DFT investigation of Au_nMo (n = 2-12) Clusters:

The Barrierless Hydrogen Adsorption Behavior of Au_9Mo

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SUPPORTING INFORMATION

Contents:

1. Structures of low-lying isomers of molecularly and dissociative adsorbed H_2 on Au_nMo clusters (n = 2-12): Figs. S1, S2 and S3.

2. Partial and total densities of states (DOS) of thermodynamically preferred configurations for hydrogen adsorbed on Au_nMo (n = 2-12) clusters: Figs. S4 and S5.

3. The energy profiles (n = 5-9) as well as the intrinsic reaction coordinates (n = 5, 7) for dissociation of H_2 on Au_nMo clusters: Figs. S6, and S7.

4. Molecular diagrams and density electronic of state for the most stable Au_9Mo and Au_9Y clusters: Figs. S8, and Figs. S9.

5. Electronic configurations and molecular diagrams for the most stable configuration of hydorgen adsorbed: Figs. S10

5. Calculated NBO Charge Distribution on the most stable of Au_nMo and $Au_nMo@H_2$ (n = 2-12). Mo represents Mo atom, while Au-1 and Au-2 label two Au atoms that bind to the corresponding H atoms, H-1 and H-2: Table S2.
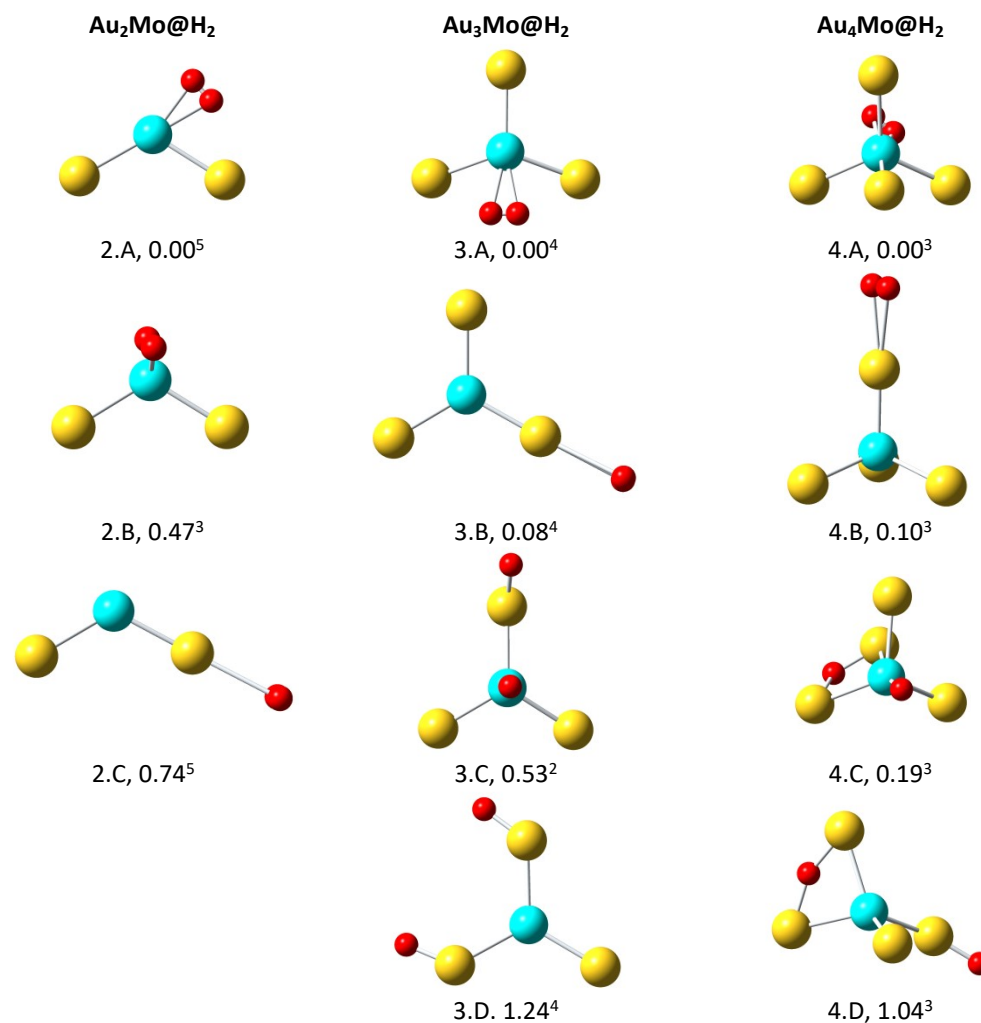
Au$_2$Mo@H$_2$ **Au$_3$Mo@H$_2$** **Au$_4$Mo@H$_2$**

2.A, 0.00^5 3.A, 0.00^4 4.A, 0.00^3

2.B, 0.47^3 3.B, 0.08^4 4.B, 0.10^3

2.C, 0.74^5 3.C, 0.53^2 4.C, 0.19^3

3.D. 1.24^4 4.D, 1.04^3

Fig. S1. *Optimized structures, spin configurations, and relative energies (in eV) of computed lowest-energy isomers of Au$_n$Mo clusters (n = 2-4) with an adsorbed hydrogen molecule. We denote each structure as **n.a,b^x**, in which n stands for number of Au atoms in Au$_n$Mo clusters, **a** is labeled as A, B, C, and D for isomers with increasing order of energy, b is the relative energy (in eV), and x refers to the spin configuration. The yellow, cyan, and red spheres represent Au, Mo, and H atoms, respectively.*

Au₅Mo@H₂
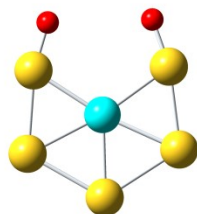
Au₆Mo@H₂

Au₇Mo@H₂

Au₈Mo@H₂

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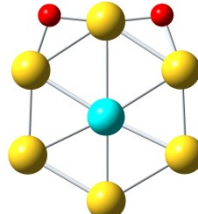
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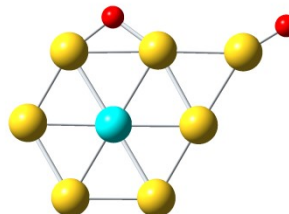
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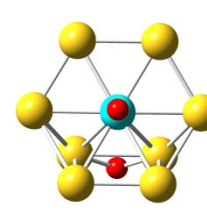
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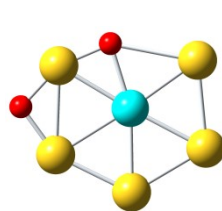
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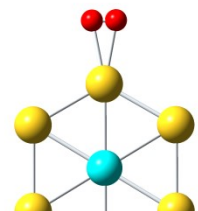
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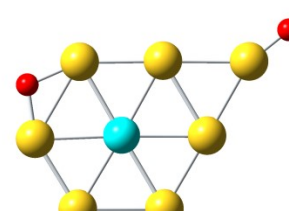
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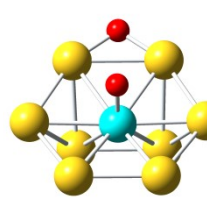
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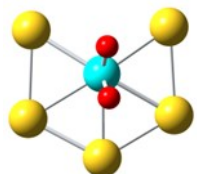
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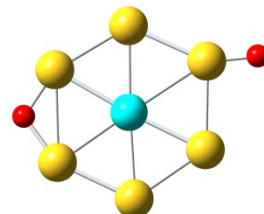
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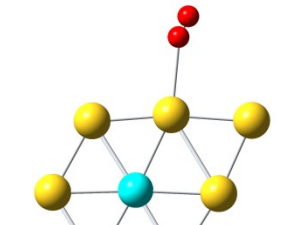
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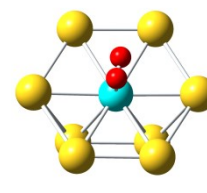
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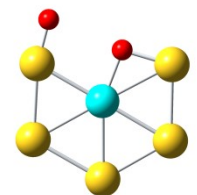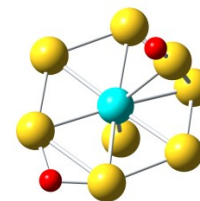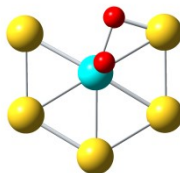
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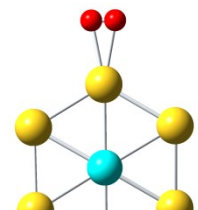
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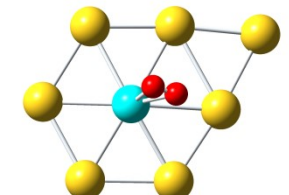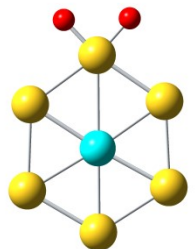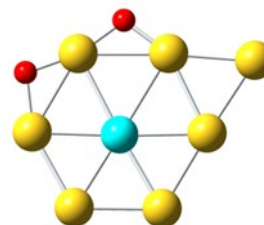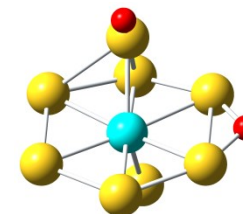
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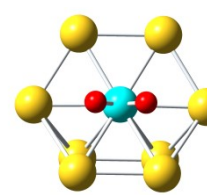
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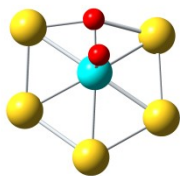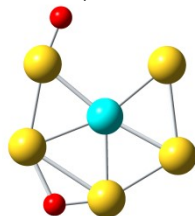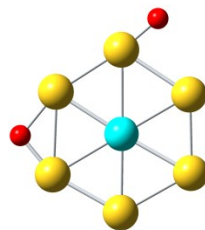
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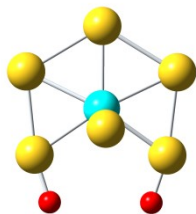
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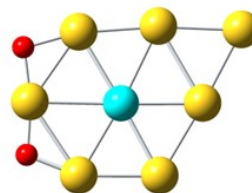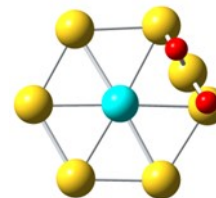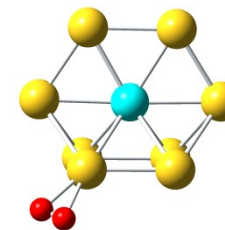
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5.F, 0.17[4]

