Electronic Supplementary Information

Geometric and Electronic Properties of Gold Clusters Doped with a Single Oxygen Atom

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Table S1 The favourite dissociation channels for Au_n^q and Au_nO^q clusters by B3LYP and PBE. Channels with Au or Au_2 as a fragment are shown in black, and other channels with O (AuO) as a fragment are shown in red (blue).

Channels for Au_n^q	Energy (eV)		Channels for Au_nO^q	Energy (eV)	
	B3LYP	PBE		B3LYP	PBE
			$AuO^- \rightarrow Au^- + O$	2.01	2.70
			$AuO \rightarrow Au + O$	1.99	2.62
			$AuO^+ \rightarrow Au^+ + O$	1.42	2.21
$Au_2^- \rightarrow Au^- + Au$	1.70	1.97	$Au_2O^- \rightarrow AuO^- + Au$	2.76	2.90
$Au_2 \rightarrow Au + Au$	1.91	2.23	$Au_2O \rightarrow AuO + Au$	1.69	2.09
$Au_2^+ \rightarrow Au^+ + Au$	2.03	2.36	$Au_2O^+ \rightarrow Au_2^+ + O$	2.45	3.16
			$\rightarrow AuO + Au^+$	2.49	2.90[a]
$Au_3^- \rightarrow Au_2 + Au^-$	2.34	2.60	$Au_3O^- \rightarrow Au_2O^- + Au$	1.67	2.11
$Au_3 \rightarrow Au_2 + Au$	0.91	1.23	$Au_3O \rightarrow Au_2 + AuO$	1.46	1.86
$Au_3^+ \rightarrow Au_2^+ + Au$	3.04	3.39	$Au_3O^+ \rightarrow Au_3^+ + O$	1.45	2.11
$Au_4^- \rightarrow Au_3^- + Au$	1.26	1.55	$Au_4O^- \rightarrow Au_2O^- + Au_2$	1.94	2.35
$Au_4 \rightarrow Au_2 + Au_2$	0.98	1.34	$Au_4O \rightarrow Au_2O + Au_2$	1.43	1.82
$Au_4^+ \rightarrow Au_3^+ + Au$	1.23	1.65	$Au_4O^+ \rightarrow Au_3^+ + AuO$	1.73	2.11
$Au_5^- \rightarrow Au_3^- + Au_2$	1.60	1.92	$Au_5O^- \rightarrow Au_4O^- + Au$	1.88	2.46
$Au_5 \rightarrow Au_4 + Au$	1.69	2.13	$Au_5O \rightarrow Au_3O + Au_2$	2.09	2.52
$Au_5^+ \rightarrow Au_3^+ + Au_2$	1.87	2.20	$Au_5O^+ \rightarrow Au_5^+ + O$	1.76	2.66
			$\rightarrow Au_4O^+ + Au$	1.83	2.36[a]
$Au_6^- \rightarrow Au_5^- + Au$	1.33	1.93	$Au_6O^- \rightarrow Au_4O^- + Au_2$	1.58	2.26
			$\rightarrow Au_5O^- + Au$	1.61	2.03[a]
$Au_6 \rightarrow Au_4 + Au_2$	2.42	2.89	$Au_6O \rightarrow Au_5O + Au$	1.62	2.06
$Au_6^+ \rightarrow Au_5^+ + Au$	1.41	2.09	$Au_6O^+ \rightarrow Au_5^+ + AuO$	1.95	2.33
			$\rightarrow Au_5O^+ + Au$	2.18	2.28[a]
$Au_7^- \rightarrow Au_5^- + Au_2$	1.85	2.39	$Au_7O^- \rightarrow Au_5O^- + Au_2$	2.29	2.70
$Au_7 \rightarrow Au_6 + Au$	1.10	1.51	$Au_7O \rightarrow Au_5O + Au_2$	2.09	2.50
$Au_7^+ \rightarrow Au_5^+ + Au_2$	2.05	2.65	$Au_7O^+ \rightarrow Au_7^+ + O$	1.80	2.75
			$\rightarrow Au_6O^+ + Au$	1.82	2.69[a]
$Au_8^- \rightarrow Au_7^- + Au$	1.77	2.23	$Au_8O^- \rightarrow Au_7O^- + Au$	1.25	1.65
$Au_8 \rightarrow Au_6 + Au_2$	1.66	2.03	$Au_8O \rightarrow Au_7O + Au$	1.51	1.96
$Au_8^+ \rightarrow Au_7^+ + Au$	1.56	2.05	$Au_8O^+ \rightarrow Au_7^+ + AuO$	2.06	2.54
			$\rightarrow Au_7O^+ + Au$	2.26	2.41[a]

[a] For Au_6O^- and $Au_{2,5,6,7,8}O^+$, PBE suggests another channels to be favourite, but the energy difference of the two channels for each cluster is small (less than 0.3 eV).

