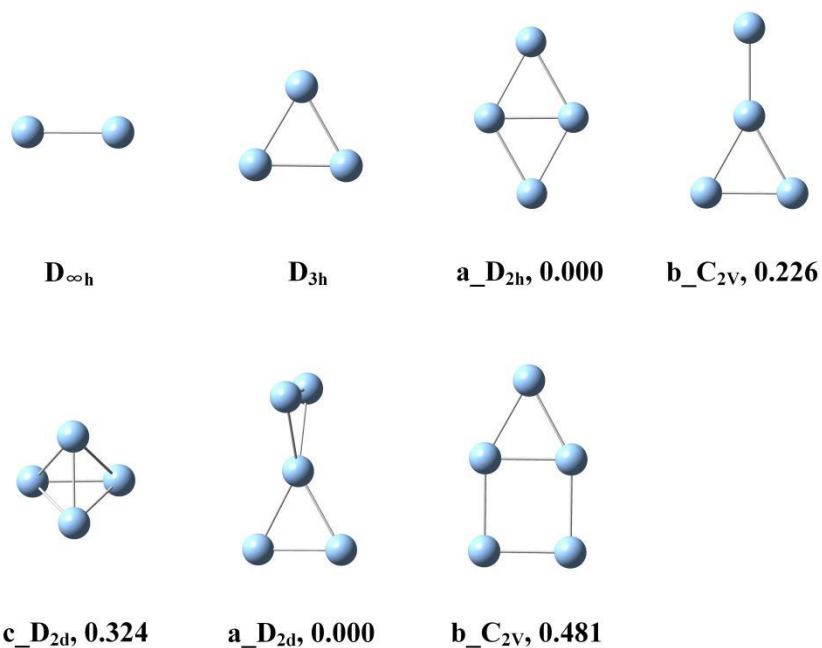


(a) Ag₂₋₅⁺



(b) Ag₆⁺

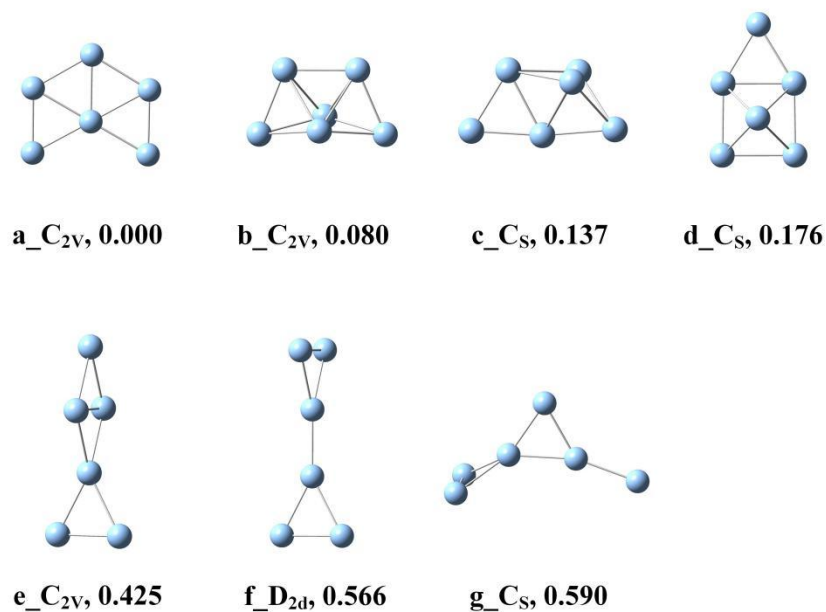
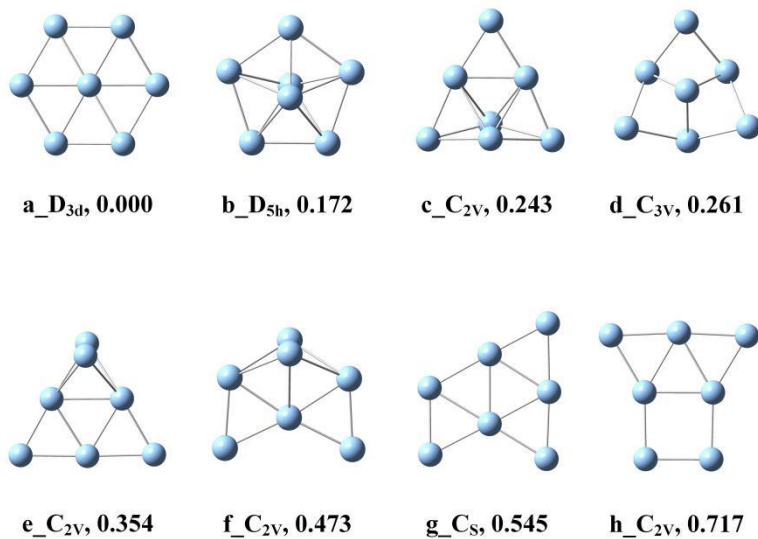