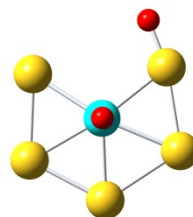6.F, 0.46[5]
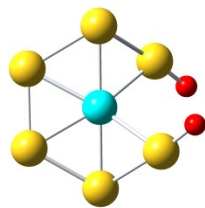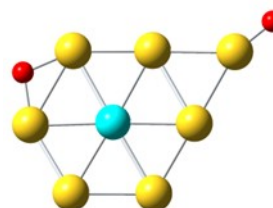
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8.F, 0.13[3]

5.G, 0.19[4]

6.G, 0.56[3]

7.G, 0.62[4]

8.G, 0.22[3]

5.H, 0.29[2]

6.H, 0.56[5]

7.H, 0.70[4]

8.H, 0.22[3]

5.I, 0.30^2

5.I, 0.62^3

7.I, 0.70^2

8.H, 0.25^3

5.K, 0.38^6

6.K, 0.83^3

7.K, 0.72^6

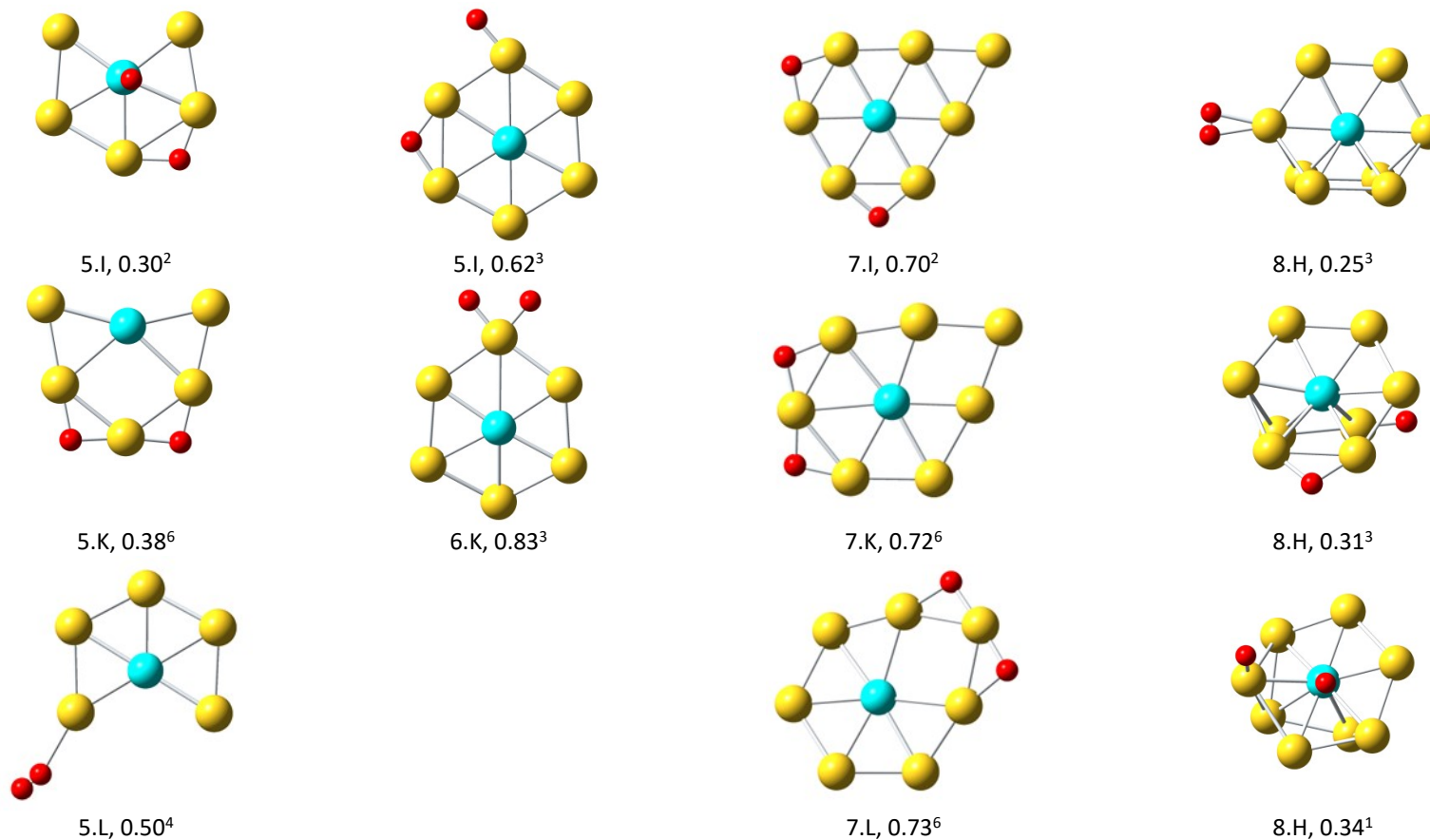8.H, 0.31^3

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7.L, 0.73^6

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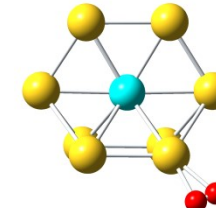
Fig. S2. *Optimized structures, spin configurations, and relative energies (in eV) of computed lowest-energy isomers of Au$_n$Mo clusters (n = 5-8) with an adsorbed hydrogen molecule. We denote each structure as **n.a,b^x**, in which n stands for number of Au atoms in Au$_n$Mo clusters, **a** is labeled as A, B, C, D, E, F, G, H, I, K, and L for isomers with increasing order of energy, b is the relative energy (in eV), and x refers to the spin configuration. The yellow, cyan, and red spheres represent Au, Mo, and H atoms, respectively.*
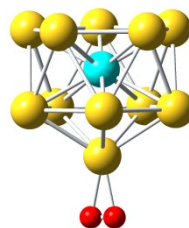
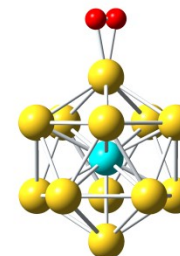**Au$_9$Mo@H$_2$**   **Au$_{10}$Mo@H$_2$**   **Au$_{11}$Mo@H$_2$**   **Au$_{12}$Mo@H$_2$**
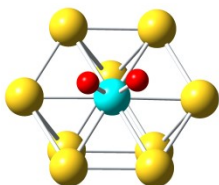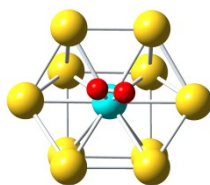
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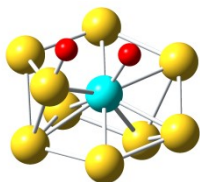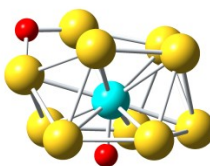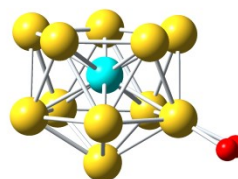
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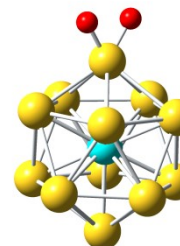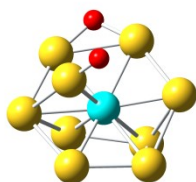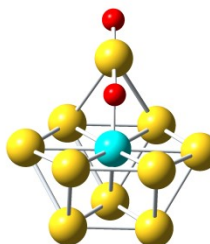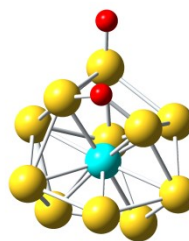
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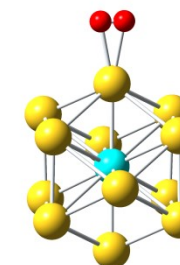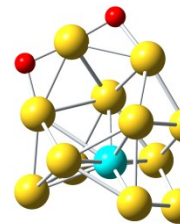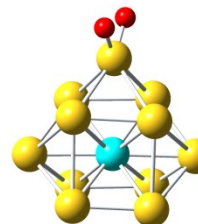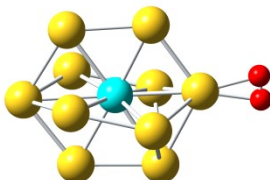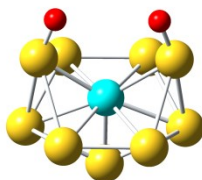
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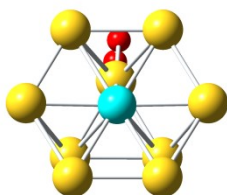
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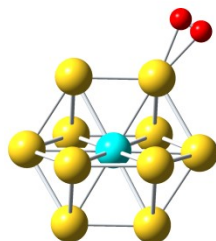
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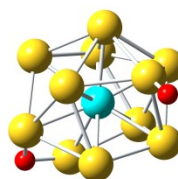
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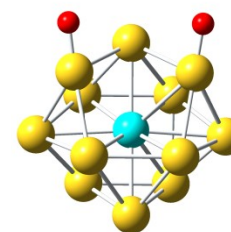
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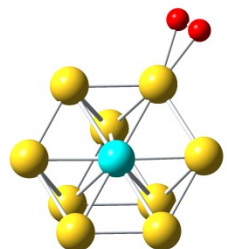
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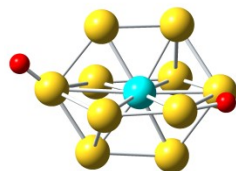
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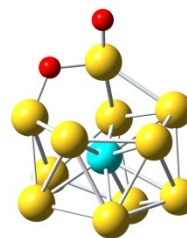
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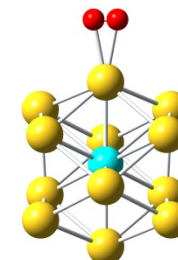
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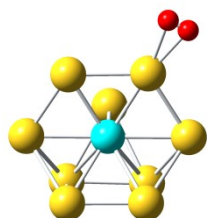
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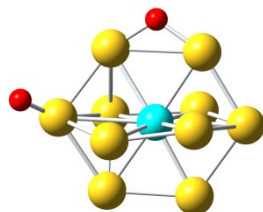
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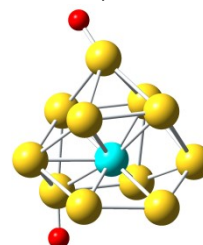
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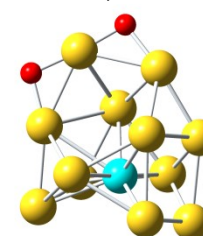
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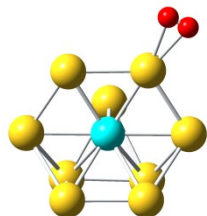
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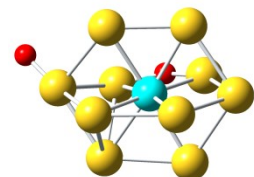
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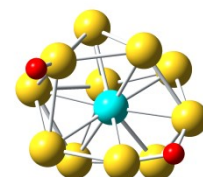
12.H, 2.08^5