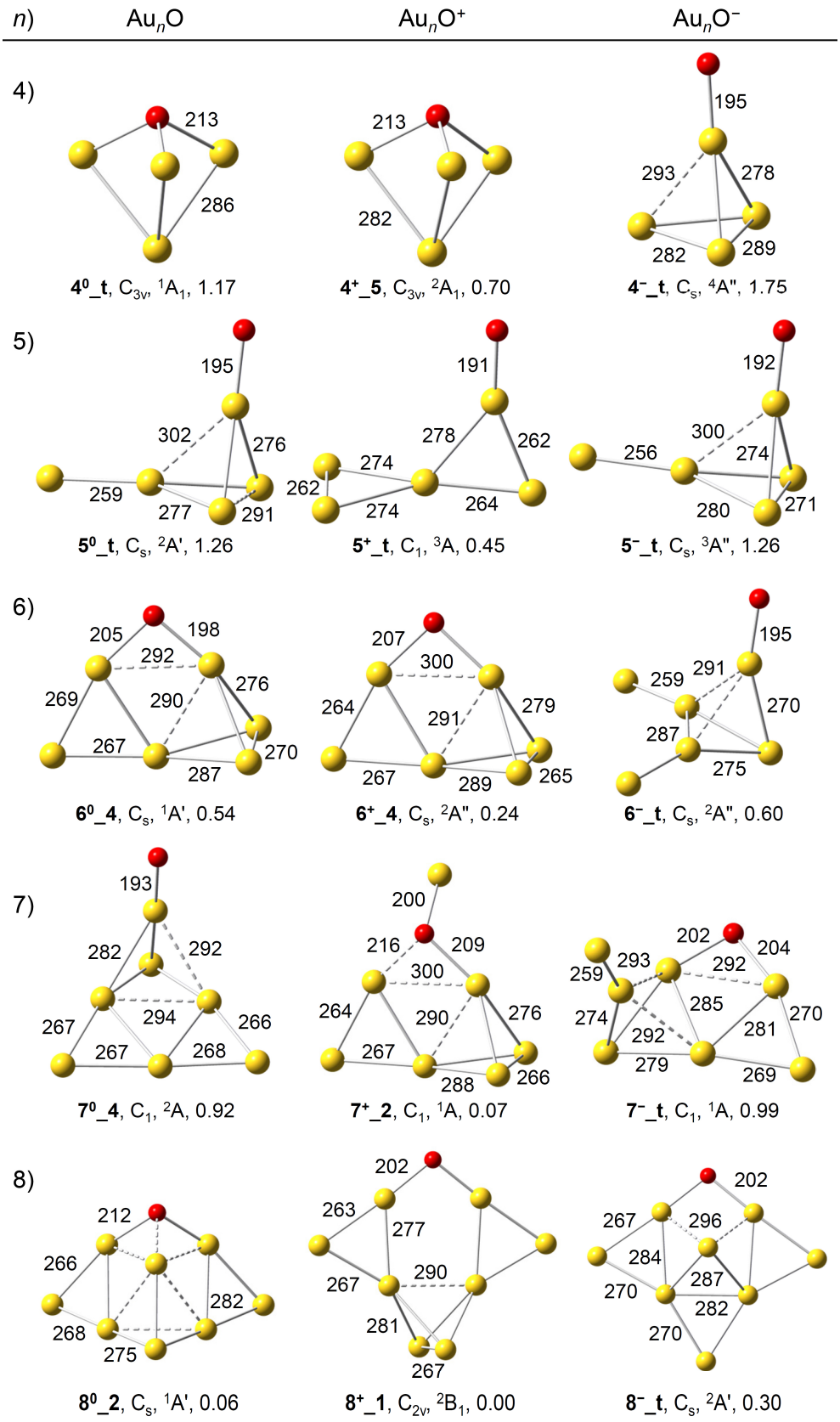

Figure S1. A replot of Figures 4-8 for B3LYP optimized most stable three-dimensional structures of Au$_n$O^q (n = 4-8, q = 0, ±1). The symmetry, electronic state, and relative energy (in eV) with respect to the ground state are listed below each structure. Bond lengths are labelled in picometre, and dashed lines denote Au−Au bonds between 290 and 310 pm or Au-O bonds in 215-230 pm.

