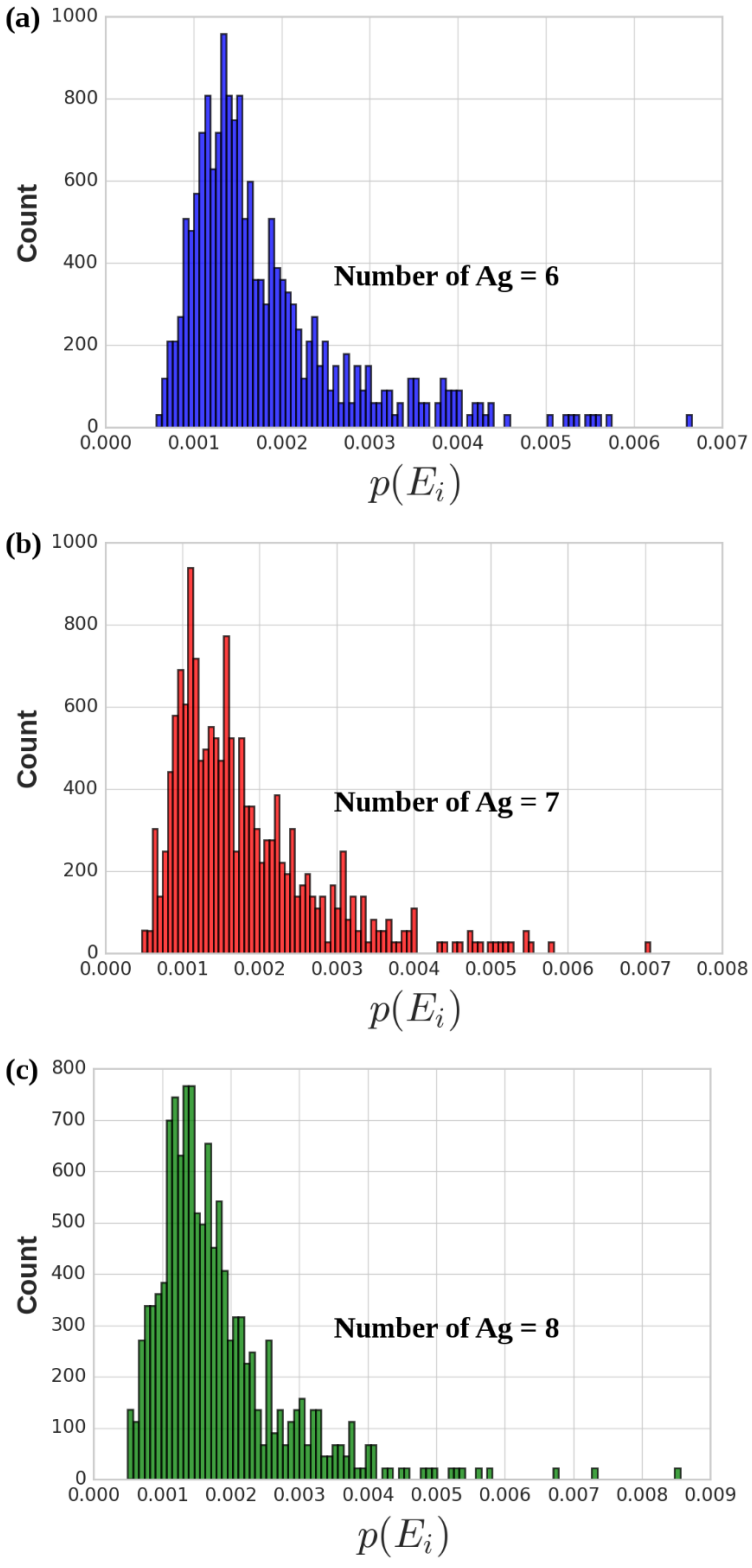


*Figure S17: Boltzmann distributions of the relative energies per atom. $p(E_i) = \exp(-[E_i-E_{min}]/k_BT) / \sum\exp(-[E_i-E_{min}]/k_BT)$, where $E_i$ is rhe energy per atom, kB is the Boltzmann constant and T is the room temperature(298K).*