9.I, 0.67^2

10.I, 0.34^3

11.I, 0.40^2

9.K, 0.67[4]   10.K, 0.35[3]   11.K, 0.52[2]
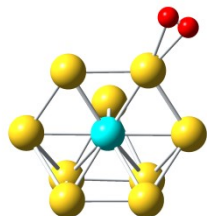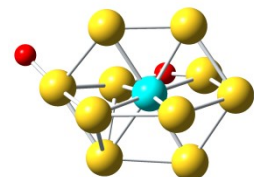
9.L, 0.69[2]   10.L, 0.38[1]   11.L, 0.54[2]
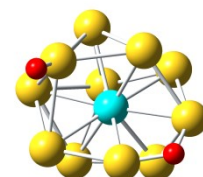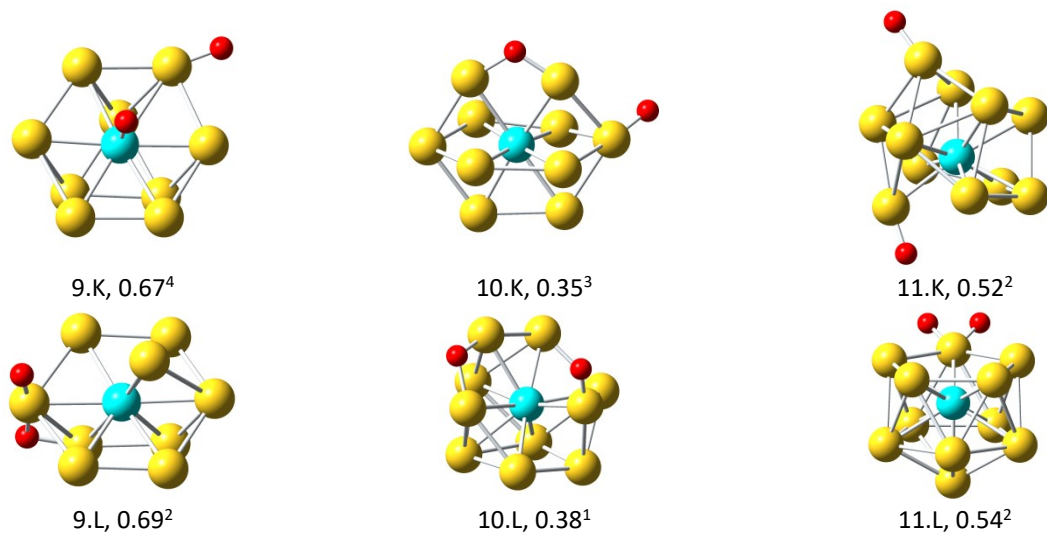
Fig. S3. *Optimized structures, spin configurations, and relative energies (in eV) of computed lowest-energy isomers of Au_nMo clusters (n = 9-12) with an adsorbed hydrogen molecule. We denote each structure as **n.a,b^x,c**, in which n stands for number of Au atoms in Au_nMo clusters, **a** is labeled as A, B, C, D, E, F, G, H, I, K, and L for isomers with increasing order of energy, b