Figure S2. The low-lying structures of Ag_n⁺ ($n = 2-6$) determined by the calculations at the PBE/def2-SVP level of theory. The even sizes are in their doublet state and the odd sizes are in their singlet state. The geometry of each structure and its energy (in eV) relative to the lowest-lying one was indicated.

(a)Ag₇⁺



(b)Ag₈⁺

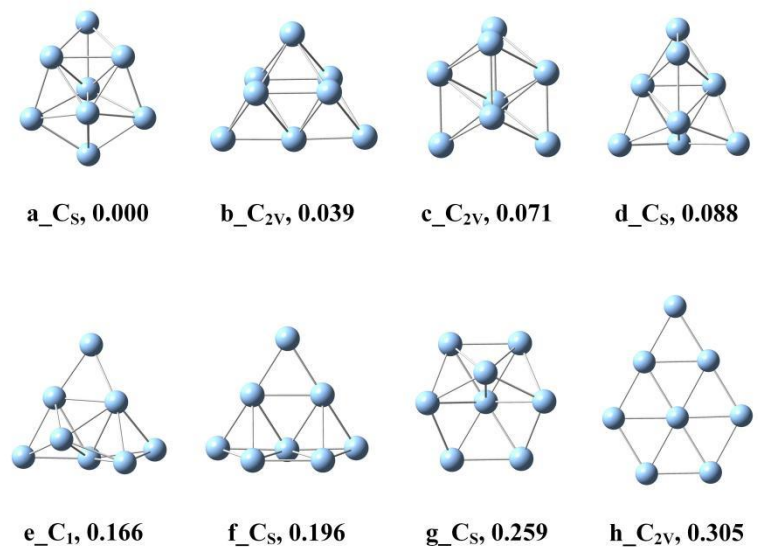
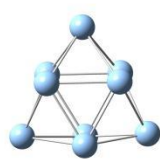
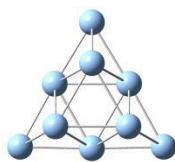


Figure S3. The low-lying eight structures of Ag₇⁺ and Ag₈⁺ determined by the calculations at the PBE/def2-SVP level of theory. The Ag₇⁺ is in its singlet state and the Ag₈⁺ is in its doublet state. The geometry of each structure and its energy (in eV) relative to the lowest-lying one was indicated.