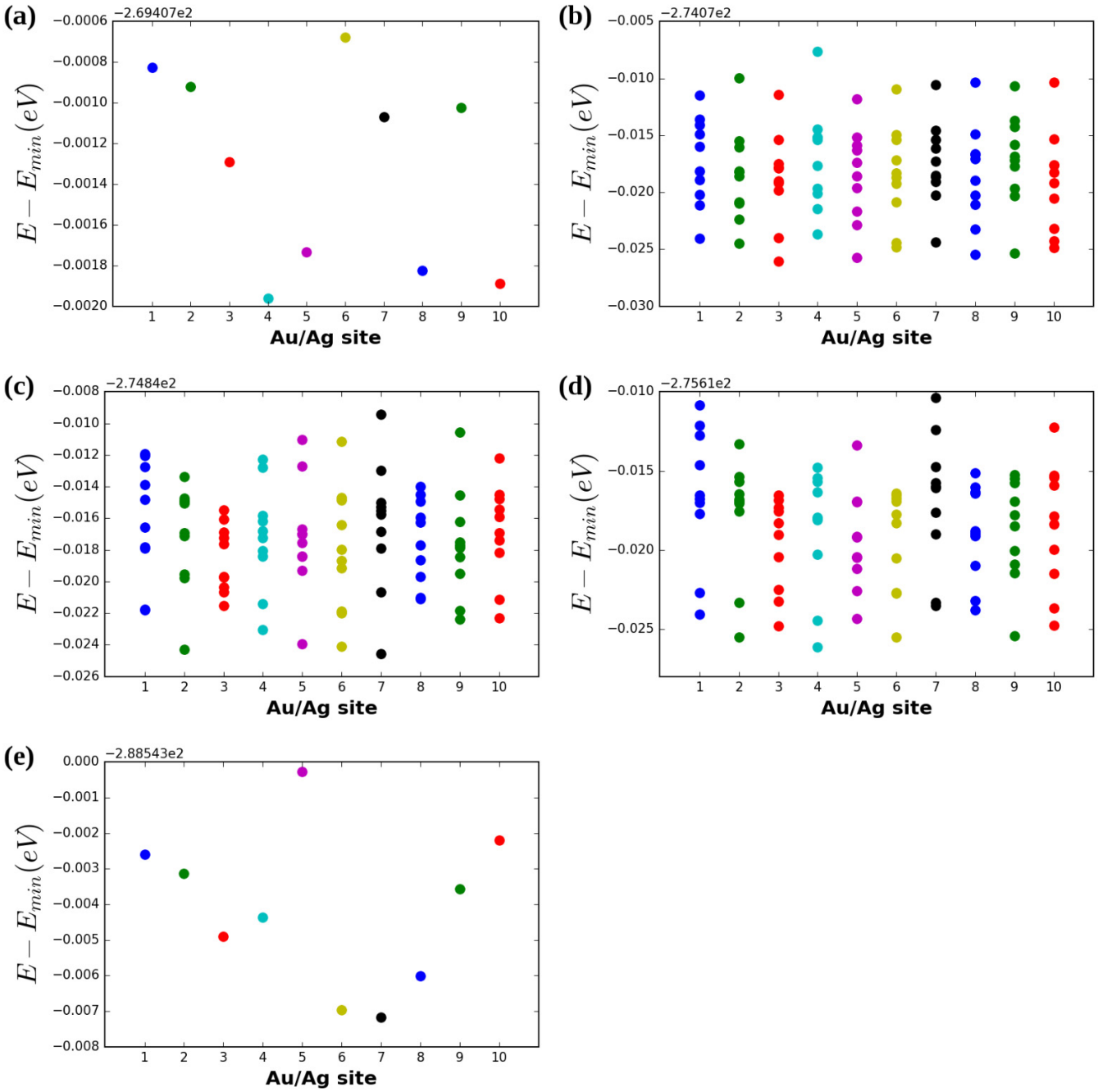


*Figure S18: Energies of CO adsorbed (a) 0-, (b) 6-, (c) 7-, (d) 8- and (e) 25-Ag alloyed isomers considered in Figure 6 of the main text.*