is the relative energy (in eV), and x refers to the spin configuration. The yellow, cyan, and red spheres represent Au, Mo, and H atoms, respectively.*
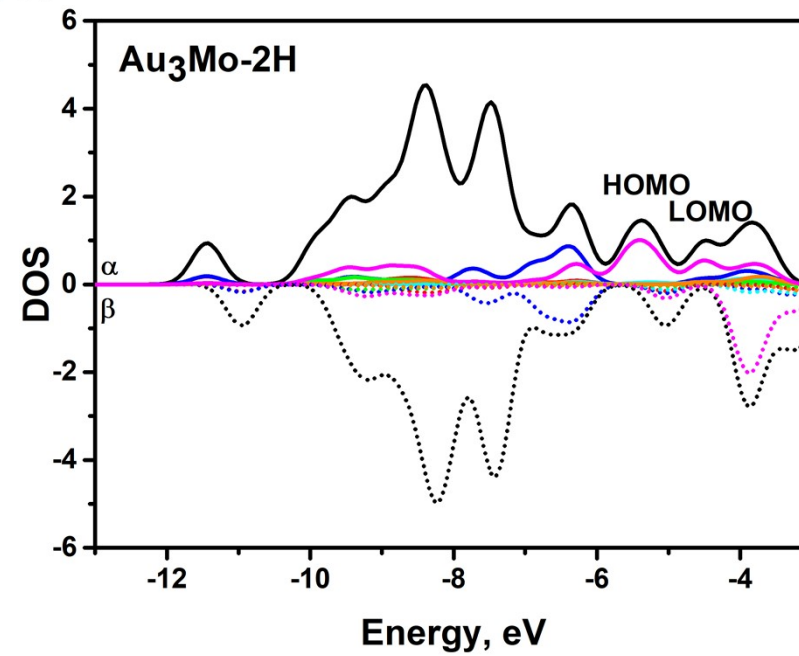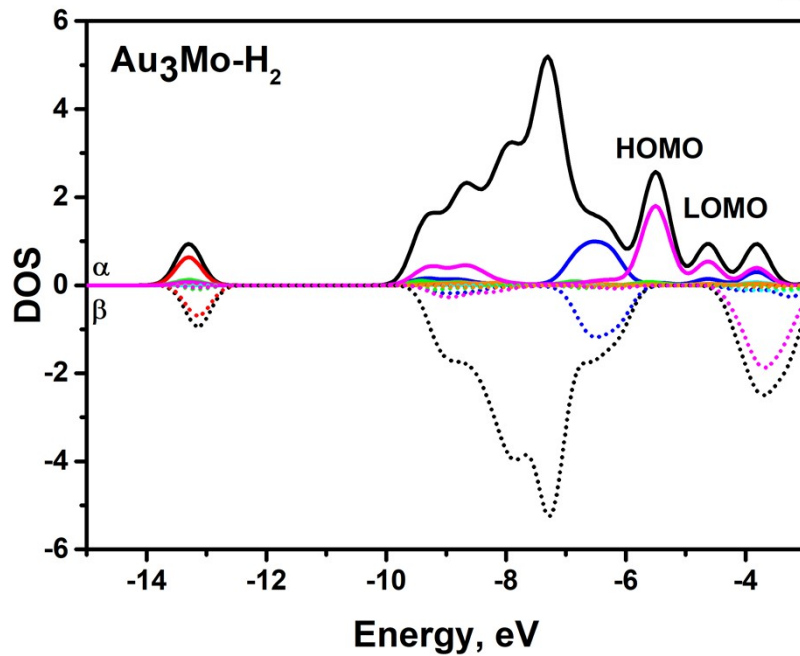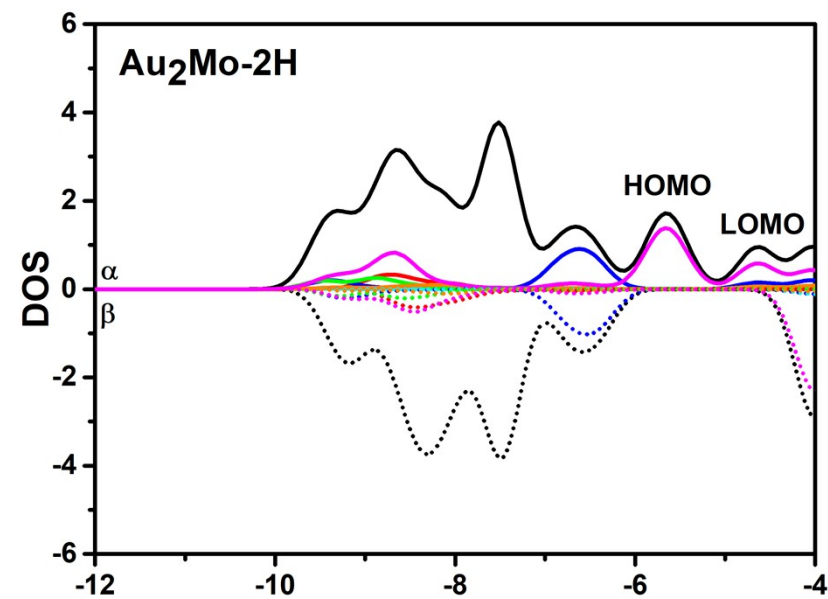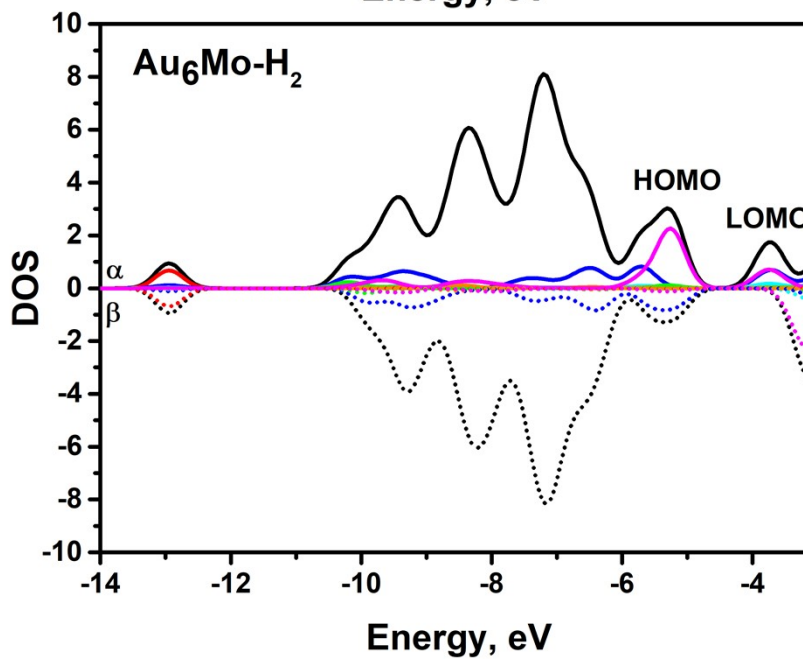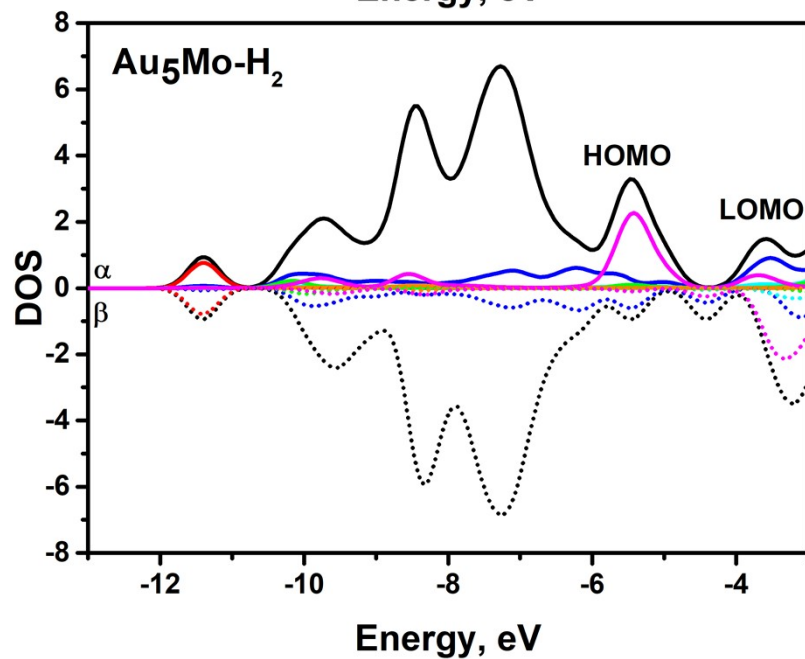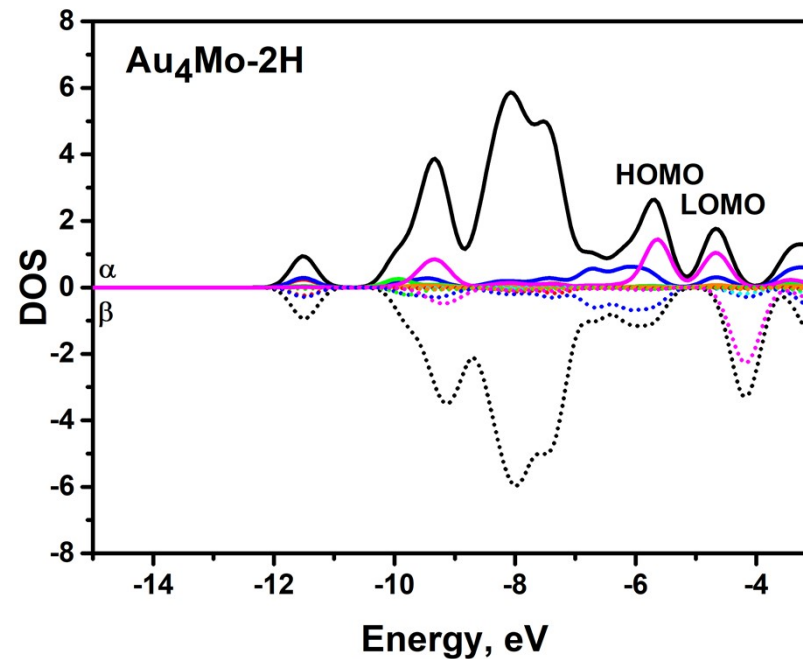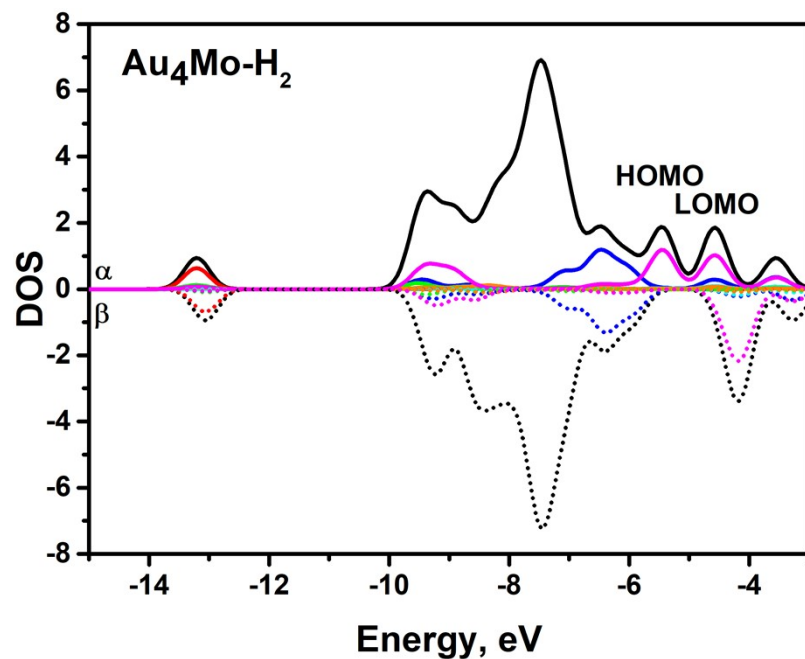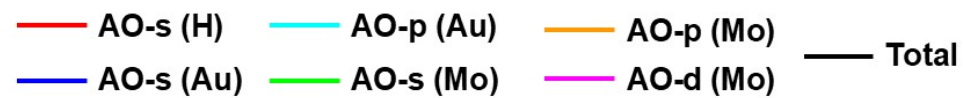
Figure S4. *Partial and total densities of states (DOS) of thermodynamically preferred configurations for hydrogen adsorbed on Au_nMo (n = 2-6) clusters.*
