

Analysis of O₂ Adsorption on Binary-Alloy Clusters of Gold: Energetics and Correlations

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Supporting Information:

(A) Assessment of the Basis Set convergence

We repeated the O₂ adsorption calculations on Pd₂, PdAu, Pt₂, and PtAu using larger basis sets cc-pVTZ (triple-zeta), cc-pVQZ (quadruple-zeta), and cc-pV5Z (quintuple-zeta) to investigate the basis set convergence issue. These basis sets include polarization functions by definition. The valence polarization functions are listed in the brackets: cc-pVTZ (4s, 3p, 2d, 1f), cc-pVQZ (5s, 4p, 3d, 2f, 1g), and cc-pV5Z (6s, 5p, 4d, 3f, 2g, 1h). Therefore, one can systematically achieve the convergence of the electronic energy to the complete basis set limit. Moreover, these basis sets are useful in systematically recovering a significant fraction of the correlation energy.

In the table below, we have compared the O₂ binding energies reported in the paper (6-311+G(3df) basis set) with the BE values calculated using the aforementioned basis sets. It is clear that the BE values are converged for the cc-pV5Z basis set. Moreover, these converged values are in good agreement with the BE values reported in the paper. We conclude that the BE values in our paper are almost converged to the complete basis set (CBS) limit.

It is also clear from the table that the BE trends on Pd₂, PdAu, Pt₂, and PtAu remain unchanged even when cc-pVTZ, cc-pVQZ, and cc-pV5Z basis sets are employed. In conclusion, the lack of any general trend for dimers cannot be attributed to the basis set limitations.

Cluster	BE (kcal/mol) of O ₂ calculated using the B3LYP functional and different basis sets for O atom as shown below. LANL2DZ was used for heavy atoms.			
	Paper: 6-311+G(3df)	cc-pVTZ	cc-pVQZ	cc-pV5Z
PdAu	6.61	6.32	6.59	6.78
PtAu	22.80	21.20	22.20	22.54
Pd ₂	26.33	25.30	25.50	25.72
Pt ₂	12.86	12.40	12.59	12.80

(B) Mulliken Spin Density analysis for O₂ adsorption

Pure and Au-alloy dimers: The atom numbers correspond to the Figures 1 and 2 in the paper.

Cluster	Spin Density on Each Atom				Spin Density	Total Spin Density
	Atom 1	Atom 2	Atom 3	Atom 4		
Au ₂ -O ₂	0.07	0.01	0.90	1.02	1.92	2.00
Ag ₂ -O ₂	-0.03	0.09	1.00	0.94	1.94	2.00
AgAu-O ₂	0.07	-0.01	1.02	0.92	1.94	2.00
Cu ₂ -O ₂	0.07	0.22	0.92	0.79	1.71	2.00
CuAu-O ₂	0.13	0.12	0.80	0.96	1.75	2.00
Na ₂ -O ₂	0.39	0.66	0.38	0.56	0.95	2.00
NaAu-O ₂	0.26	-0.07	0.83	0.97	1.80	2.00
Pd ₂ -O ₂	0.36	0.36	0.64	0.64	1.28	2.00
PdAu-O ₂	-0.34	-0.27	0.87	0.73	1.61	1.00
Pt ₂ -O ₂	0.26	0.78	0.45	0.50	0.96	2.00
PtAu-O ₂	-0.04	0.03	0.56	0.45	1.01	1.00

Pure and Au-alloy trimers: The atom numbers correspond to the Figures 3 to 7 in the paper.

Cluster	Spin Density on Each Atom					Spin Density	Total Spin Density
	Atom 1	Atom 2	Atom 3	Atom 4	Atom 5		
Au ₃	0.51	0.51	-0.02	---	---	---	1.00
Au ₃ -O ₂	-0.08	-0.08	-0.02	0.59	0.60	1.19	1.00
Ag ₃	0.54	-0.09	0.54	---	---	---	1.00
Ag ₃ -O ₂	-0.03	-0.01	-0.03	0.54	0.54	1.07	1.00
Ag ₂ Au	0.24	0.24	0.52	---	---	---	1.00
Ag ₂ Au-O ₂	-0.02	-0.02	-0.01	0.52	0.53	1.05	1.00
AgAu ₂	0.00	0.50	0.50	---	---	---	1.00
AgAu ₂ -O ₂	-0.03	-0.03	-0.02	0.56	0.53	1.08	1.00
Cu ₃	0.11	0.45	0.45	---	---	---	1.00
Cu ₃ -O ₂	-0.01	0.00	0.00	0.50	0.50	1.00	1.00
Cu ₂ Au	0.48	0.26	0.26	---	---	---	1.00