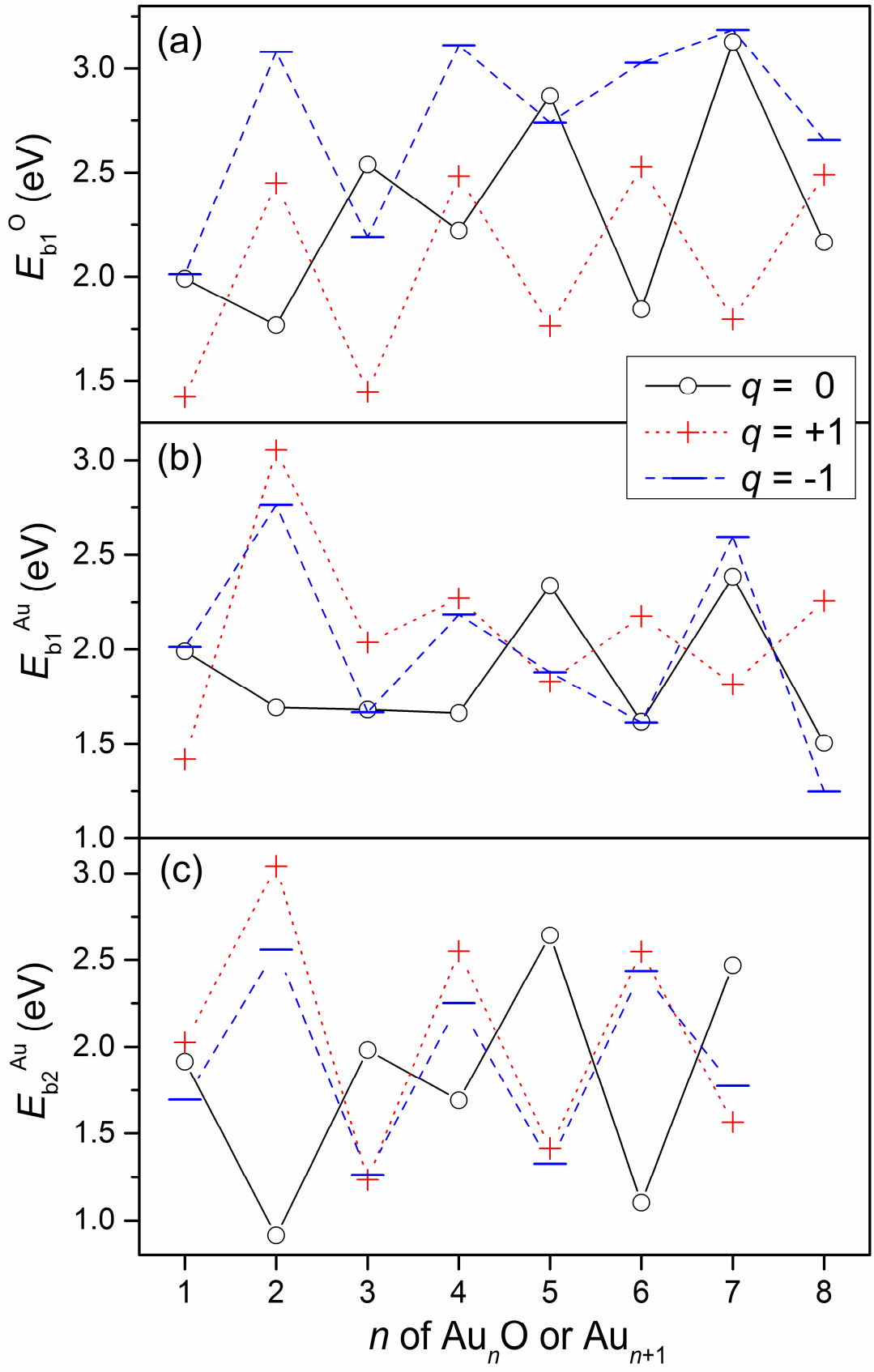

Figure S2. A replot of Figure 11 for the binding energies of an O or Au in Au_nO^q, or an Au in Au_n^q, as shown in (a) $E_{b1}{}^{O}$, (b) $E_{b1}{}^{Au}$, and (c) $E_{b2}{}^{Au}$, respectively. Clusters with different charge states (i.e., $q = 0, \pm 1$) are shown in each panel.