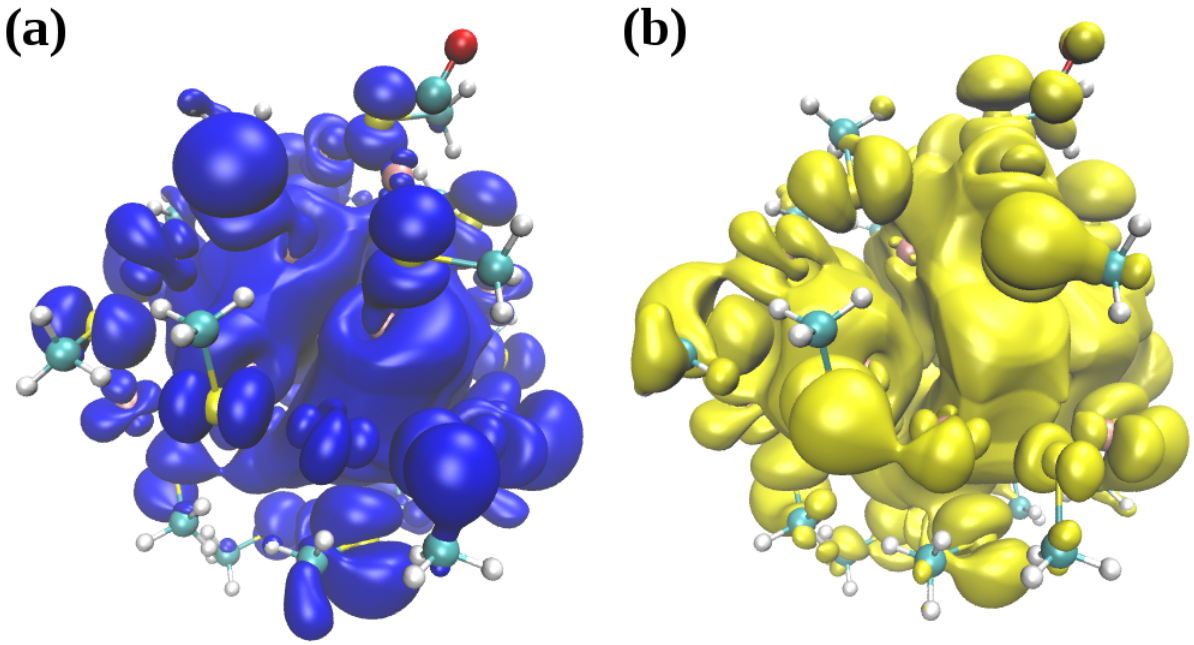


*Figure S19: (a) HOMO and (b) LUMO electron densities of Ag25 nanoculster (isovalue = 0.0002).*