Cu ₂ Au-O ₂	-0.01	0.01	0.01	0.49	0.49	0.99	1.00
CuAu ₂	0.02	0.49	0.49	---	---	---	1.00
CuAu ₂ -O ₂	0.13	-0.26	-0.26	0.69	0.69	1.39	1.00
Na ₃	0.51	0.51	-0.02	---	---	---	1.00
Na ₃ -O ₂	-0.01	0.00	0.00	0.50	0.50	1.01	1.00
Na ₂ Au	0.16	0.42	0.42	---	---	---	1.00
Na ₂ Au-O ₂	0.00	0.00	0.00	0.50	0.50	1.01	1.00
NaAu ₂	-0.04	0.52	0.52	---	---	---	1.00
NaAu ₂ -O ₂	0.00	0.00	-0.03	0.49	0.54	1.03	1.00
Pd ₃	0.75	0.75	0.50	---	---	---	2.00
Pd ₃ -O ₂	0.39	0.35	0.35	0.46	0.45	0.91	2.00
Pd ₂ Au	0.03	0.49	0.49	---	---	---	1.00
Pd ₂ Au-O ₂	-0.02	0.04	0.04	0.47	0.47	0.95	1.00
PdAu ₂	0.41	-0.20	-0.20	---	---	---	0.00
PdAu ₂ -O ₂	0.36	0.01	0.01	0.77	0.84	1.62	2.00
Pt ₃	0.43	0.78	0.78	---	---	---	2.00
Pt ₃ -O ₂	0.20	0.88	0.20	0.36	0.36	0.72	2.00
Pt ₂ Au	-0.05	0.52	0.52	---	---	---	1.00
Pt ₂ Au-O ₂	-0.03	0.14	0.14	0.37	0.37	0.74	1.00
PtAu ₂	0.08	-0.04	-0.04	---	---	---	0.00
PtAu ₂ -O ₂	0.40	0.05	0.07	0.68	0.79	1.47	2.00

(C) Investigation of fragmentation of bare and O₂-covered clusters

We investigated all possible combinations in which the clusters might decompose to form smaller clusters or separated constituent atoms. The energy required for decomposition/fragmentation of bare and O₂-covered clusters (ΔE_{Frag} = sum of energy of fragments – energy of intact cluster or cluster-O₂ complex) was calculated. This data is provided in the table below. Clearly, all the bare and O₂-covered clusters reported in our paper are more stable than their fragments and hence stability of these clusters is not a concern.

Fragmentation Channel	Fragmentation Energy ΔE_{Frag} (kcal/mol)	Fragmentation Channel	Fragmentation Energy ΔE_{Frag} (kcal/mol)
Au ₂ = 2Au	43.20	Au ₃ -O ₂ = Au + Au ₂ -O ₂	24.44
Ag ₂ = 2Ag	35.81	Ag ₃ -O ₂ = Ag + Ag ₂ -O ₂	34.66
Cu ₂ = 2Cu	46.48	Cu ₃ -O ₂ = Cu + Cu ₂ -O ₂	57.84
Na ₂ = 2Na	17.37	Na ₃ -O ₂ = Na + Na ₂ -O ₂	26.05
Pd ₂ = 2Pd	22.13	Pd ₃ -O ₂ = Pd + Pd ₂ -O ₂	28.11
Pt ₂ = 2Pt	84.19	Pt ₃ -O ₂ = Pt + Pt ₂ -O ₂	78.46

