Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary information

O_2 adsorption and dissociation on neutral, positively and negatively charged Au_n (n = 5-79) clusters

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For each cluster and charge state considered in this work, we report the full set of optimized geometries, thermodynamic stabilities and transition state barriers. The material is organized according to cluster size (Au_n, n = 5, 13, 25, 38, 55 and 79). We also report in a schematic representation the binding energy (E_B) defined in equation 1, the activation barrier ($\Delta E^{\#}$), i.e. the difference between the energy of the transition state and the initial state, and the reaction energy (E_R), defined as the energy difference between the final state and the initial state.

$$E_B = E_{sys} - \left(E_{Au_n} + E_{O_2}\right) \qquad \text{Eq. 1}$$

The O_2 dissociation profiles are plotted for each charge state: dashed-line cationic cluster, solid-line neutral cluster, dotted-line negatively charged cluster. Ionization potential (in red-dashed) and electron affinity (in blue-dot) are also shown.

Au_5

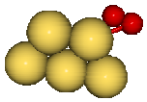
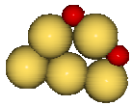
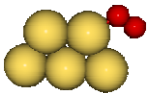
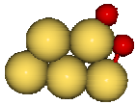
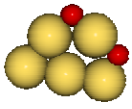
O_2-$Au_5^+ \rightarrow 2O$-Au_5^+		
Initial state	**Transition state**	**Final state**
		
E_B= -0.47 eV	$\Delta E^{\#}$= 2.89 eV	E_R= 0.05 eV
O_2-$Au_5 \rightarrow 2O$-Au_5		
		
E_B= -0.54 eV	$\Delta E^{\#}$= 2.81 eV	E_R= -0.58 eV
O_2-$Au_5^- \rightarrow 2O$-Au_5^-		
		
E_B= -0.39 eV	$\Delta E^{\#}$= 2.23 eV	E_R= -0.90 eV

Figure 1 – Geometrical structures and energies of initial state (molecular adsorption), transition state, and final dissociative state for O_2 interacting with a $Au_5^{(-1,0,+1)}$ cluster.

