Supporting Information

Supplementary Information I

Table 1 presents a comparison of our current results on gold dimer i.e Au_2 cluster with the previously published results. The nice agreement of our results with both the experimentally measured and theoretically reported values firmly establishes the accuracy of the computational method and the reliability of atomic pseudo-potentials used in this work.

Table 1. Bond length (BL), binding energy per atom (E_b/n), ionization potential (IP), electron affinity (EA) and vibrational frequency (ω_e) of pure gold dimer (Au_2)

	BL Å	E_b/n (in eV)	IP (in eV)	EA (in eV)	ω_e (in cm^{-1})
Current value	2.55	1.09	9.42	2.05	167
Literature value(Experimental)	2.47[81]	1.16[81]	9.50[81]	1.94[82]	191[83]
Literature value (Theoretical)	2.52[84], 2.53[85]	1.155[84]	9.31[85], 9.37[86]	2.05[85]	170[85]

*Ionization potential (IP) was estimated as difference in ground state energies between neutral and cationic clusters at their optimized geometries.
*Electron affinity (EA) was calculated as difference in ground state energies between neural and anionic clusters at their optimized geometries.

Supplementary information II

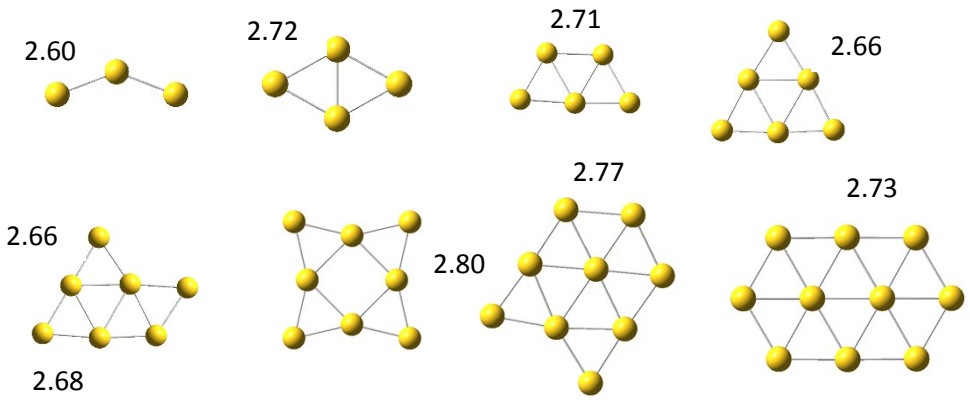


Figure 1. Optimized geometries of neutral Au_n (n=3-10) clusters. Numbers denote the Au-Au bond length in Å

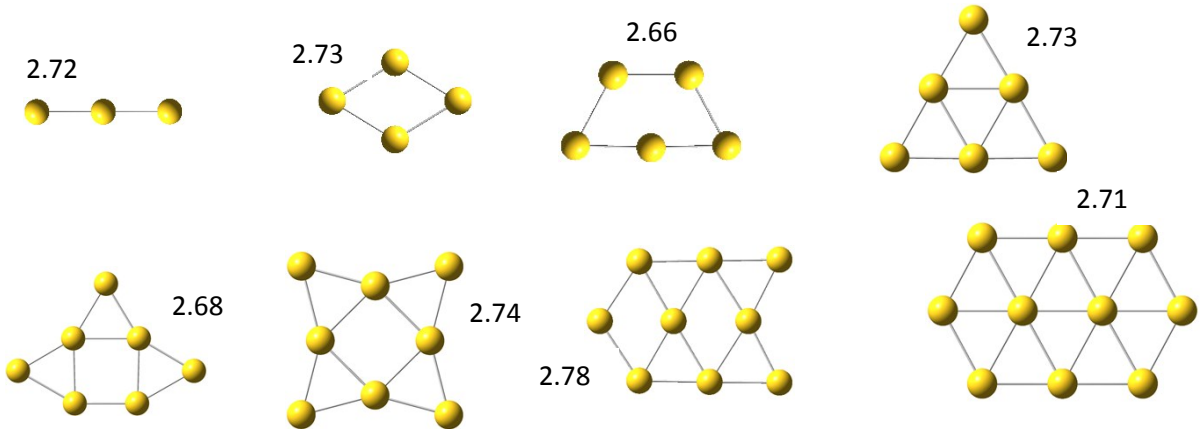


Figure 2. Optimized geometries of anion Au_n^- (n=3-10) clusters. Numbers indicate the Au-Au bond length in Å