AgAu = Ag + Au	44.18	Au3-O2 = Au2 + Au1-O2	25.90
CuAu = Cu + Au	52.86	Ag3-O2 = Ag2 + Ag1-O2	31.55
NaAu = Na + Au	57.08	Cu3-O2 = Cu2 + Cu1-O2	49.57
PdAu = Pd + Au	36.04	Na3-O2 = Na2 + Na1-O2	24.27
PtAu = Pt + Au	54.52	Pd3-O2 = Pd2 + Pd1-O2	37.60
		Pt3-O2 = Pt2 + Pt1-O2	59.51
Au3 = 3Au	63.47		
Ag3 = 3Ag	51.19	Ag2Au-O2 = Au + Ag2-O2	46.54
Cu3 = 3Cu	69.55	Ag2Au-O2 = Ag + AgAu-O2	37.09
Na3 = 3Na	23.27	AgAu2-O2 = Ag + Au2-O2	33.49
Pd3 = 3Pd	58.96	AgAu2-O2 = Au + AgAu-O2	33.45
Pt3 = 3Pt	157.42	Cu2Au-O2 = Au + Cu2-O2	68.42
		Cu2Au-O2 = Cu + CuAu-O2	59.50
Au3 = Au + Au2	20.27	CuAu2-O2 = Cu + Au2-O2	53.23
Ag3 = Ag + Ag2	15.38	CuAu2-O2 = Au + CuAu-O2	36.04
Cu3 = Cu + Cu2	23.08	Na2Au-O2 = Au + Na2-O2	80.86
Na3 = Na + Na2	5.89	Na2Au-O2 = Na + NaAu-O2	69.07
Pd3 = Pd + Pd2	36.83	NaAu2-O2 = Na + Au2-O2	61.78
Pt3 = Pt + Pt2	73.23	NaAu2-O2 = Au + NaAu-O2	46.73
		Pd2Au-O2 = Au + Pd2-O2	46.89
Ag2Au = Ag2 + Au	26.25	Pd2Au-O2 = Pd + PdAu-O2	52.70
AgAu2 = Ag + Au2	24.13	PdAu2-O2 = Pd + Au2-O2	43.30
Cu2Au = Cu2 + Au	33.89	PdAu2-O2 = Au + PdAu-O2	46.67
CuAu2 = Cu + Au2	36.65	Pt2Au-O2 = Au + Pt2-O2	57.64
Na2Au = Na2 + Au	53.94	Pt2Au-O2 = Pt + PtAu-O2	77.37
NaAu2 = Na + Au2	44.56	PtAu2-O2 = Pt + Au2-O2	68.97
Pd2Au = Pd2 + Au	55.09	PtAu2-O2 = Au + PtAu-O2	37.67
PdAu2 = Pd + Au2	34.95		
Pt2Au = Pt2 + Au	40.81	Ag2Au-O2 = AgAu + Ag1-O2	35.04
PtAu2 = Pt + Au2	54.14	Ag2Au-O2 = Ag2 + Au1-O2	45.98
		AgAu2-O2 = AgAu + Au1-O2	33.97
Au2O2 = Au1 + Au1-O2	44.67	AgAu2-O2 = Au2 + Ag1-O2	32.39
Ag2O2 = Ag1 + Ag1-O2	32.69	Cu2Au-O2 = CuAu + Cu1-O2	53.76
Cu2O2 = Cu1 + Cu1-O2	38.20	Cu2Au-O2 = Cu2 + Au1-O2	74.88
Na2O2 = Na1 + Na1-O2	15.60	CuAu2-O2 = CuAu + Au1-O2	45.04
Pd2O2 = Pd1 + Pd1-O2	31.62	CuAu2-O2 = Au2 + Cu1-O2	39.97
Pt2O2 = Pt1 + Pt1-O2	65.24	Na2Au-O2 = NaAu + Na1-O2	39.38
		Na2Au-O2 = Na2 + Au1-O2	111.42
AgAu-O2 = Au1 + Ag1-O2	42.14	NaAu2-O2 = NaAu + Au1-O2	49.37
AgAu-O2 = Ag1 + Au1-O2	44.71	NaAu2-O2 = Au2 + Na1-O2	30.92
CuAu-O2 = Au1 + Cu1-O2	47.12	Pd2Au-O2 = PdAu + Pd1-O2	42.47
CuAu-O2 = Cu1 + Au1-O2	61.86	Pd2Au-O2 = Pd2 + Au1-O2	71.86
NaAu-O2 = Au1 + Na1-O2	27.39	PdAu2-O2 = PdAu + Au1-O2	51.92
NaAu-O2 = Na1 + Au1-O2	59.72	PdAu2-O2 = Au2 + Pd1-O2	29.28
PdAu-O2 = Au1+ Pd1-O2	25.81	Pt2Au-O2 = PtAu + Pt1-O2	68.36
PdAu-O2 = Pd1+ Au1-O2	41.29	Pt2Au-O2 = Pt2 + Au1-O2	69.15
PtAu-O2 = Au1 + Pt1-O2	45.52	PtAu2-O2 = PtAu + Au1-O2	59.11
PtAu-O2 = Pt1 + Au1-O2	75.96	PtAu2-O2 = Au2 + Pt1-O2	39.99