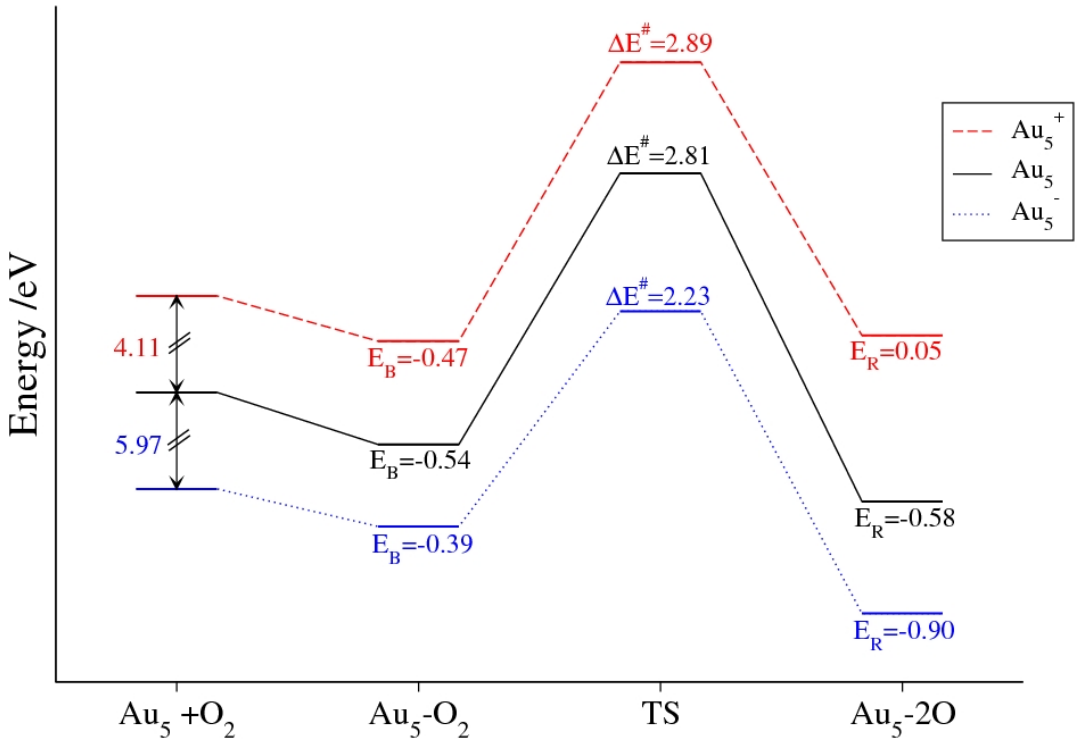


Figure 2 – Reaction energy profiles for O_2 interacting with a $Au_5^{(-1,0,+1)}$ cluster.

Au_{13}

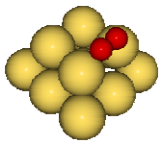
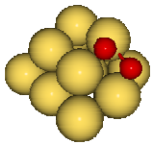
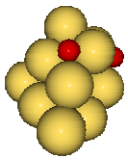
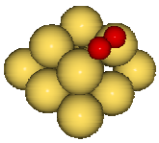
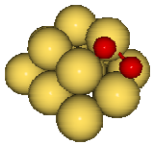
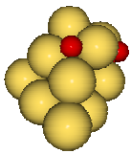
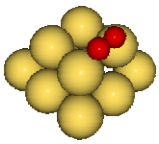
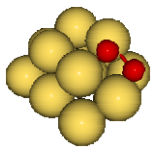
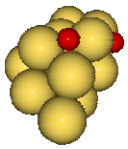
O_2-$Au_{13}^+ \rightarrow 2O$-Au_{13}^+		
Initial state	**Transition state**	**Final state**
		
E_B= -0.29 eV	$\Delta E^{\#}$= 1.81 eV	E_R= -1.45 eV
O_2-$Au_{13} \rightarrow 2O$-Au_{13}		
		
E_B= -0.51 eV	$\Delta E^{\#}$= 1.79 eV	E_R= -1.46 eV
O_2-$Au_{13}^- \rightarrow 2O$-Au_{13}^-		
		
E_B= -0.83 eV	$\Delta E^{\#}$= 1.66 eV	E_R= -1.79 eV

Figure 3 – Geometrical structures and energies of initial state (molecular adsorption), transition state, and final dissociative state for O_2 interacting with a $Au_{13}^{(-1,0,+1)}$ cluster.