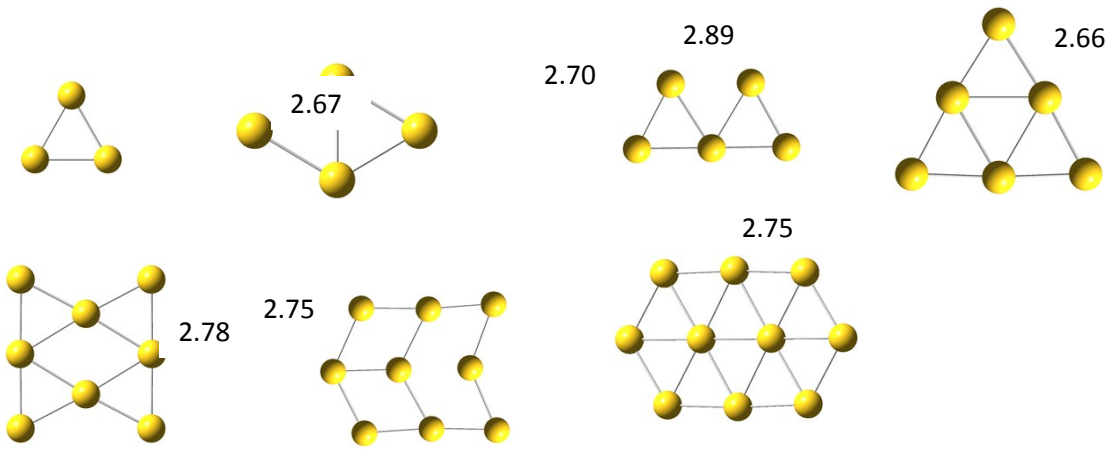
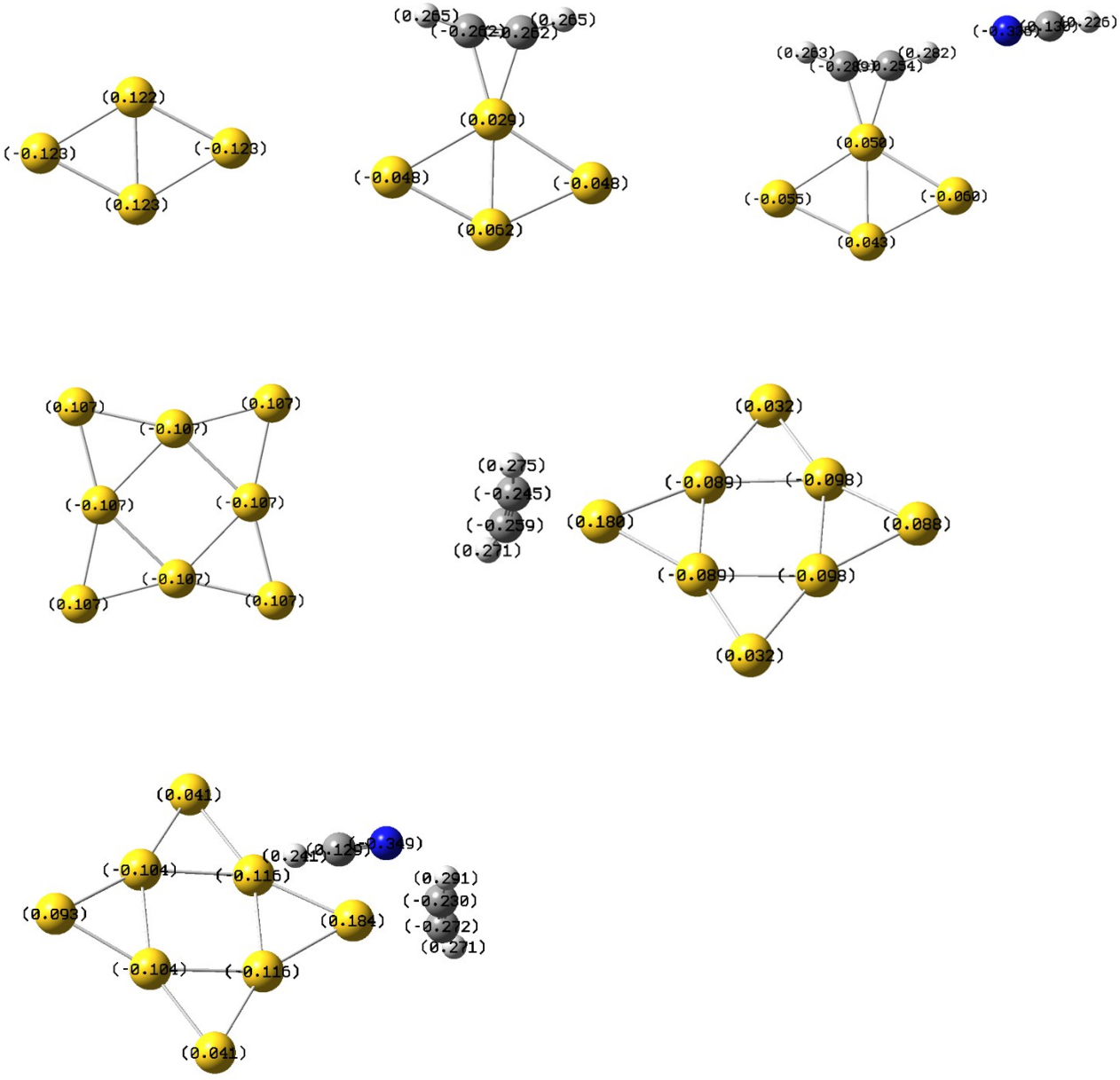