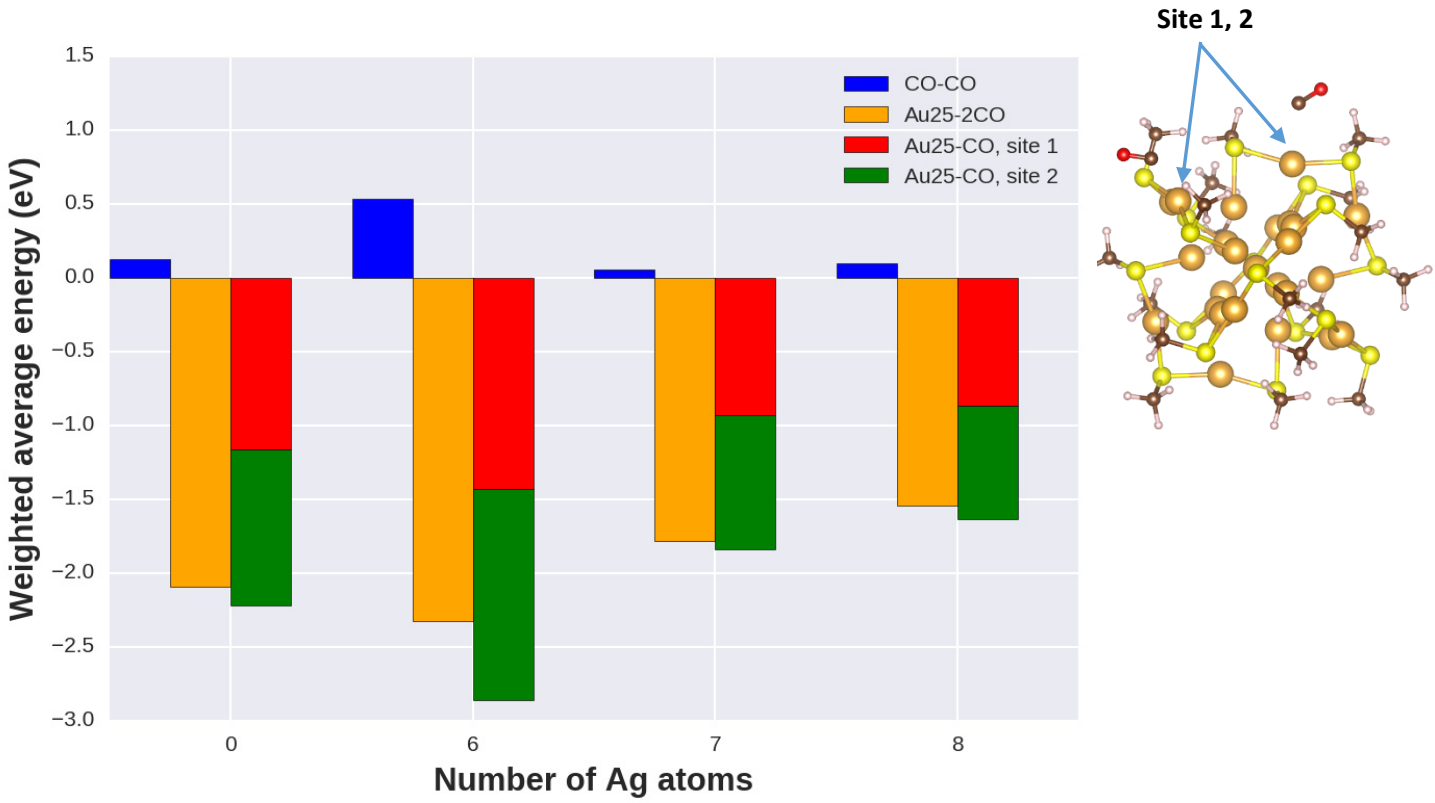


*Figure 20: Adsorption energies of Au25/2CO systems. Energies are weighted using the Boltzmann weights calculated based on the energy of the two-CO-adsorbed isomers. The corresponding numerical values are given in Table S1.*

<u>Derivation of the CO-CO interaction energy and the Ag contribution to the adsorption energy in the Au25/2CO system</u>

In the following derivation, adsorption energies are indicated with the superscript, 'ads'. All the other quantities are total energies.

$Au25/2CO^{ads} = Au25/CO(site1)^{ads} + Au25/CO(site2)^{ads} + CO\text{-}CO^{intr}$

$= [1] + [2] + [3]$

$[1] = Au25/CO(site1) – EAu25 – CO$

$= Au25/CO(site1, Ag=0) + Au25/CO(site1, Ag \neq 0) – Au25(Ag=0) – Au25(Ag \neq 0) – CO$

$= Au25/CO(site1, Ag=0) – Au25(Ag=0) – CO + Au25/CO(site1, Ag \neq 0) – EAu25(Ag \neq 0)$

$= Au25/CO(site1,Ag=0)^{ads} + Ag\text{-}contribution(site1)$

Similarly,
[2] = Au25/CO(site2,Ag=0) $^{ads}$ + Ag-contribution(site2)

Therefore, the total Ag contribution is,

Ag-contribution(site1) + Ag-contribution(site2) = [1] - Au25/CO(site1,Ag=0) $^{ads}$ + [2] - Au25/CO(site2,Ag=0) $^{ads}$
= Au25/CO(site1)$^{ads}$ - Au25/CO(site1,Ag=0) $^{ads}$ +
Au25/CO(site2)$^{ads}$ - Au25/CO(site2,Ag=0) $^{ads}$
= Difference between the adsorption energies when CO is at sites 1 and 2 seperately

Table S1: Numerical values of Au25/2CO adsorption energy (**Au25-2CO**), CO-CO interaction energy (**CO-CO**), Au25/CO adsorption energy at site 1 (**Au25-CO (site1)**), Au25/CO adsorption energyat site 2 (**Au25-CO (site2)**), and the relative energy ($E_{rel}$) of ten lowest energy CO alloyed bimetallic clusters. All the energies are in eV.

