

Supplemental Data

Direct Observation of Size Dependent Activation of NO on Gold Clusters

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Details of the structures, energetics and vibrational frequencies of Au_nNO^+ and Au_nCO^+ complexes from DFT calculations.

Figure S1: Optimized structures of bare gold cluster cations Au_n^+ ($n=2-8$) and of their complexes with CO or NO.

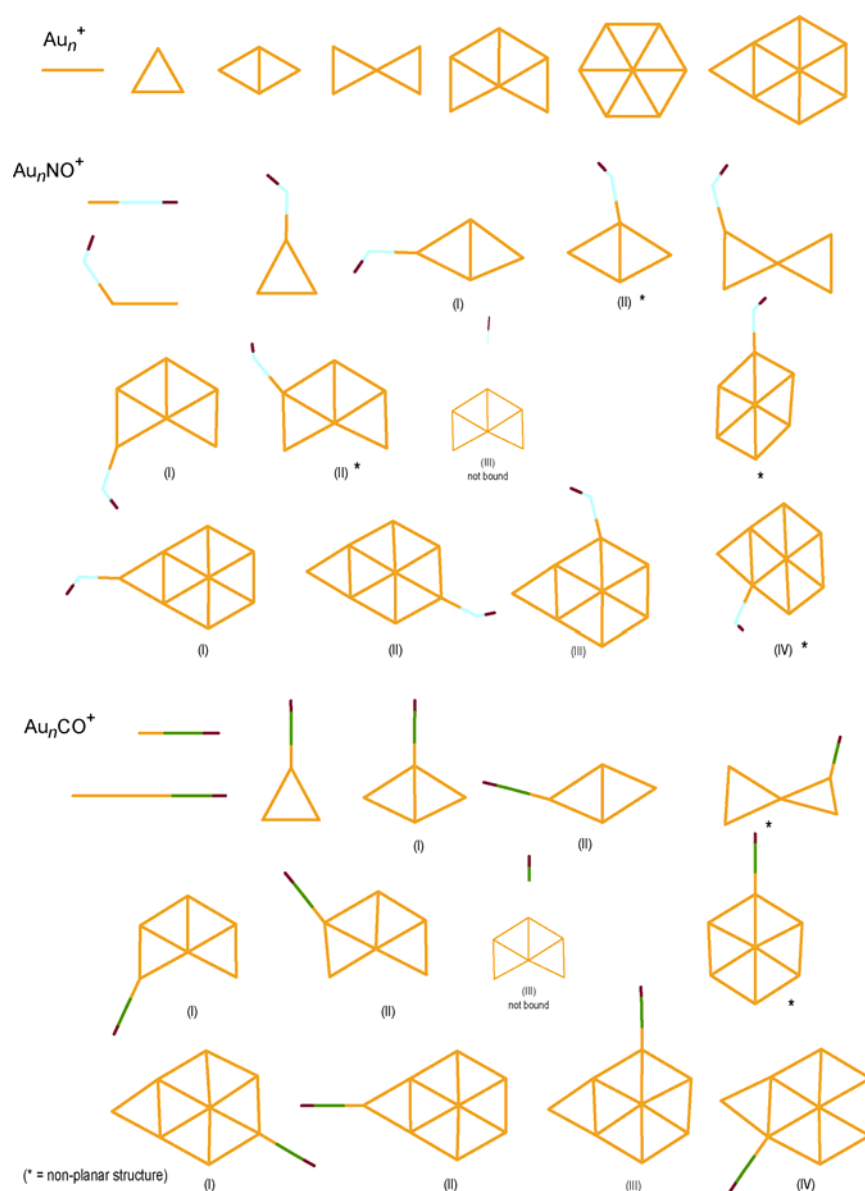


Table S1: Calculated binding energies of NO and CO to gold cluster cations and calculated and experimental frequencies of the internal stretch vibrations of the ligands.

	$E(\text{SCF})$ +ZPVE (h)	ΔE (eV) $E(\text{Au}_n\text{NO}) - E(\text{NO}) - E(\text{Au}_n)$	ΔG^{298} (kJ/mol)	$\nu(\text{NO})$ (cm^{-1})	$\nu(\text{NO})$, scaled (cm^{-1})	$\nu(\text{NO})$ exp. (cm^{-1})
NO	-129.87919			1973.4	1876.0	
AuNO ⁺	-265.25038	-0.78	-82	2030.8	1930.6	1917.8 ^{10a}
Au ₂ NO ⁺	-401.03079	-1.42	-111	2034.6	1934.2	
Au ₃ NO ⁺	-536.79967	-0.80	-49	1968.2	1871.0	1875
Au ₄ NO ⁺ (I)	-672.52850	-0.85	-50	1932.0	1836.6	1854
Au ₄ NO ⁺ (II)	-672.52217	-0.68	-36	1941.0	1845.2	
Au ₅ NO ⁺	-808.29599	-0.65	-30	1949.0	1852.8	1865
Au ₆ NO ⁺ (I)	-944.02892	-0.69	-31	1921.2	1826.4	1827
Au ₆ NO ⁺ (II)	-944.02501	-0.58	-21	1916.8	1822.2	
Au ₆ NO ⁺ (III)	(not bound)					
Au ₇ NO ⁺	-1079.79375	-0.46	-15	1936.9	1841.3	1862
Au ₈ NO ⁺ (I)	-1215.53489	-0.62	-26	1916.6	1822.0	1817
Au ₈ NO ⁺ (II)	-1215.53470	-0.61	-23	1909.7	1815.4	
Au ₈ NO ⁺ (III)	-1215.53049	-0.50	-13	1918.9	1824.2	
Au ₈ NO ⁺ (IV)	-1215.52201	-0.27	+9	1903.2	1809.3	
	$E(\text{SCF})$ +ZPVE (h)	ΔE (eV) $E(\text{Au}_n\text{CO}) - E(\text{CO}) - E(\text{Au}_n)$	ΔG^{298} (kJ/mol)	$\nu(\text{CO})$ (cm^{-1})	$\nu(\text{CO})$, scaled (cm^{-1})	$\nu(\text{CO})$ exp. (cm^{-1})
CO	-113.29927			2215.9	2143.0	
AuCO ⁺	-248.71079	-1.87	-184	2308.1	2232.2	2236.8 ^{10b}
Au ₂ CO ⁺	-384.45234	-1.46	-163	2282.0	2206.9	
Au ₃ CO ⁺	-520.23722	-1.27	-137	2267.0	2192.4	
Au ₄ CO ⁺ (I)	-655.95826	-1.12	-119	2254.1	2179.9	2157
Au ₄ CO ⁺ (II)	-655.95213	-0.95	-97	2259.4	2185.1	
Au ₅ CO ⁺	-791.73343	-1.13	-118	2248.8	2174.8	2152
Au ₆ CO ⁺ (I)	-927.45990	-0.99	-98	2250.6	2176.6	2152
Au ₆ CO ⁺ (II)	-927.45585	-0.88	-87	2240.1	2166.4	
Au ₆ CO ⁺ (III)	(not bound)					
Au ₇ CO ⁺	-1063.22667	-0.81	-77	2240.7	2167.0	2152
Au ₈ CO ⁺ (I)	-1198.96420	-0.87	-80	2236.9	2163.3	2143
Au ₈ CO ⁺ (II)	-1198.95984	-0.75	-67	2245.0	2171.1	
Au ₈ CO ⁺ (III)	-1198.95738	-0.68	-58	2235.9	2162.3	
Au ₈ CO ⁺ (IV)	-1198.94900	-0.45	-28	2228.2	2154.9	