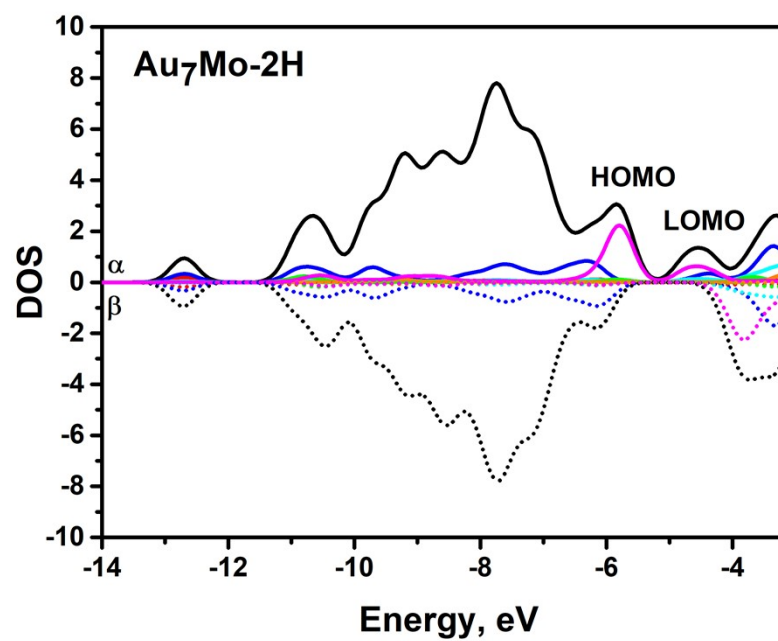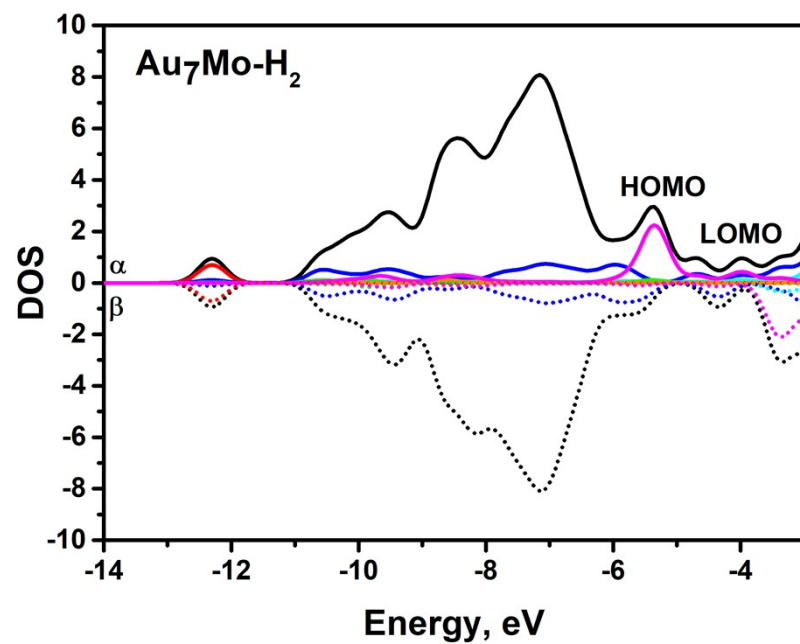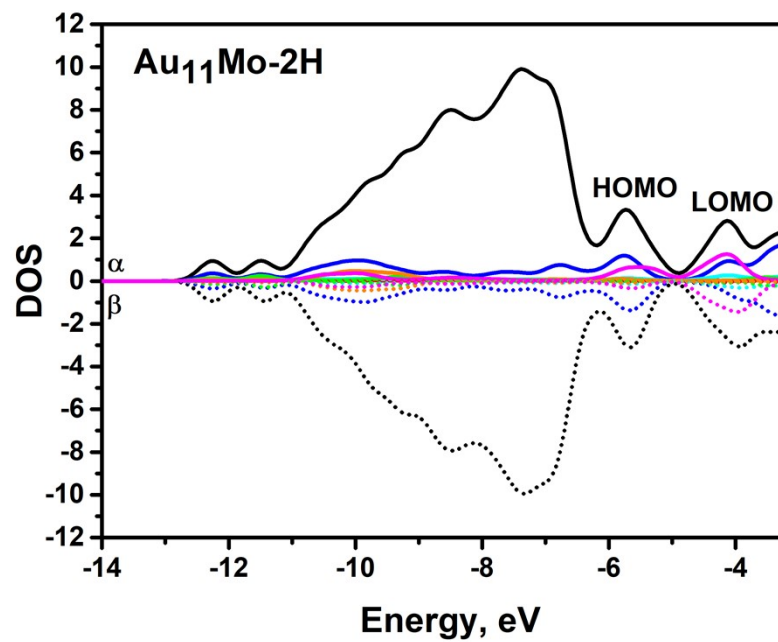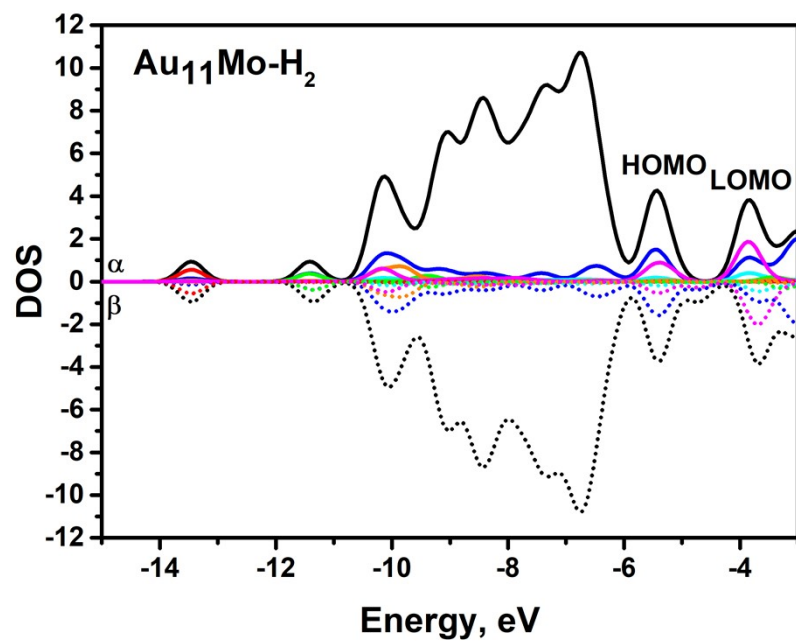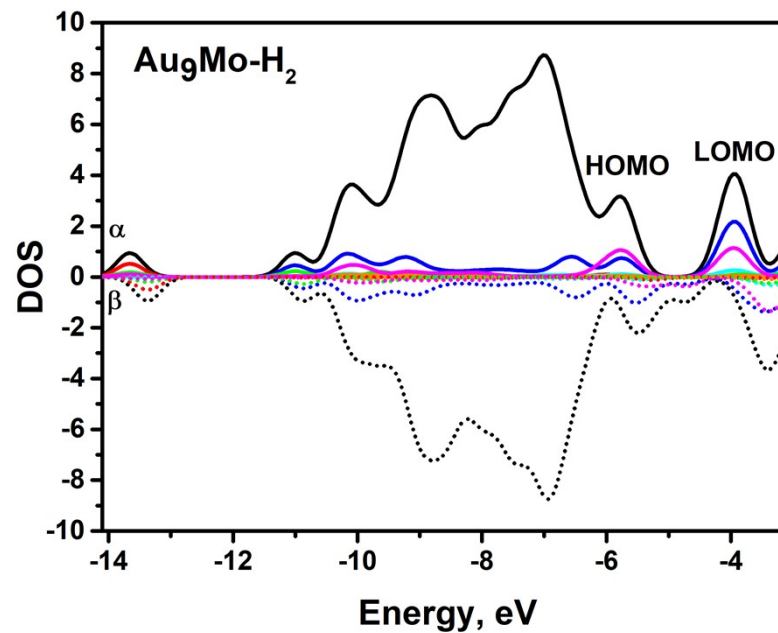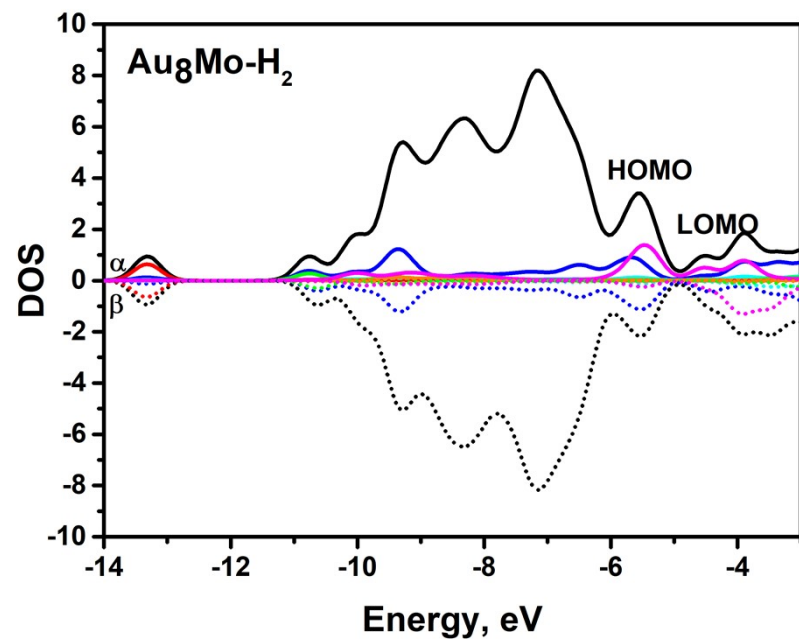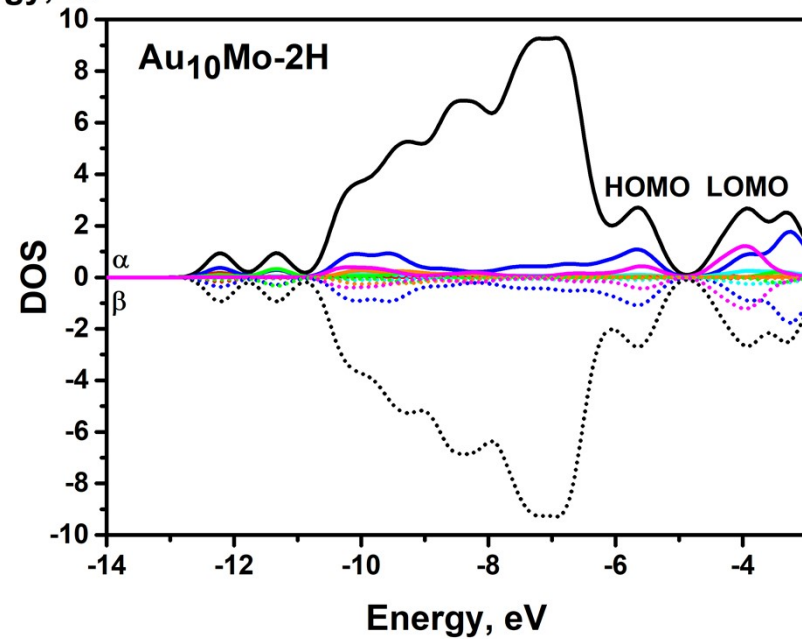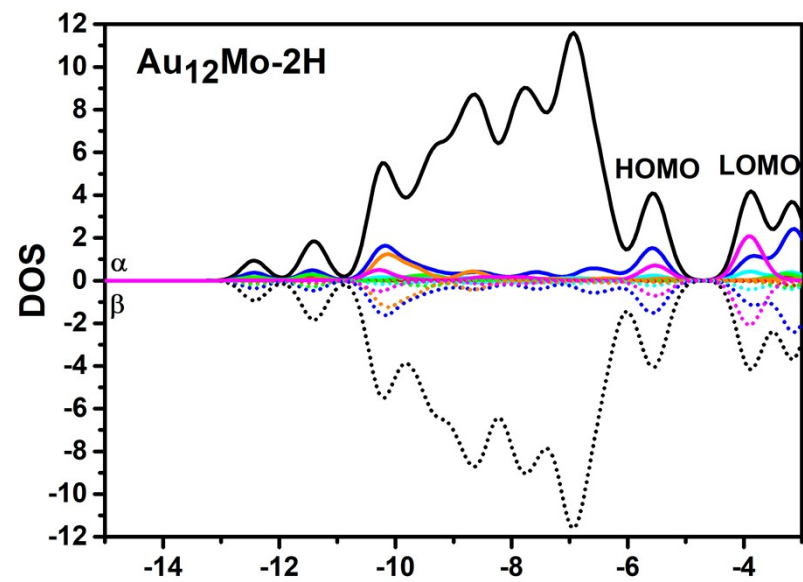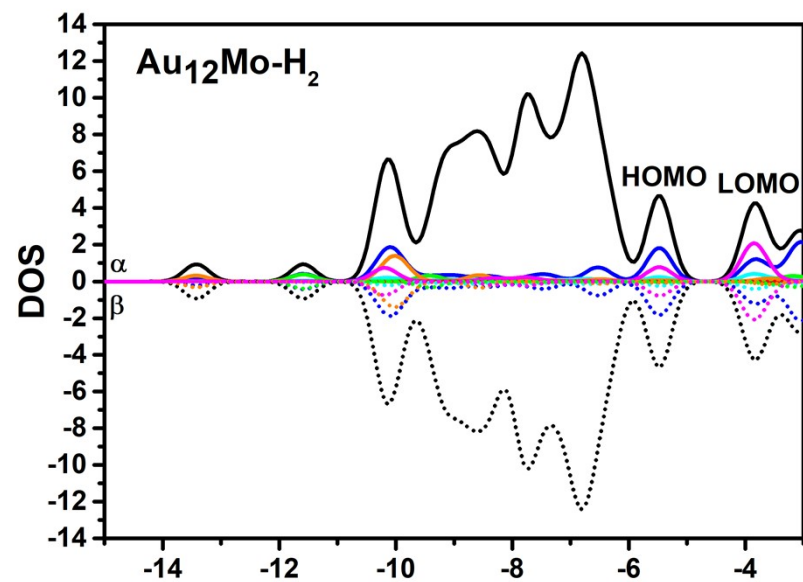
Fig. S5. *Partial and total densities of states (DOS) of thermodynamically preferred configurations for hydrogen adsorbed on Au_nMo (n =7-12) clusters.*
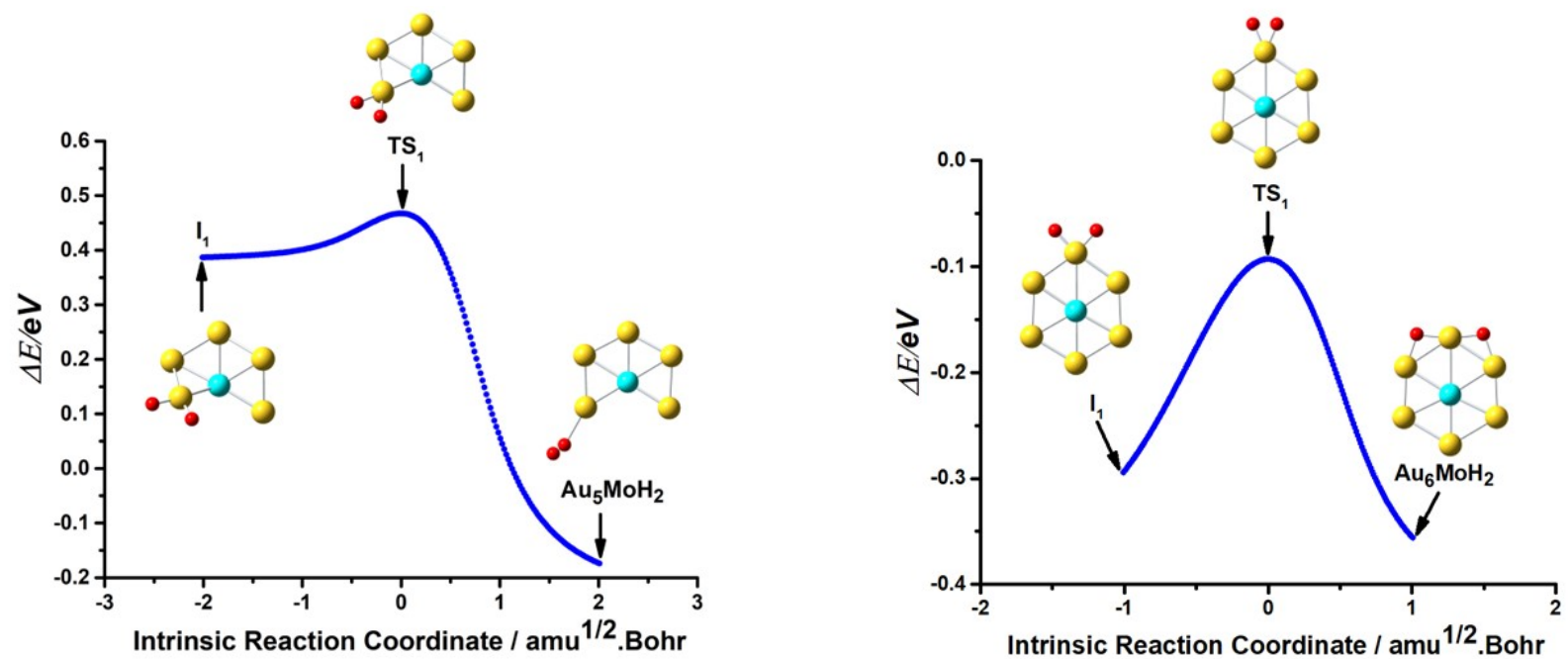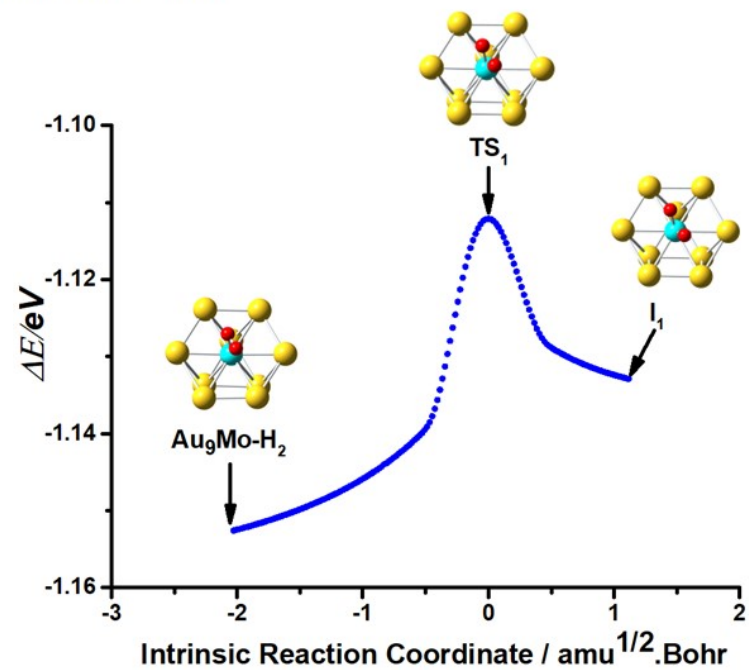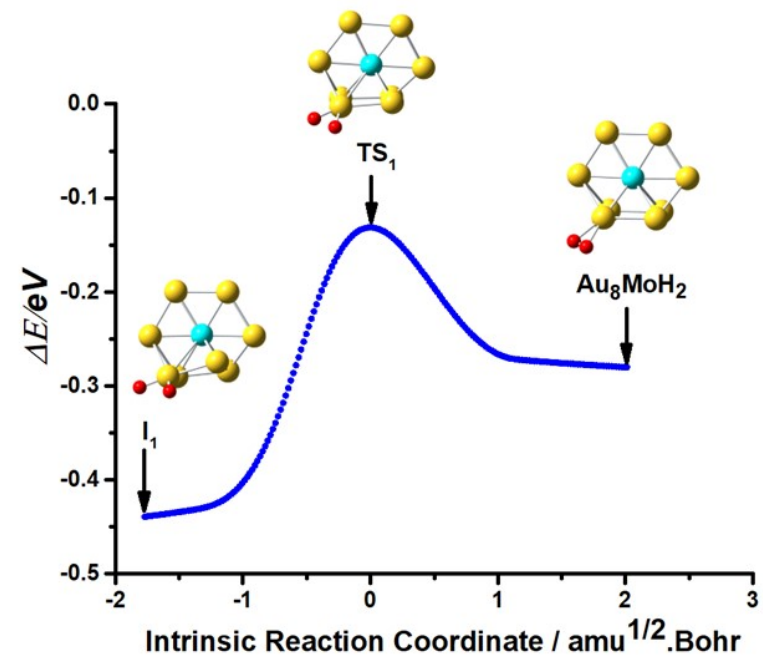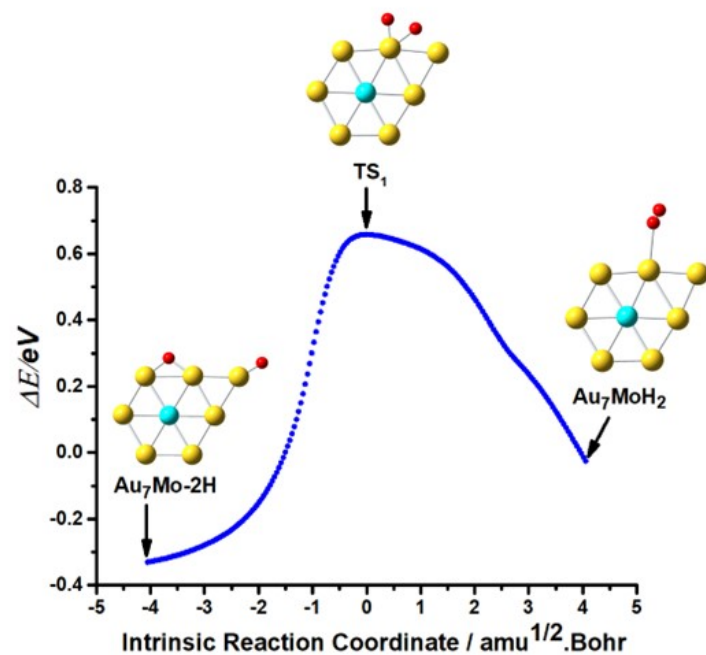