| | **Au25-2CO** | **CO-CO** | **Au25-CO (site1)** | **Au25-CO (site2)** | $E_{rel}$ |
|---|---|---|---|---|---|
| **#Ag = 0** | -2.0948 | 0.1234 | -1.162 | -1.0562 | 0 |
| | | | | | |
| **#Ag = 6** | -2.4656 | 0.6338 | -1.609 | -1.4904 | 0 |
| | -2.8147 | 0.6815 | -1.8871 | -1.6091 | 0.1915 |
| | -2.3227 | -0.0515 | -1.0234 | -1.2478 | 0.5886 |
| | -2.3853 | 0.8325 | -1.6168 | -1.601 | 0.602 |
| | -2.4244 | 0.8604 | -1.4406 | -1.8442 | 0.6383 |
| | -2.2838 | 0.8337 | -1.6821 | -1.4354 | 0.8626 |
| | -2.2139 | 0.1917 | -1.2397 | -1.166 | 0.9161 |
| | -2.1574 | 0.6828 | -1.3561 | -1.4841 | 1.0404 |
| | -2.129 | 0.3044 | -1.1814 | -1.252 | 1.1496 |
| | -1.6913 | 0.1708 | -0.9544 | -0.9077 | 1.8896 |
| | | | | | |
| **#Ag = 7** | -1.4542 | 0.0999 | -0.5897 | -0.9644 | 0 |
| | -2.0599 | 0.2627 | -1.312 | -1.0106 | 0.278 |

| | | | | | |
|---|---|---|---|---|---|
| | -2.1369 | 0.2622 | -1.5578 | -0.8414 | 0.292 |
| | -1.821 | 0.4149 | -1.0522 | -1.1838 | 0.3806 |
| | -2.0352 | 0.0728 | -1.0153 | -1.0927 | 0.4083 |
| | -1.9269 | 0.0782 | -0.6765 | -1.3285 | 0.4452 |
| | -1.6662 | -0.026 | -0.9749 | -0.6654 | 0.5701 |
| | -1.8604 | -0.0636 | -0.9082 | -0.8885 | 0.6342 |
| | -1.5682 | -0.5072 | -0.595 | -0.466 | 0.6625 |
| | -1.249 | -0.1619 | -0.6046 | -0.4824 | 0.8195 |
| | | | | | |
| **#Ag = 8** | -1.5429 | 0.1962 | -0.7699 | -0.9692 | 0 |
| | -1.9612 | 0.5989 | -1.1435 | -1.4166 | 0.284 |
| | -1.9742 | -0.0547 | -0.9307 | -0.9887 | 0.5933 |
| | -2.0051 | 0.4247 | -1.3528 | -1.077 | 0.7056 |
| | -1.7334 | 0.3652 | -1.1388 | -0.9597 | 0.7296 |
| | -1.9958 | 0.0148 | -0.9734 | -1.0372 | 0.7641 |
| | -1.662 | 0.1137 | -0.8599 | -0.9158 | 0.8461 |
| | -0.8518 | -0.3602 | -0.4559 | -0.0357 | 0.9457 |
| | -1.3883 | 0.0815 | -0.6764 | -0.7934 | 0.9698 |
| | 0.0093 | -0.6709 | -0.2386 | 0.9188 | 1.0919 |

Atomic coordinates of the lowest energy isomers shown in Figure 2 of the main text.

6-Ag

| | | | |
|---|---|---|---|
| Au | 5.3033210 | 8.8058220 | 9.0034970 |
| Au | 7.6682770 | 9.8188730 | 10.8394830 |
| Au | 9.6811940 | 6.5600820 | 11.2876340 |
| Ag | 7.5860790 | 4.2159630 | 9.7855380 |
| Au | 3.3207570 | 6.8642560 | 10.2852740 |
| Au | 2.2075780 | 9.7736920 | 9.2047420 |
| Au | 4.7849240 | 10.5354120 | 6.2455860 |
| Ag | 6.4906920 | 8.0744630 | 6.5241750 |
| Ag | 6.0317920 | 7.1931440 | 11.1919970 |
| Au | 4.1132420 | 6.2499960 | 13.3122130 |
| Au | 1.5970540 | 4.6139080 | 11.1034480 |
| Au | 2.9938770 | 4.7020330 | 8.3458550 |
| Au | 5.4785660 | 6.0211200 | 8.5727700 |
| S | 5.5596680 | 10.9881260 | 10.3758790 |
| S | 9.8628230 | 8.9869370 | 11.6120000 |