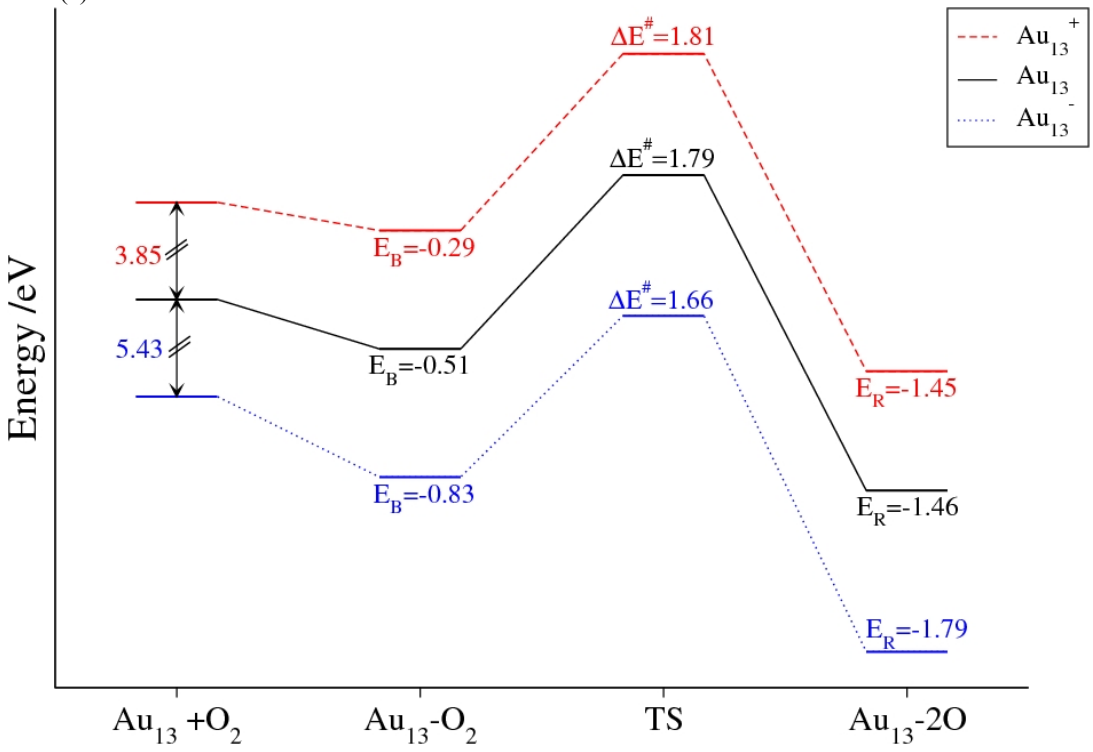


Figure 4 – Reaction energy profiles for O_2 interacting with a $Au_{13}^{(-1,0,+1)}$ cluster.

Au_{25}

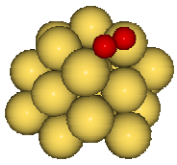
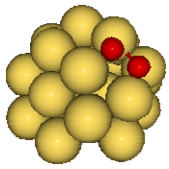
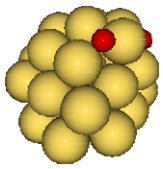
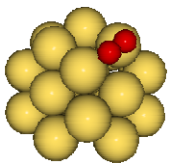
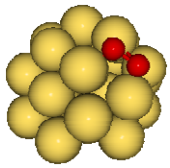
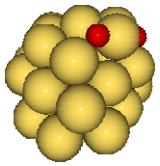
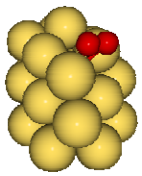
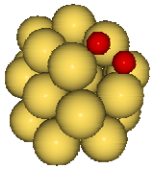
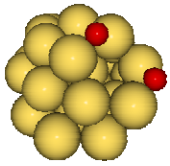
O_2-$Au_{25}^+ \rightarrow 2O$-Au_{25}^+		
Initial state	**Transition state**	**Final state**
		
E_B= -0.58 eV	$\Delta E^{\#}$= 1.65 eV	E_R= -0.61 eV
O_2-$Au_{25} \rightarrow 2O$-Au_{25}		
		
E_B= -0.51 eV	$\Delta E^{\#}$= 0.53 eV	E_R= -1.55 eV
O_2-$Au_{25}^- \rightarrow 2O$-Au_{25}^-		
		
E_B= -1.37 eV	$\Delta E^{\#}$= 1.75 eV	E_R= -0.49 eV

Figure 5 – Geometrical structures and energies of initial state (molecular adsorption), transition state, and final dissociative state for O_2 interacting with a $Au_{25}^{(-1,0,+1)}$ cluster.