Fig. S6. Calculated intrinsic reaction coordinates for H_2 dissociation on Au_nMo clusters (n =5-9). The intermediates and transition states are denoted as I_i and TS_i. The yellow, cyan, and red spheres represent Au, Mo, and H atoms, respectively.
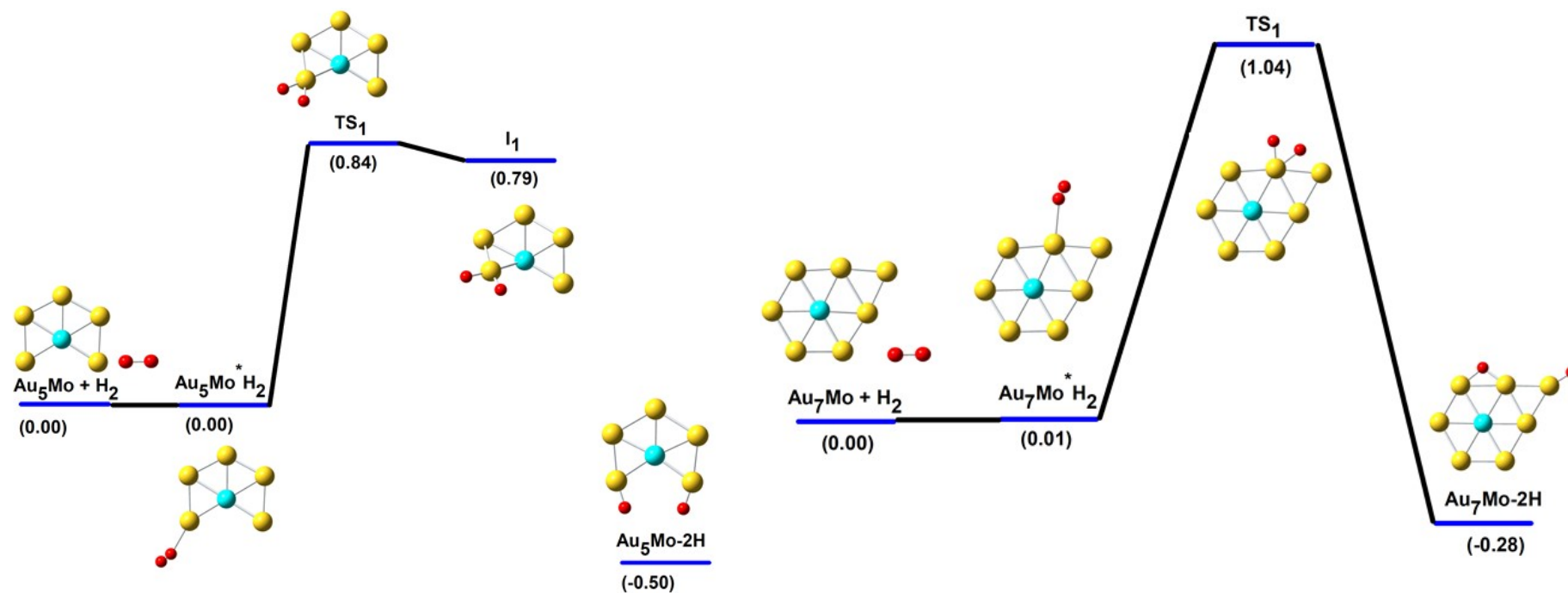
Fig. S7. Calculated reaction pathways and relative energies (in eV) for single H_2 adsorption and dissociation on Au_5Mo and Au_7Mo clusters. The intermediates and transition states are denoted as I_i and TS_i. The yellow, cyan, and red spheres represent Au, Mo, and H atoms, respectively.
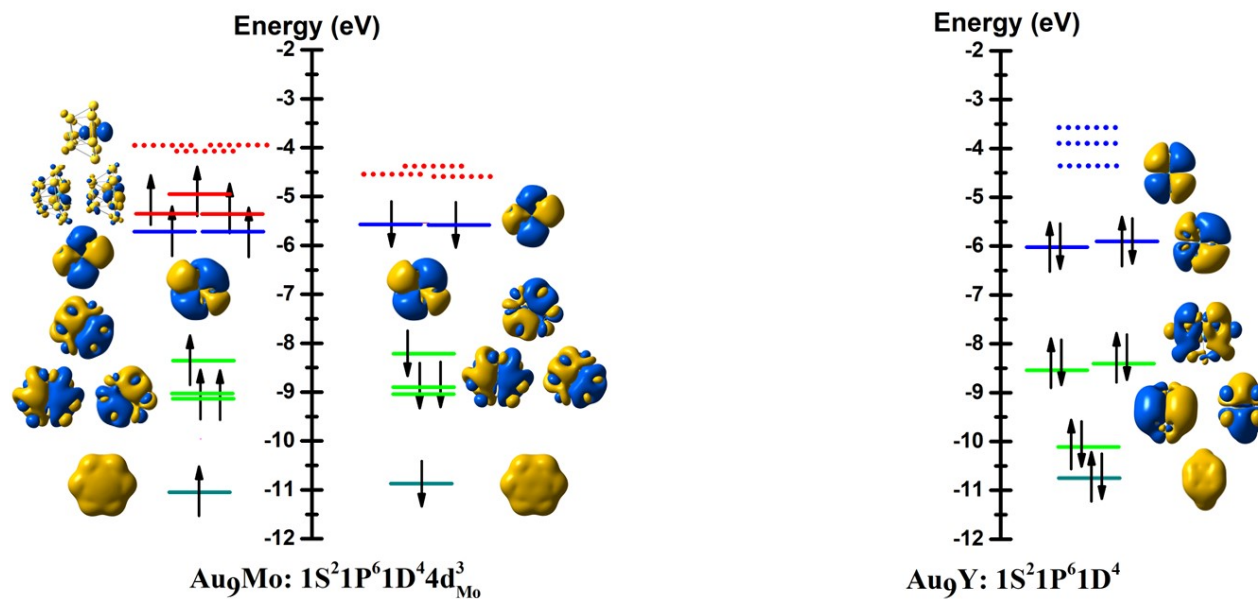
Figure S8. Molecular diagrams for the most stable Au$_9$Mo and Au$_9$Y clusters with pictures of the delocalized