(D) Sources of scatter in correlations: Geometric effect

We found an approximate linear correlation between the $E_{\text{HOMO-Cluster}} - E_{\text{LUMO-O}_2}$ and the NBO charge on adsorbed O₂ (Paper: Figure 12, $R^2 = 0.69$). There is also an approximate linear relationship between the O₂ BE and $E_{\text{HOMO-Cluster}} - E_{\text{LUMO-O}_2}$ (Paper: Figure 13). There are several potential sources of scatter in these correlations as discussed in the paper. The geometric effect can be isolated using a simple test as described below.

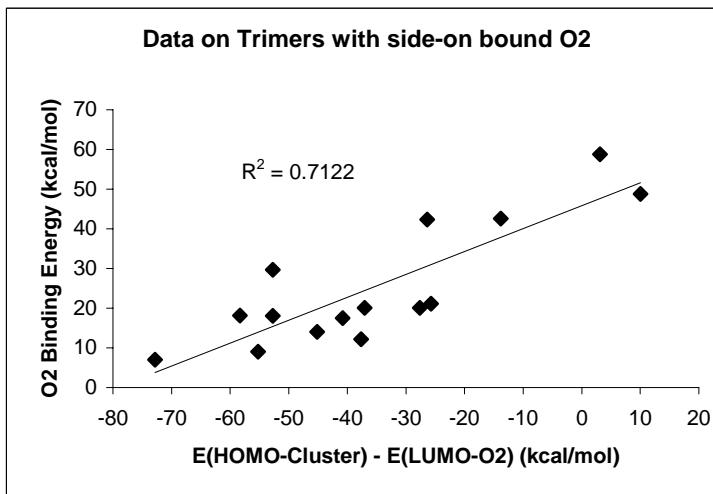
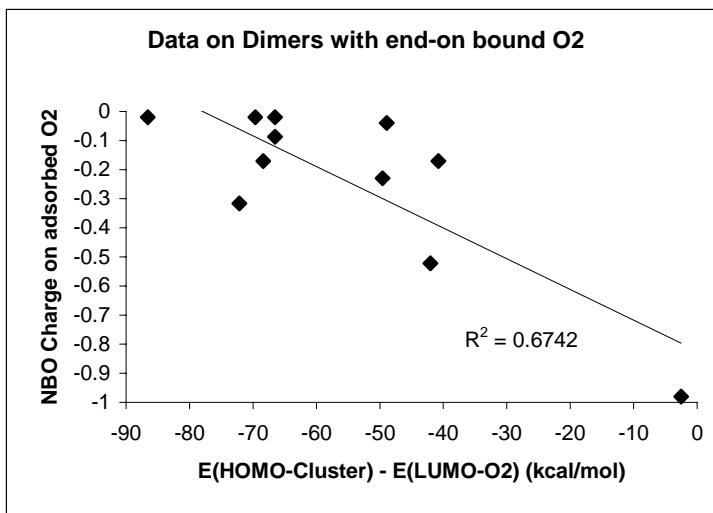
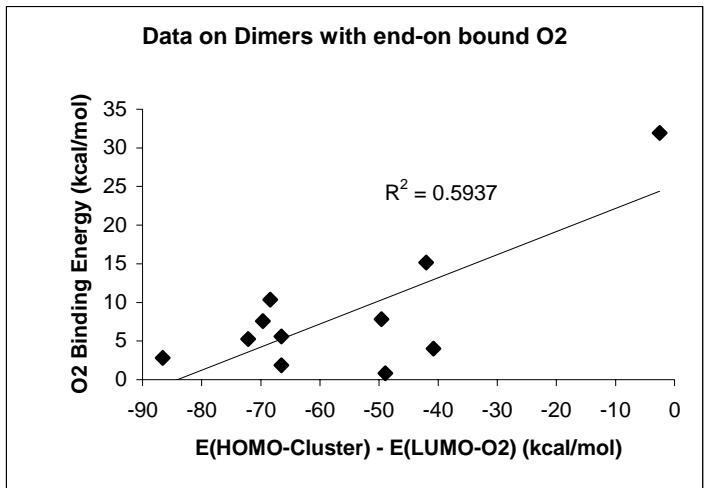
Since we have data for several different binding orientations of O₂ on each cluster, we selected the cluster-O₂ geometries with uniform (similar) binding orientations and examined the aforementioned correlations for dimers and trimers separately. For example, we used the BE and NBO charge data for geometries with O₂ end-on bound on dimers and side-on bound on trimers. We note that some of these geometries are not the ground state geometries. We made plots of BE versus $E_{\text{HOMO-Cluster}} - E_{\text{LUMO-O}_2}$ and charge-transfer versus $E_{\text{HOMO-Cluster}} - E_{\text{LUMO-O}_2}$ for dimers (end-on O₂) and separately for trimers (side-on O₂). We found that the R^2 values for these correlations (uniform binding orientation of O₂) are somewhat better than the R^2 values corresponding to the data reported in the paper (for ground state cluster-O₂ geometries). Therefore, part of the scatter in the correlations reported in the paper is due to geometric effects, i.e., due to the differences in the ground-state O₂ binding orientation on different clusters.