| | | | |
|---|---|---|---|
| S | 9.6782590 | 4.1056680 | 11.3326180 |
| S | 2.9913390 | 11.5235930 | 7.6203960 |
| S | 6.5553230 | 9.8638460 | 4.6620050 |
| S | 6.3752300 | 7.1826640 | 13.7608490 |
| S | 1.7712910 | 5.4817750 | 13.4312050 |
| S | 0.8205130 | 3.4794140 | 9.0453930 |
| Au | 5.4461250 | 3.2360400 | 8.2249400 |
| Au | 3.2595600 | 2.1599040 | 6.2244260 |
| Au | 1.2441420 | 5.4929500 | 5.8330520 |
| Ag | 3.0514610 | 7.5877790 | 7.5583770 |
| Ag | 8.0568070 | 5.1116360 | 6.9490340 |
| Au | 8.6667280 | 1.9997130 | 7.8220640 |
| Au | 6.1573770 | 1.7413400 | 10.8540430 |
| Au | 4.5256350 | 4.3229140 | 10.6983580 |
| Ag | 4.5052050 | 4.8693060 | 5.9406330 |
| Au | 6.7961790 | 5.7515020 | 3.5570750 |
| Au | 9.5840580 | 7.5188820 | 6.0270650 |
| Au | 7.9245840 | 7.3067490 | 8.8373690 |
| S | 5.3787900 | 1.0743880 | 6.7799640 |
| S | 1.0673170 | 3.0522390 | 5.4941110 |
| S | 1.1582830 | 7.9524010 | 5.8041720 |
| S | 8.0355570 | 0.5525560 | 9.7315830 |
| S | 4.3039510 | 2.3878880 | 12.3680410 |
| S | 4.5245020 | 4.8839350 | 3.3364190 |
| S | 9.1307660 | 6.5284120 | 3.7798370 |
| S | 10.1238360 | 8.5728110 | 8.1758910 |
| S | 8.9772220 | 3.0687950 | 5.6457050 |
| S | 0.9671660 | 8.0601440 | 10.4410510 |

7-Ag

| | | | |
|---|---|---|---|
| Ag | 5.3390010 | 9.0668000 | 8.8378030 |
| Au | 7.7879590 | 9.9362840 | 10.9015060 |
| Au | 9.7875050 | 6.5421480 | 11.3440120 |
| Ag | 8.1551180 | 4.4898010 | 9.5374570 |
| Ag | 3.0478770 | 6.7331930 | 10.2017040 |
| Au | 1.9456580 | 9.7717300 | 8.9797260 |
| Au | 4.6529870 | 10.5060520 | 6.0961060 |
| Ag | 6.6329920 | 7.9048110 | 6.4615500 |
| Ag | 6.5449640 | 6.5927520 | 11.3750320 |
| Au | 4.1350570 | 6.2168670 | 13.5524710 |
| Au | 1.4785990 | 4.4313980 | 11.1839360 |
| Au | 2.9713640 | 4.7113170 | 8.2515960 |
| Au | 5.4877380 | 6.0308910 | 8.5874320 |
| S | 5.6757890 | 11.0614430 | 10.4499090 |
| S | 9.9227270 | 8.9788890 | 11.6460670 |
| S | 9.8684670 | 4.0722550 | 11.4275240 |
| S | 2.9186990 | 11.5111240 | 7.5207410 |
| S | 6.5248650 | 9.8125800 | 4.6602580 |
| S | 6.3606870 | 7.1944010 | 13.9072600 |

