Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Fig. S1 Linear fitting of $-\ln(I/I_0)$ vs CO flows in the kinetic measurements of reactions between Ag_nO^- (n = 1-8) and CO at 150 K. The I and I_0 stand for the intensities of Ag_nO^- with and without CO, respectively. Because the intensity of certain Ag_nO^- from the cluster source was not constant during a series of measurements, we always took one spectrum without CO to get the instant I_0 immediately after the experiment at a defined CO flow. The obtained slopes, their uncertainties, and the cofficients of determination (R^2) in linear fitting were indicated. The mass spectra on the right column qualitatively show the disappearing of Ag_nO^- and the generation of Ag_n^- or $Ag_nCO_2^-$.

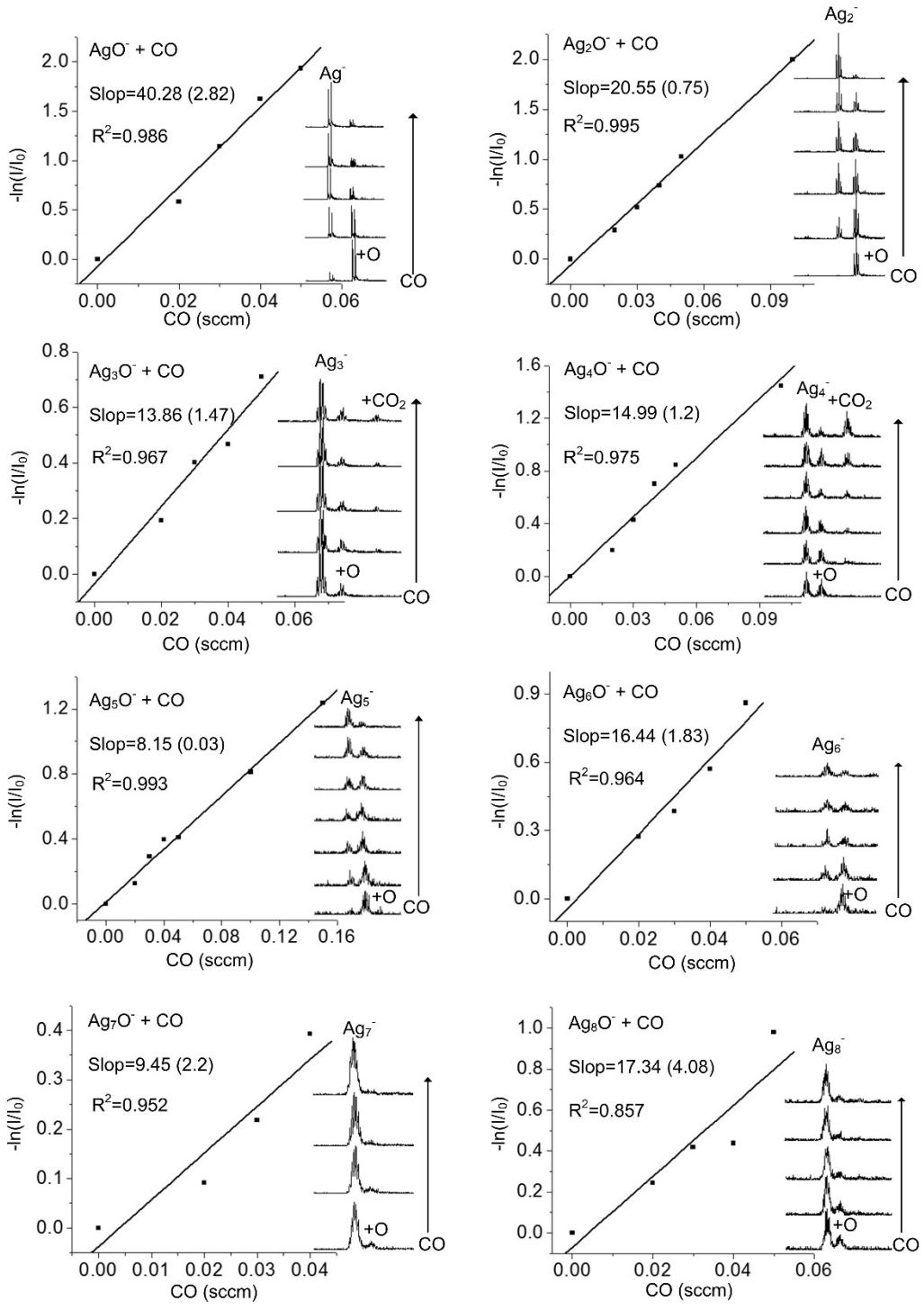


Fig. S2 The lower lying structural candidates of Ag_nO^- (n = 1-8) optimized by B3LYP method with the Aug-cc-pvtz-pp basis set for Ag and the 6-311g* basis sets for C and O. The Ag_nO^- (n = 1, 3, 5, 7) are at their singlet states, and the Ag_nO^- (n = 2, 4, 6, 8) are at their doublet states. The numerals show their relative energies in eV.