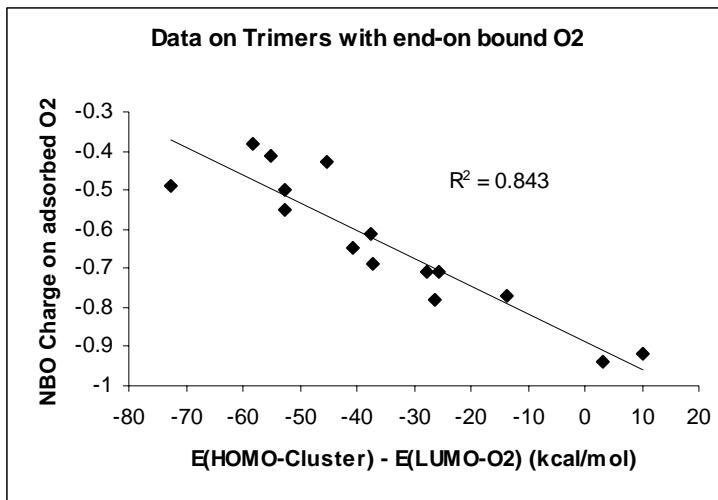
We note that the best results were obtained when data for only end-on O₂ binding was used for dimers and data for only side-on O₂ binding was used for trimers. In the following table we have compared the R^2 values for the data in the paper with the data for uniform O₂ adsorption site.

For dimers: the BE versus $E_{\text{Cluster-HOMO}} - E_{\text{O}_2\text{-LUMO}}$ correlation improved significantly when data on end-on bound O₂ was used. Still, the R^2 value is only 0.59. The Charge-transfer versus $E_{\text{Cluster-HOMO}} - E_{\text{O}_2\text{-LUMO}}$ correlation improved only slightly.

For trimers: the the BE versus $E_{\text{Cluster-HOMO}} - E_{\text{O}_2\text{-LUMO}}$ correlation became slightly worse when data on side-on bound O₂ was used. On the other hand, the Charge-transfer versus $E_{\text{Cluster-HOMO}} - E_{\text{O}_2\text{-LUMO}}$ correlation improved significantly ($R^2 = 0.84$). Plots are shown below.

R^2 values for data in the Original Manuscript		R^2 values for data on similar O ₂ binding sites	
BE versus $E_{\text{Cluster-HOMO}} - E_{\text{O}_2\text{-LUMO}}$	O ₂ NBO Charge versus $E_{\text{Cluster-HOMO}} - E_{\text{O}_2\text{-LUMO}}$	BE versus $E_{\text{Cluster-HOMO}} - E_{\text{O}_2\text{-LUMO}}$	O ₂ NBO Charge versus $E_{\text{Cluster-HOMO}} - E_{\text{O}_2\text{-LUMO}}$
Ground State of Dimer-O ₂		Dimer-O ₂ : Data for end-on binding	
$R^2 = 0.31$	$R^2 = 0.63$	$R^2 = 0.59$	$R^2 = 0.67$
Ground State of Trimer-O ₂		Trimer-O ₂ : Data for side-on binding	
$R^2 = 0.74$	$R^2 = 0.70$	$R^2 = 0.71$	$R^2 = 0.84$





Overall, these results suggest that the scatter in correlations can be attributed to some extent to O₂ adsorption on different sites. However, a significant portion of the scatter is still unexplained.