| | | | |
|---|---|---|---|
| S | 1.8059070 | 5.4176170 | 13.4373250 |
| S | 0.8255110 | 3.4349180 | 9.0499680 |
| Ag | 5.1900820 | 3.0201630 | 8.3775110 |
| Au | 3.1817000 | 2.0676100 | 6.1086340 |
| Au | 1.2782000 | 5.5636440 | 5.9201000 |
| Au | 3.3973170 | 7.5401640 | 7.3955820 |
| Au | 7.7393790 | 5.2374290 | 6.8498470 |
| Au | 8.6878650 | 2.0583380 | 7.9039620 |
| Au | 6.1770050 | 1.6098830 | 11.0696170 |
| Au | 4.6034090 | 4.3743620 | 10.7362570 |
| Ag | 4.2561280 | 5.3885230 | 5.7530670 |
| Au | 6.8187160 | 5.6490580 | 3.6620760 |
| Au | 9.5717050 | 7.4574800 | 6.0641890 |
| Au | 7.9830800 | 7.2638650 | 8.8445770 |
| S | 5.2975070 | 1.0129100 | 6.7406910 |
| S | 1.0465970 | 3.1142030 | 5.4821750 |
| S | 1.2764440 | 8.0348320 | 5.9371730 |
| S | 8.0370390 | 0.5922770 | 9.7869710 |
| S | 4.2894900 | 2.4025920 | 12.4141630 |
| S | 4.5499440 | 4.8246700 | 3.2349930 |
| S | 9.1415810 | 6.4879440 | 3.8108170 |
| S | 10.1037120 | 8.6144820 | 8.1758860 |
| S | 8.8684200 | 3.1927270 | 5.7387110 |
| S | 0.8381030 | 8.1254820 | 10.4142590 |

8-Ag

| | | | |
|---|---|---|---|
| Ag | 5.4280300 | 9.1043240 | 9.0475300 |
| Au | 7.7759680 | 10.0703530 | 11.0797840 |
| Au | 9.6788220 | 6.5122570 | 11.4112260 |
| Au | 7.5307490 | 4.4253720 | 9.7293830 |
| Ag | 3.0186240 | 6.7935080 | 10.2730930 |
| Au | 1.8791770 | 9.9465270 | 9.1032280 |
| Au | 4.7205780 | 10.6325920 | 6.1155480 |
| Ag | 6.5573420 | 7.7797050 | 6.2332340 |
| Ag | 6.6019250 | 6.6135190 | 11.4683750 |
| Au | 4.0624690 | 6.3170230 | 13.6510710 |
| Au | 1.3136410 | 4.5105860 | 11.2027840 |
| Au | 3.0111360 | 4.6755660 | 8.2512160 |
| Au | 5.4656900 | 6.0857140 | 8.5446060 |
| S | 5.6825230 | 11.1955490 | 10.5174190 |
| S | 9.8886100 | 8.9631080 | 11.7184160 |
| S | 9.6149730 | 4.0620450 | 11.2650020 |
| S | 2.9151630 | 11.5601290 | 7.5363980 |
| S | 6.5197860 | 9.8298650 | 4.6418800 |
| S | 6.3087210 | 7.2600200 | 13.9500040 |
| S | 1.7594200 | 5.4550570 | 13.4596260 |
| S | 0.7888650 | 3.4791140 | 9.0538710 |
| Au | 5.6396630 | 3.1930740 | 8.1419270 |
| Au | 3.2464950 | 2.1853230 | 6.2483370 |
| Au | 1.1549110 | 5.5315260 | 5.7992030 |
| Ag | 3.0168760 | 7.5202370 | 7.3747320 |

| | | | |
|---|---|---|---|
| Au | 7.5305420 | 5.0662680 | 6.8680930 |
| Au | 8.5232170 | 2.2915520 | 7.9280660 |
| Au | 6.2855920 | 1.6703260 | 10.9902100 |
| Ag | 4.5204490 | 3.8956520 | 10.5877860 |
| Ag | 4.7224870 | 4.7099240 | 5.9278470 |
| Au | 6.8068930 | 5.6959310 | 3.6469220 |
| Au | 9.6248000 | 7.5225630 | 5.9722990 |
| Ag | 8.4117720 | 6.9663560 | 8.7817210 |
| S | 5.3371950 | 1.0029430 | 6.7425330 |
| S | 1.0561840 | 3.0831240 | 5.5311430 |
| S | 1.0682770 | 7.9942570 | 5.7323190 |
| S | 8.1010290 | 0.5941300 | 9.7140480 |
| S | 4.3814690 | 2.1532750 | 12.5198580 |
| S | 4.5273170 | 4.8428650 | 3.3427210 |
| S | 9.1403470 | 6.5037270 | 3.7653670 |
| S | 10.2393490 | 8.6756730 | 8.0654540 |
| S | 8.8724270 | 3.2025140 | 5.6486310 |
| S | 0.8051180 | 8.2282890 | 10.4692680 |