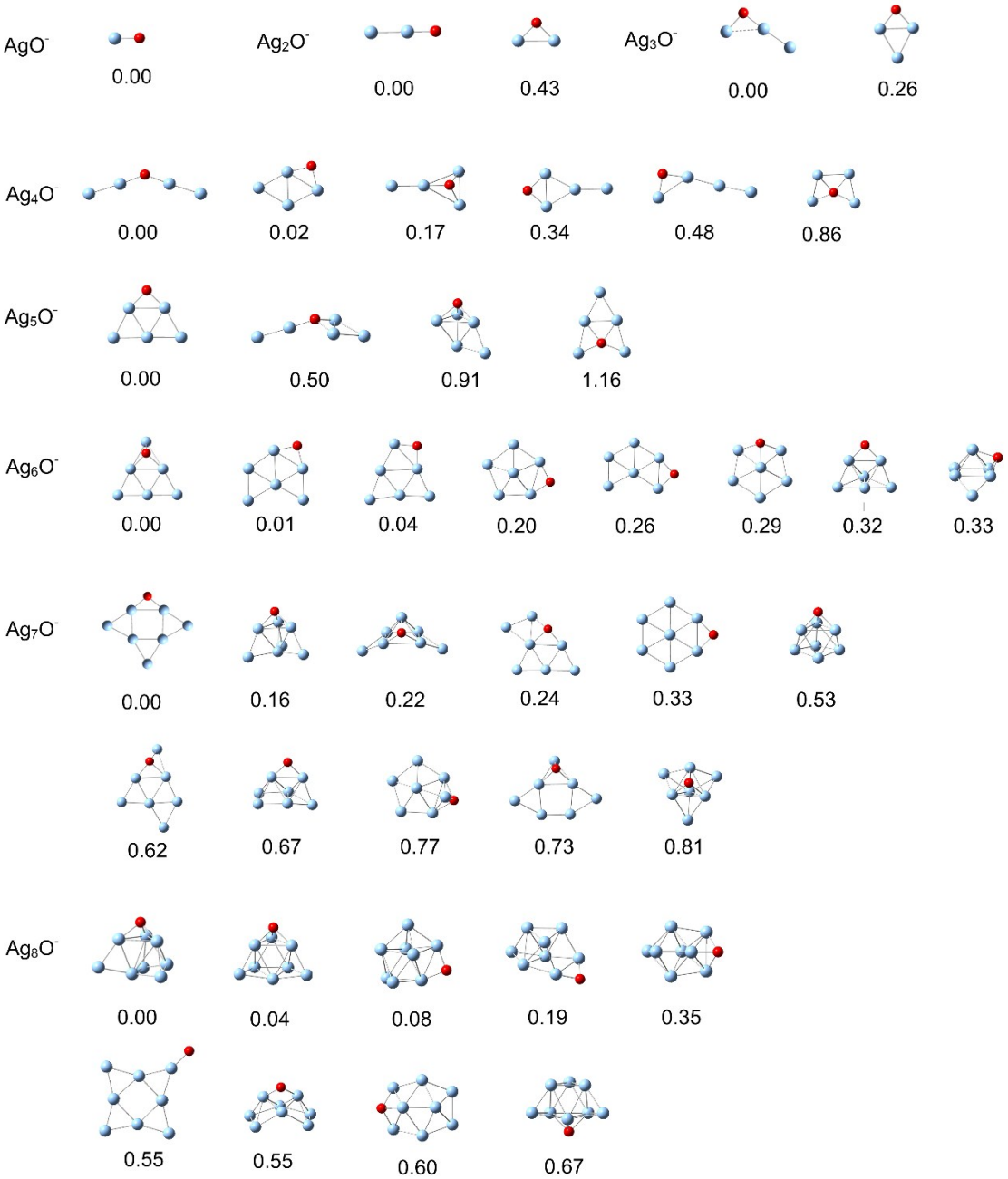


Fig. S3 The spins and negative charges (in a.u.) on the oxygen atoms in the lowest lying structures of Ag_nO^- (n = 1-8) from the natural bond orbital (NBO) analysis.