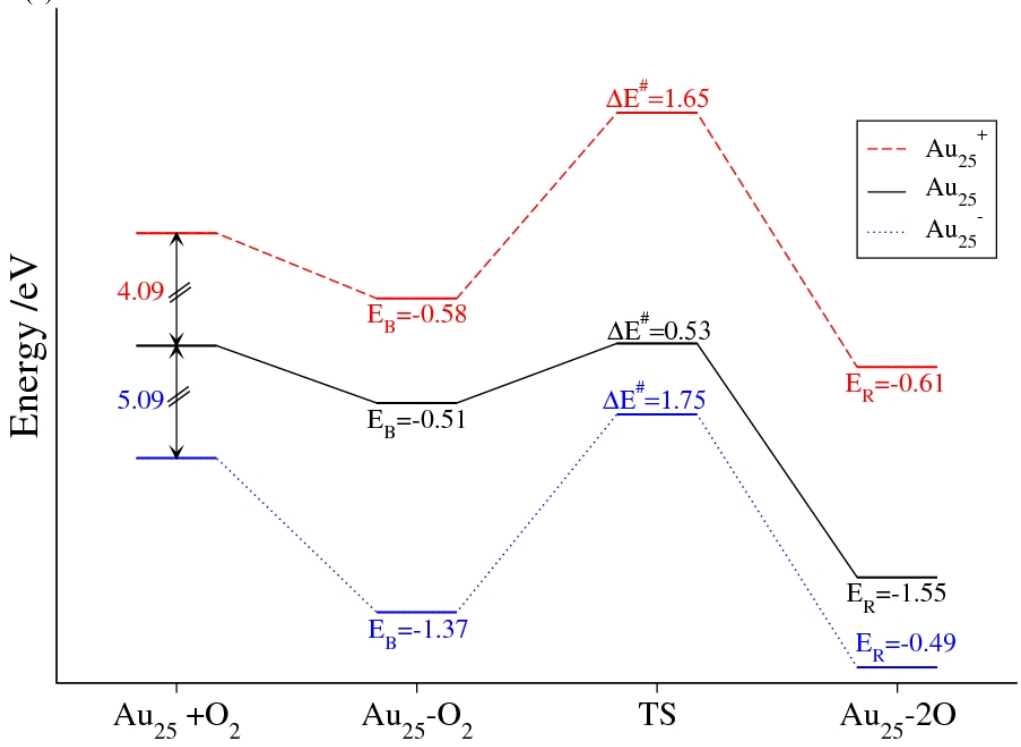


Figure 6 – Reaction energy profiles for O_2 interacting with a $Au_{25}^{(-1,0,+1)}$ cluster.

Au_{38}

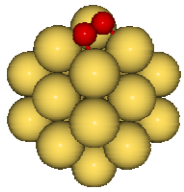
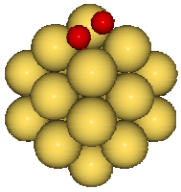
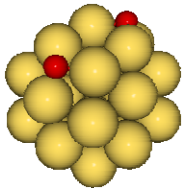
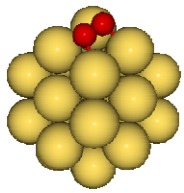
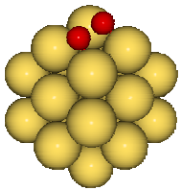
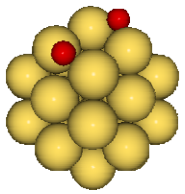
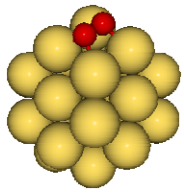
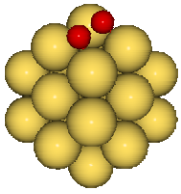
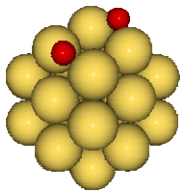
O_2-$Au_{38}^+ \rightarrow 2O$-Au_{38}^+		
Initial state	**Transition state**	**Final state**
		
E_B= -0.89 eV	$\Delta E^{\#}$= 0.46 eV	E_R= -0.74 eV
O_2-$Au_{38} \rightarrow 2O$-Au_{38}		
		
E_B= -0.96 eV	$\Delta E^{\#}$= 0.45 eV	E_R= -0.55 eV
O_2-$Au_{38}^- \rightarrow 2O$-Au_{38}^-		
		
E_B= -1.07 eV	$\Delta E^{\#}$= 0.45 eV	E_R= -0.59 eV

Figure 7 – Geometrical structures and energies of initial state (molecular adsorption), transition state, and final dissociative state for O_2 interacting with a $Au_{38}^{(-1,0,+1)}$ cluster.