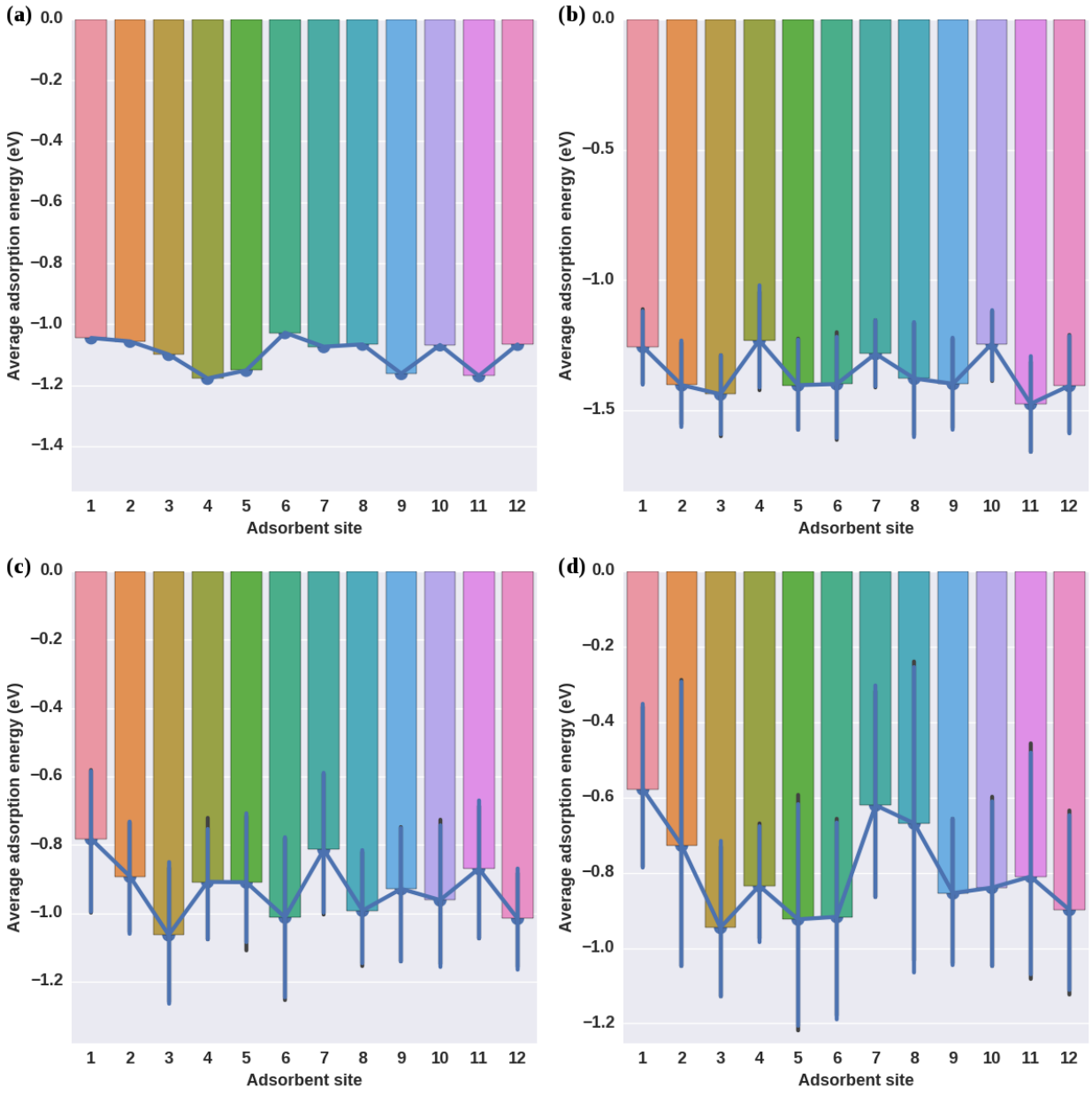


*Figure 21: Average CO adsorption energies at the 12 adsorbent sites in the outer shell for (a) 0, (b) 6-, (c) 7- and (d) 8-Ag alloyed structures. Adsorption energies are calculates considering the adsorption on 10 lowest energy isomers.*

# References

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