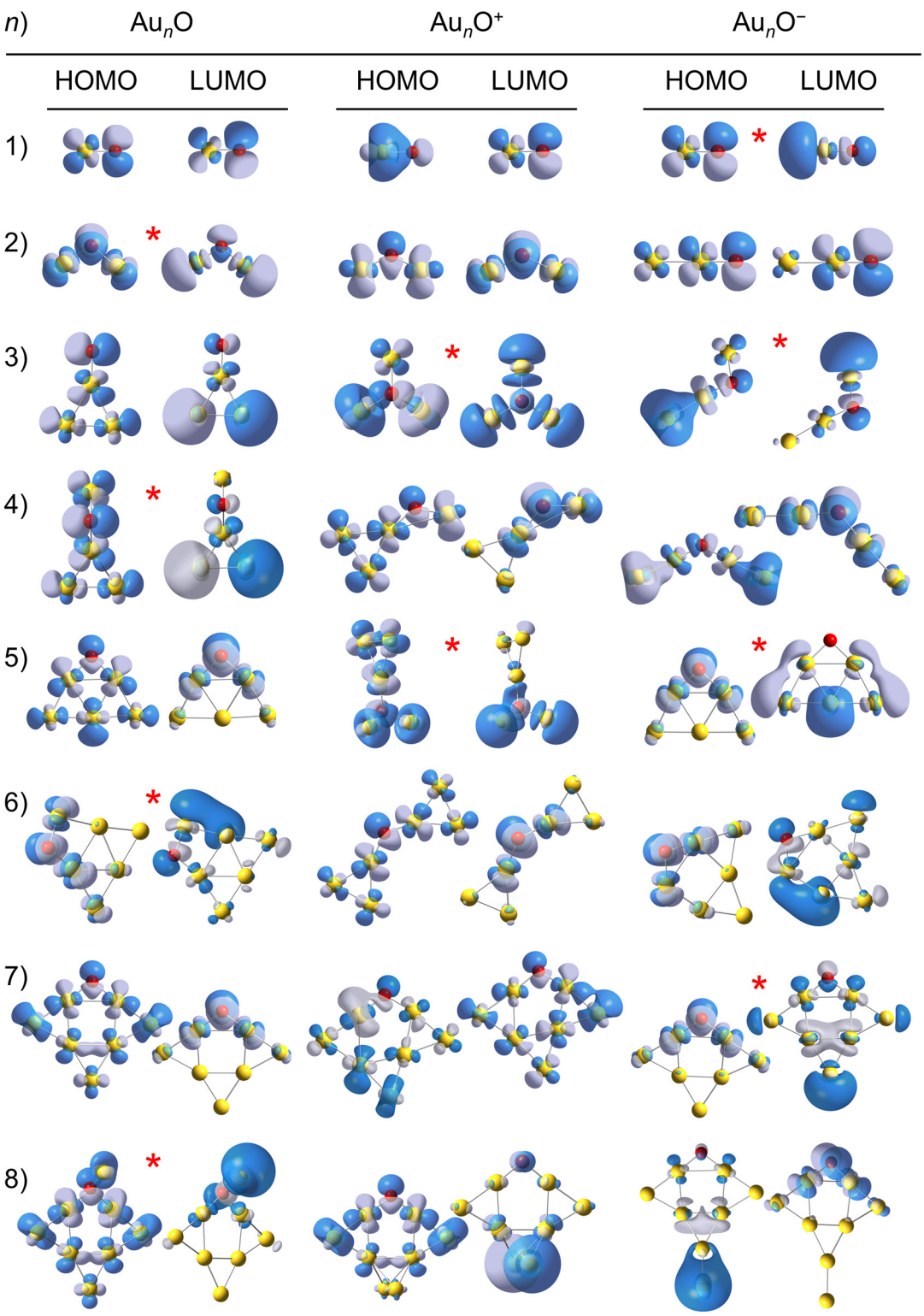

Figure S3. The highest-occupied and lowest-unoccupied spin-down molecular orbitals (MO) of Au_nO^q clusters (n = 1−8 in the n^{th} panel, and q = 0, ±1). Note that spin-up and spin-down MOs are identical for singlet states (denoted with stars), and clusters whose HOMO (Au_6O^- and Au_7O^+) or LUMO (Au_3O) are spin-up have been illustrated in Figure 12.