Figure 3. Optimized geometries of cation Au_n^+ clusters. Numbers correspond to the Au-Au bond length in Å

Neutral as well as charged Au_n , Au_n^- and Au_n^+ clusters have been systematically studied. All the relevant information is provided in the supplementary information II. It can be clearly perceived in the Figures 1-3 in the Supplementary information II that the geometries of gold clusters remain unchanged upon charging. However, a marginal variation in the bond lengths has been observed between the neutral, anionic and cationic Au_n clusters. Therefore, we have considered neutral Au_n clusters only for the adsorption of C_2H_2 and HCN upon it.

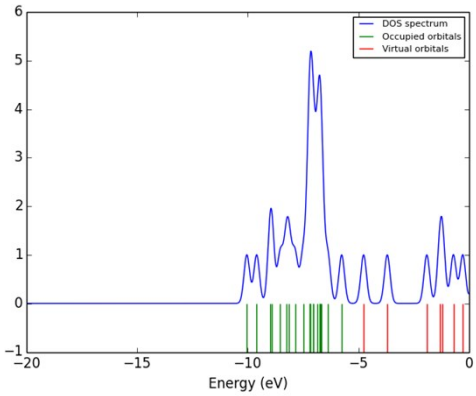
Supplementary information III



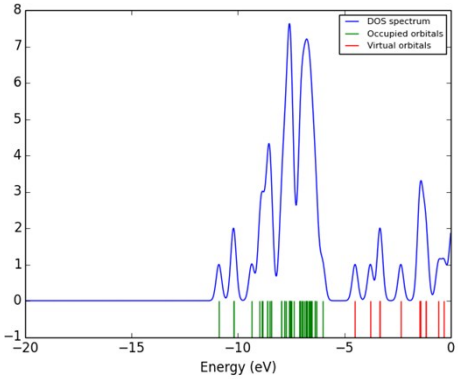
Natural Population analysis of Au_4, Au_4-C_2H_2, $Au_4C_2H_2$-HCN and Au_8, $Au_8C_2H_2$, Au_8-C_2H_2-HCN. Numbers in parenthesis represent charges on the corresponding atoms.