and localized orbitals. Dark cyan, green, and blue lines indicate orbitals corresponding to 1S, 1P, and 1D shells, respectively, while the red ones represent the localized 4d orbitals of the transition metal atom. The continuous and dashed lines imply occupied and unoccupied orbitals, respectively.
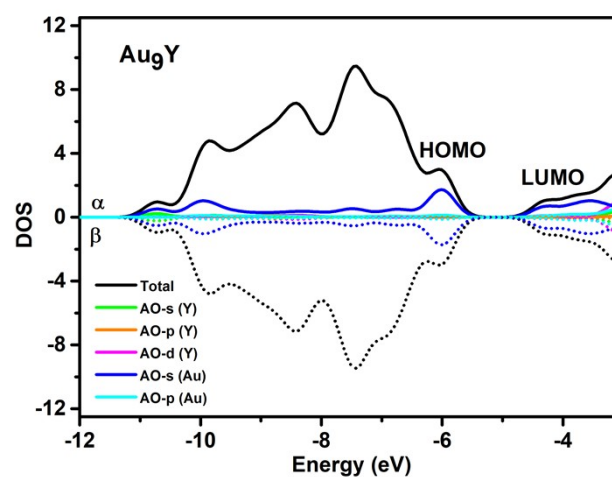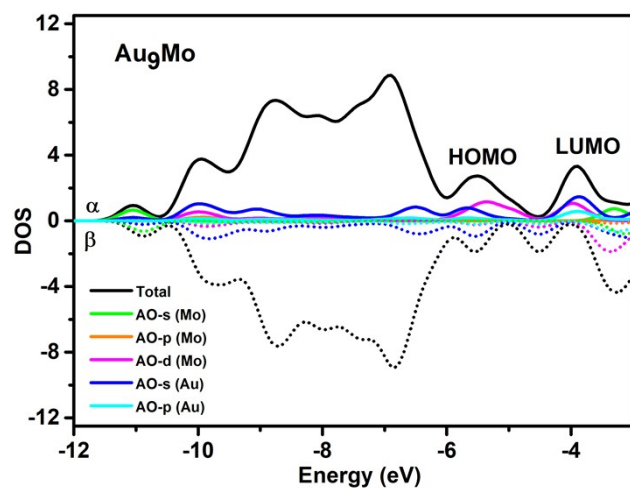
Figure S9. Density of electronic states (DOS) for Au$_9$Mo and Au$_9$Y clusters. The solid lines represent α (alpha) spin, while the short dotted lines represent β (beta) spin. HOMO and LUMO stand for the highest occupied molecular orbitals and lowest unoccupied molecular orbitals, respectively.