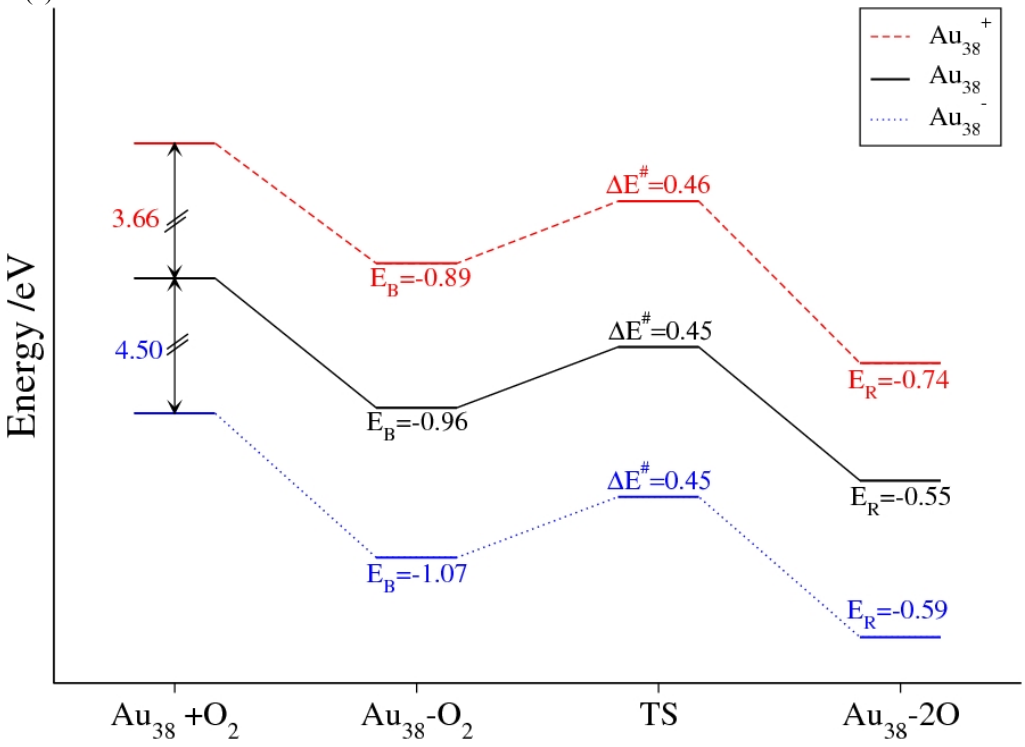


Figure 8 – Reaction energy profiles for O_2 interacting with a $Au_{38}^{(-1,0,+1)}$ cluster.

Au_{55}

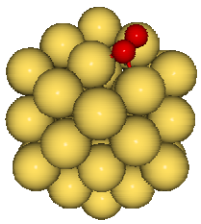
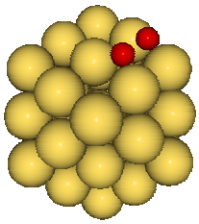
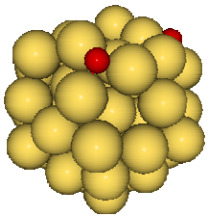
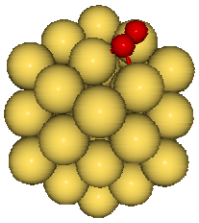
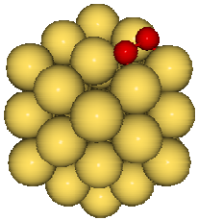
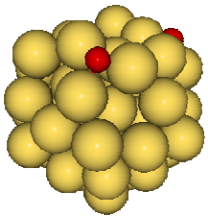
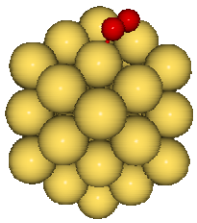
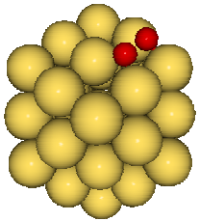
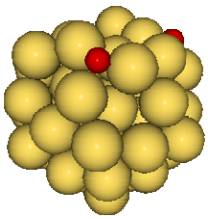
O_2-$Au_{55}^+ \rightarrow 2O$-Au_{55}^+		
Initial state	**Transition state**	**Final state**
		
E_B= -0.50 eV	$\Delta E^{\#}$= 0.87 eV	E_R= -2.24 eV
O_2-$Au_{55} \rightarrow 2O$-Au_{55}		
		
E_B= -0.23 eV	$\Delta E^{\#}$= 0.54 eV	E_R= -2.32 eV
O_2-$Au_{55}^- \rightarrow 2O$-Au_{55}^-		
		
E_B= -0.21 eV	$\Delta E^{\#}$= 0.88 eV	E_R= -2.15 eV

Figure 9 – Geometrical structures and energies of initial state (molecular adsorption), transition state, and final dissociative state for O_2 interacting with a $Au_{55}^{(-1,0,+1)}$ cluster.