Supplementary information IV

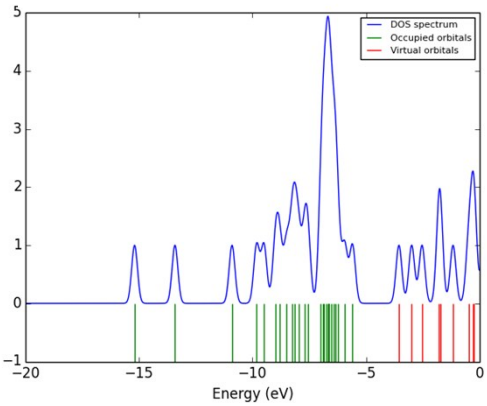
Au_4



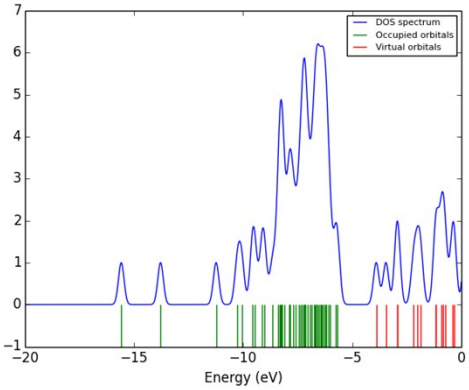
Au_8



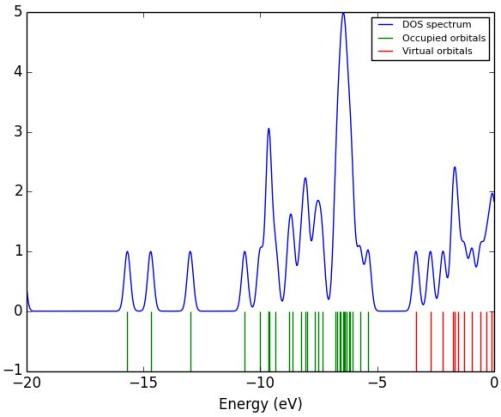
C_2H_2/Au_4



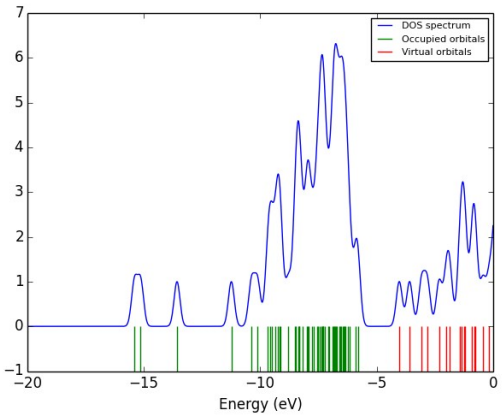
C_2H_2/Au_8



HCN/Au_4-C_2H_2



HCN/Au_8-C_2H_2



Density of states (DOS) plots of Au_n, C_2H_2/Au_n and HCN/Au_n-C_2H_2 (n = 4, 8)

Supplementary Information V

Table. Natural electronic configuration based on DFT calculations at GGA-PW91 level for C, H and N in free and adsorbed acetylene and HCN molecules.

Cluster	Atom	Natural Charge	Natural Electronic Configuration	Natural Charge on Acetylene
C_2H_2	C C H H	-0.22758 -0.22758 0.22758 0.22758	[core] 2S(1.03) 2p(3.19) [core] 2S(1.03) 2p(3.19) 1S(0.77) 1S(0.77)	0.00000
HCN	H C N	0.21882 0.07886 -0.29768	1S(0.78) [core] 2S(0.99) 2p(2.90) 3S(0.01) 4p(0.01) [core] 2S(1.61) 2p(3.67) 3S(0.01) 3d(0.01)	0.00000
Au_4	Au Au Au Au	0.12230 -0.12261 -0.12261 0.12293	[core] 6S(0.73) 5d(9.93) 6p(0.22) [core] 6S(1.22) 5d(9.87) 6p(0.03) [core] 6S(1.22) 5d(9.87) 6p(0.03) [core] 6S(0.73) 5d(9.93) 6p(0.22)	0.00000
$Au_4C_2H_2$	Au Au Au Au C C H	0.02899 -0.04849 -0.04844 0.06162 -0.26208 -0.26205 0.26522	[core] 6S(0.75) 5d(9.67) 6p(0.54) [core] 6S(1.12) 5d(9.90) 6p(0.02) [core] 6S(1.12) 5d(9.90) 6p(0.02) [core] 6S(0.85) 5d(9.89) 6p(0.20) [core] 2S(1.05) 2p(3.20) 4S(0.01) 4p(0.01) [core] 2S(1.05) 2p(3.20) 4S(0.01) 4p(0.01) 1S(0.73)	0.00631

	H	0.26522	1S(0.73)	
$Au_4C_2H_2$ HCN	Au	0.05049	[core] 6S(0.74) 5d(9.65) 6p(0.54)	Charge on C_2H_2 0.00227
	Au	-0.06049	[core] 6S(1.13) 5d(9.90) 6p(0.03)	
	Au	-0.05519	[core] 6S(1.13) 5d(9.90) 6p(0.02)	Charge on HCN 0.02008
	Au	0.04286	[core] 6S(0.87) 5d(9.89) 6p(0.20)	
	C	-0.28911	[core] 2S(1.04) 2p(3.23) 4p(0.01)	
	C	-0.25360	[core] 2S(1.06) 2p(3.18) 3S(0.01) 4p(0.01)	
	H	0.26317	1S(0.73)	
	H	0.28181	1S(0.71)	
	N	-0.33568	[core] 2S(1.60) 2p(3.72) 4S(0.01) 3d(0.01)	
	C	0.12951	[core] 2S(0.99) 2p(2.86) 3S(0.01) 4p(0.01)	
	H	0.22625	1S(0.77)	