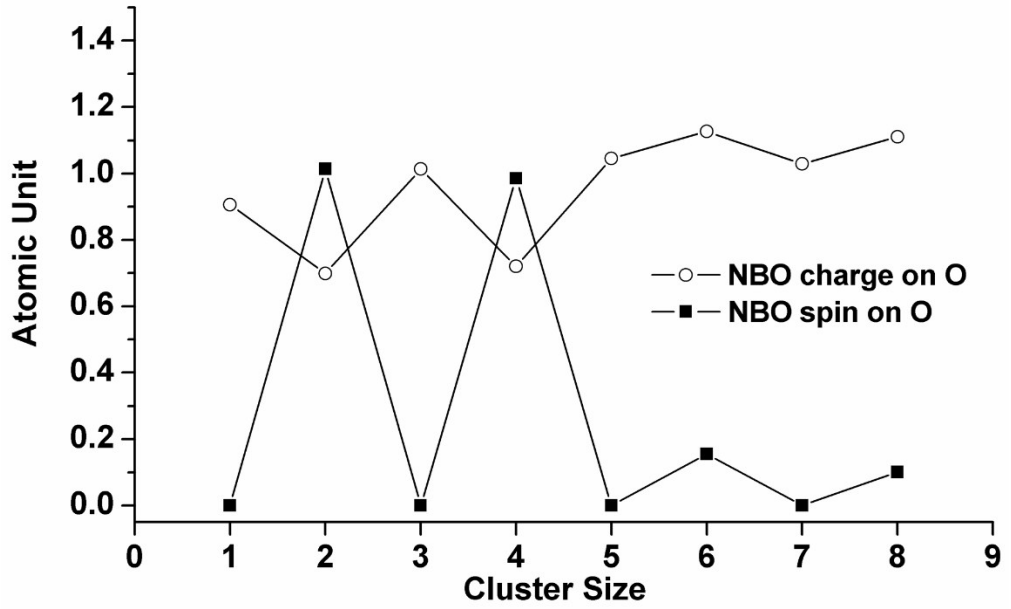
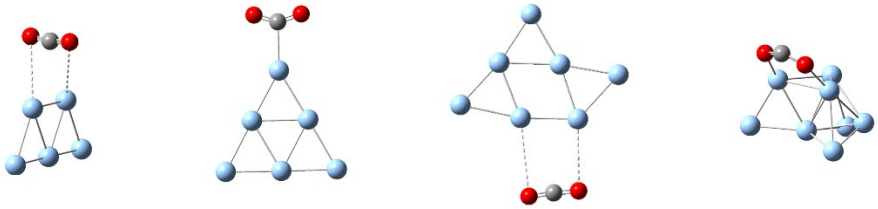


Fig. S4 Theoretical structures of $Ag_nCO_2^-$ (n = 1-8) with CO_2 molecularly bonded on the Ag_n^- frames of the lowest lying Ag_nO^- (n = 1, 2, 5-8) and the lowest lying structures of Ag_3^- and Ag_4^-. The Eb values [=$E(Ag_n^-)$ + E (CO_2)- $E(Ag_nCO_2^-)$], indicate CO_2 binding energies in eV. All structures and energies were obtained using B3LYP method with the Aug-cc-pvtz-pp basis set for Ag and the 6-311g* basis sets for C and O. The $Ag_nCO_2^-$ (n = 1, 3, 5, 7) are at their singlet states, and the $Ag_nCO_2^-$ (n = 2, 4, 6, 8) are at their doublet states. For $Ag_4CO_2^-$, the CO_2 binding strength is too weak to locate a minimum structure at the present theoretical level.

Eb = 0.13 **0.20** **0.08** **~0.00**



Eb = 0.11 **0.09** **0.09** **0.36**

Fig. S5 Structural candidates for $Ag_nCO_2^-$ (n = 3 and 4) except those with weakly bonded CO_2. The ΔE values indicate the energies (in eV) of these structures relative to those of $Ag_3CO_2^-$ or $Ag_4CO_2^-$ in Fig. S4. All structures and energies were obtained using B3LYP method with the Aug-cc-pvtz-pp basis set for Ag and the 6-311g* basis sets for C and O.