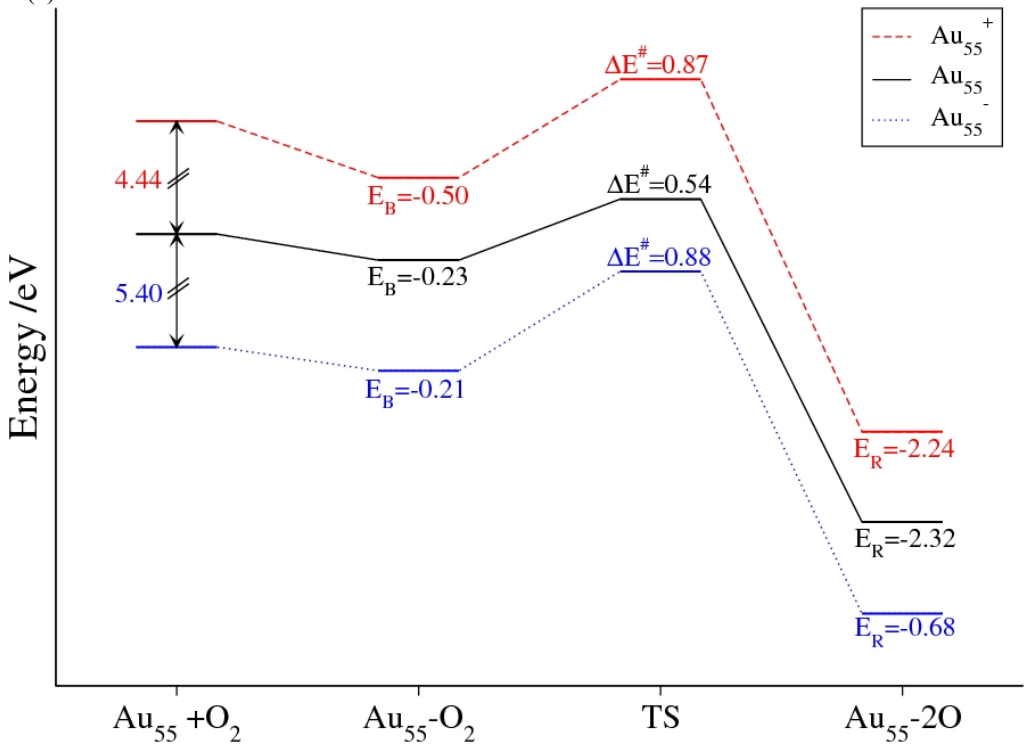


Figure 10 – Reaction energy profiles for O_2 interacting with a $Au_{55}^{(-1,0,+1)}$ cluster.

Au_{79}

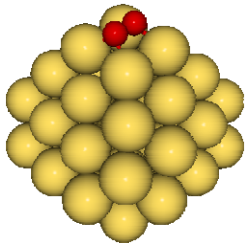
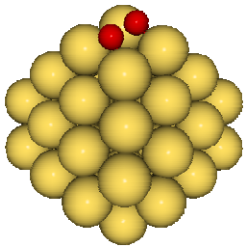
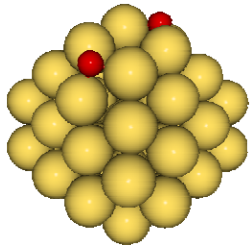
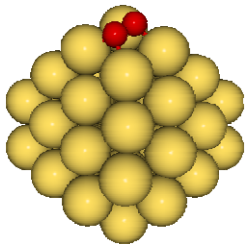
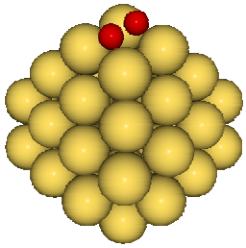
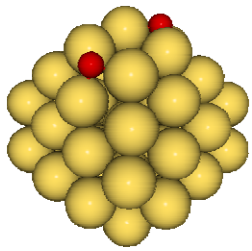
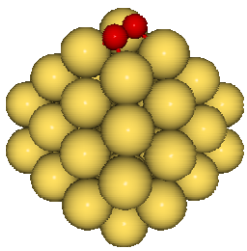
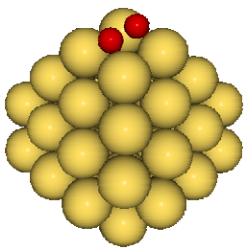
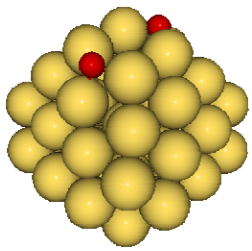
O_2-$Au_{79}^+ \rightarrow 2O$-Au_{79}^+		
Initial state	**Transition state**	**Final state**
		