Au$_3$Mo-H$_2$: 1s$_H^2$1S^{2}1P^{4}4d$_{Mo}^3$

Au$_4$Mo-H$_2$: 1s$_H^2$1S^{2}1P^{6}4d$_{Mo}^2$

Au$_7$Mo-2H: 1S^{2}1P^{6}1D^{4}4d$_{Mo}^3$

$Au_{11}Mo\text{-}H_2$: $1s_H^2 1S^2 1P^6 1D^8 4d_{Mo}^1$

$Au_{12}Mo\text{-}H_2$: $1s_H^2 1S^2 1P^6 1D^{10}$
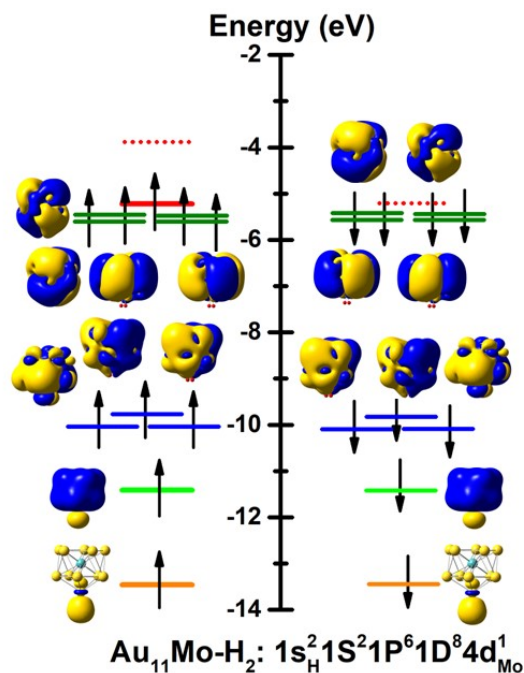
Figs 10. Electronic configurations and molecular diagrams for the most stable configuration of hydorgen adsorbed on Au_nMo (n = 2, 5-6, 8, 9 and 10) clusters with pictures of the delocalized and localized orbitals. The Orange, green, blue, and olive lines indicate orbitals corresponding to $1s_H$, 1S, 1P, and 1D shell, while the red ones represent the localized 4d orbitals of the Mo atom. Continous and dashed lines imply occupied and unoccupied orbitals, respectively.

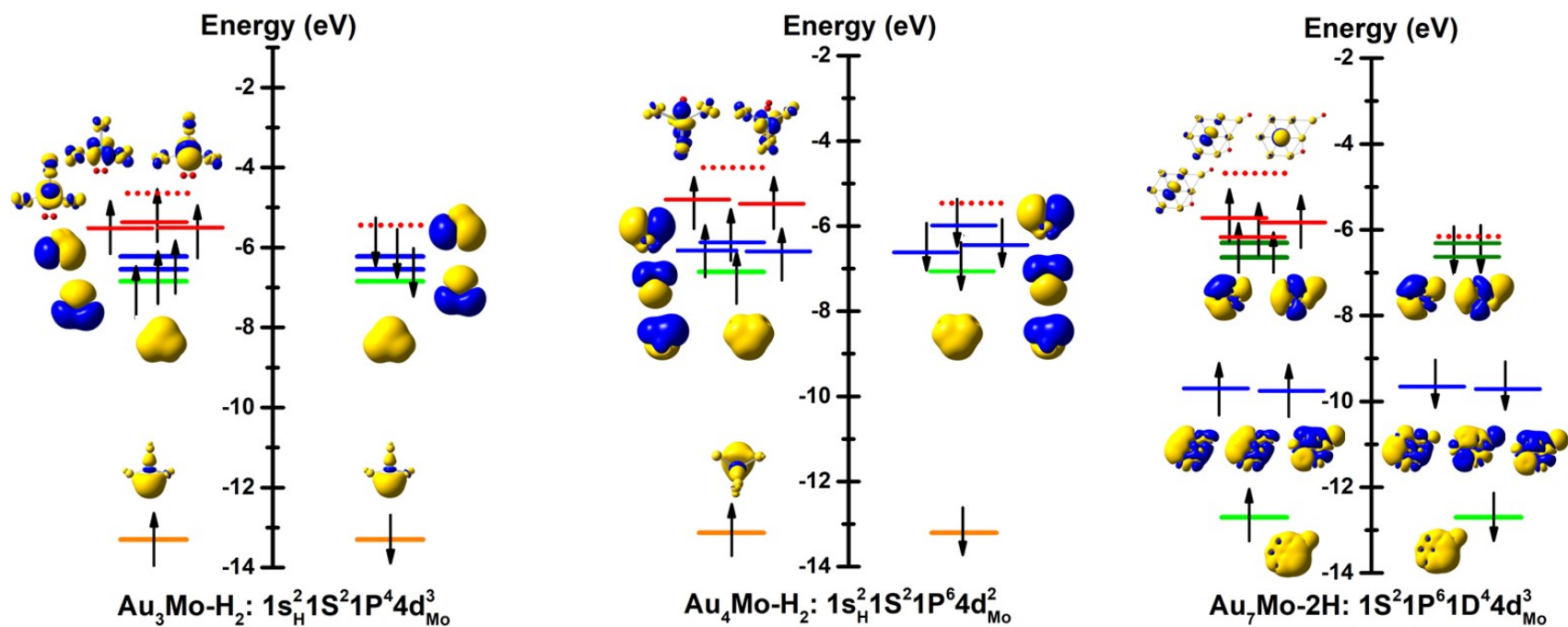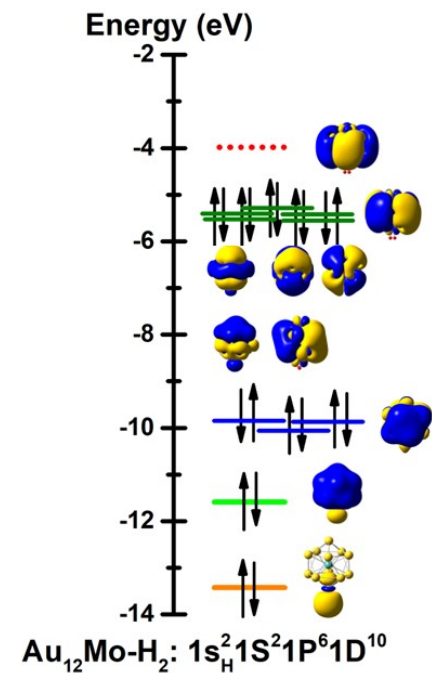**Table S2.** Calculated NBO Charge Distribution on the most stable of Au_nMo and $Au_nMo@H_2$ (n = 2-12). Mo represents Mo atom, while Au-1 and Au-2 label two Au atoms that bind to the corresponding H atoms, H-1 and H-2.

Cluster	q(Mo)	q(Au-1)	q(Au-2)	q(H-1)	q(H-2)
Au_2Mo-H_2	0.386		-0.204	0.08	0.09
Au_2Mo	0.385		-0.192		
Au_3Mo-H_2	-0.150			0.058	0.057
Au_3Mo	0.141				
Au_4Mo-H_2	-0.805			0.096	0.095
Au_4Mo	-0.416				
Au_5Mo-2H	-0.346	0.125	0.124	-0.017	-0.017
Au_5Mo	-0.228	0.039	0.038		
Au_6Mo-2H	-0.378	0.209		-0.129	-0.129
Au_6Mo	-0.563	0.083			
Au_7Mo-2H	-0.412	-0.035	0.180	-0.089	-0.063
Au_7Mo	-0.434	0.118	0.082		
Au_8Mo-2H	-1.905	0.272	0.272	-0.74	0.069
Au_8Mo	-1.841	0.274	0.274		
Au_9Mo-2H	-2.472			0.126	0.125
Au_9Mo	-2.281				
$Au_{10}Mo$-H_2	-3.756			0.176	0.176
$Au_{10}Mo$	-3.331				
$Au_{11}Mo$-H_2	-4.167	0.413		0.070	0.069
$Au_{11}Mo$	-4.145	0.410			
$Au_{12}Mo$-H_2	-4.914	0.404		0.068	0.069
$Au_{12}Mo$	-4.961	0.413			