E_B= -0.32 eV	$\Delta E^{\#}$= 0.52 eV	E_R= -0.68 eV
O_2-$Au_{79} \rightarrow 2O$-Au_{79}		
		
E_B= -0.28 eV	$\Delta E^{\#}$= 0.42 eV	E_R= -0.65 eV
O_2-$Au_{79}^- \rightarrow 2O$-Au_{79}^-		
		
E_B= -0.25 eV	$\Delta E^{\#}$= 0.49 eV	E_R= -0.66 eV

Figure 11 – Geometrical structures and energies of initial state (molecular adsorption), transition state, and final dissociative state for O_2 interacting with a $Au_{79}^{(-1,0,+1)}$ cluster.

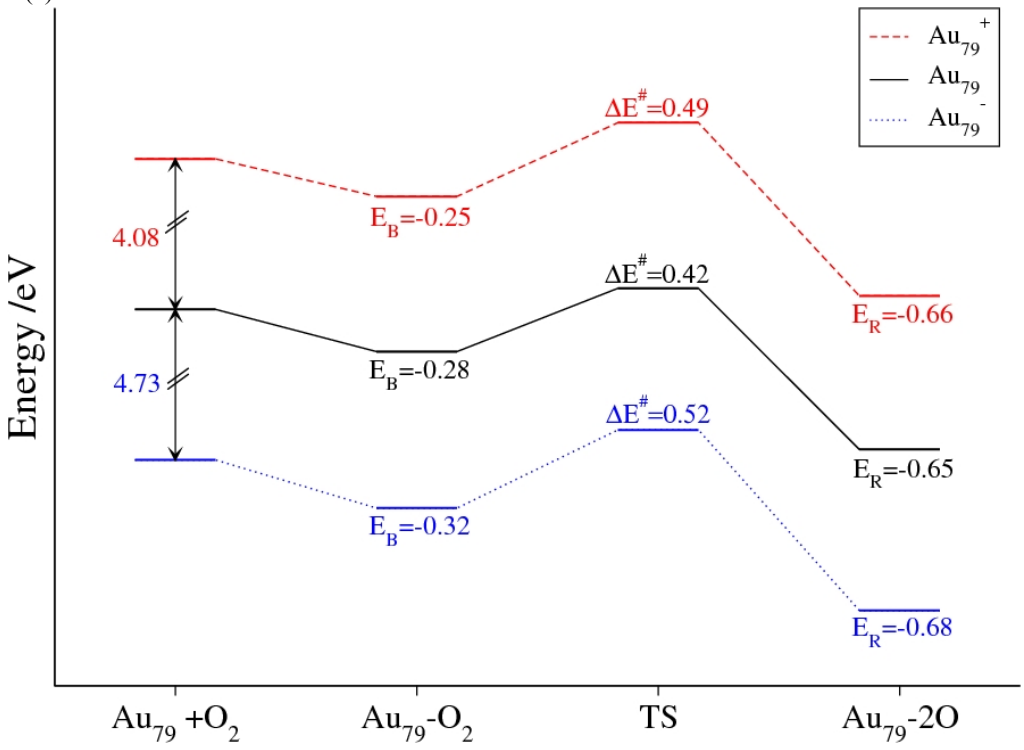


Figure 12 – Reaction energy profiles for O_2 interacting with a $Au_{79}^{(-1,0,+1)}$ cluster.