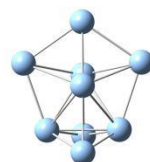
(a)Ag₉⁺



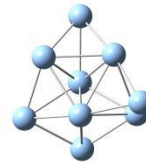
a_D_{3h}, 0.000



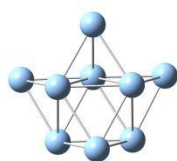
b_C_{3v}, 0.029



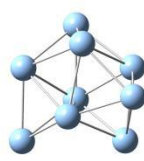
c_C_{2v}, 0.049



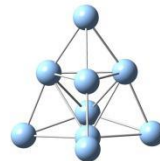
d_C₂, 0.105



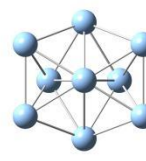
e_C_s, 0.130



f_C₁, 0.134

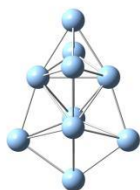


g_C_s, 0.179

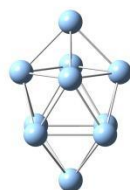


h_C_{2v}, 0.207

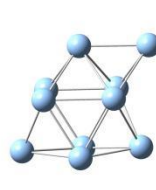
(b)Ag₁₀⁺



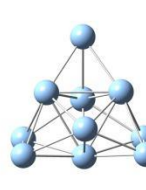
a_D_{2d}, 0.000



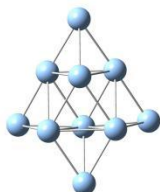
b_D_{4d}, 0.058



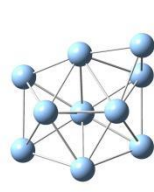
c_C_s, 0.083



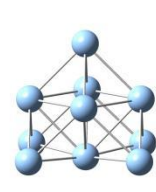
d_C_s, 0.116



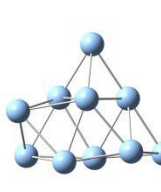
e_C_s, 0.127



f_C₁, 0.137



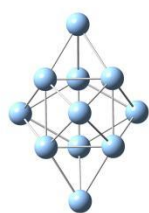
g_C_{4v}, 0.137



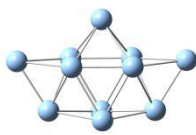
h_C₁, 0.139

Figure S4. The low-lying eight structures of Ag₉⁺ and Ag₁₀⁺ determined by the calculations at the PBE/def2-SVP level of theory. The Ag₉⁺ is in its singlet state and the Ag₁₀⁺ is in its doublet state. The geometry of each structure and its energy (in eV) relative to the lowest-lying one was indicated.

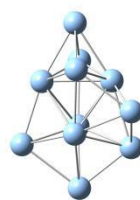
(a)Ag₁₁⁺



a_D_{3h}, 0.000



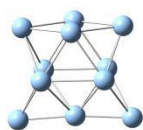
b_C_{2v}, 0.170



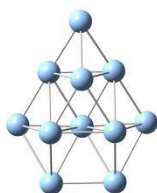
c_C₂, 0.238



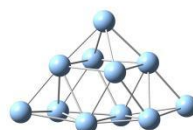
d_C₁, 0.259



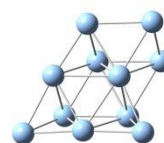
e_C_{2v}, 0.282



f_C_s, 0.288

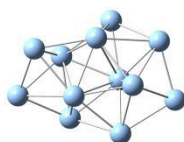


g_C₂, 0.288

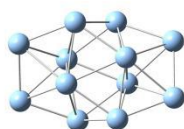


h_C₁, 0.293

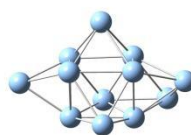
(b)Ag₁₂⁺



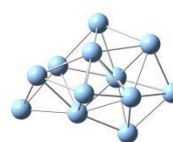
a_C₁, 0.000



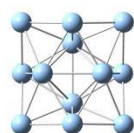
b_D₂, 0.012



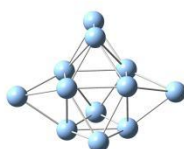
c_C_s, 0.020



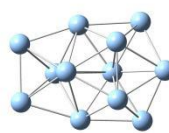
d_C₁, 0.117



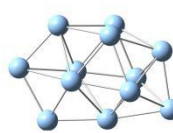
e_D_{2d}, 0.117



f_C_s, 0.118



g_C_s, 0.142



h_C_s, 0.154

Figure S5. The low-lying eight structures of Ag₁₁⁺ and Ag₁₂⁺ determined by the calculations at the PBE/def2-SVP level of theory. The Ag₁₁⁺ is in its singlet state and the Ag₁₂⁺ is in its doublet state. The geometry of each structure and its energy (in eV) relative to the lowest-lying one was indicated.

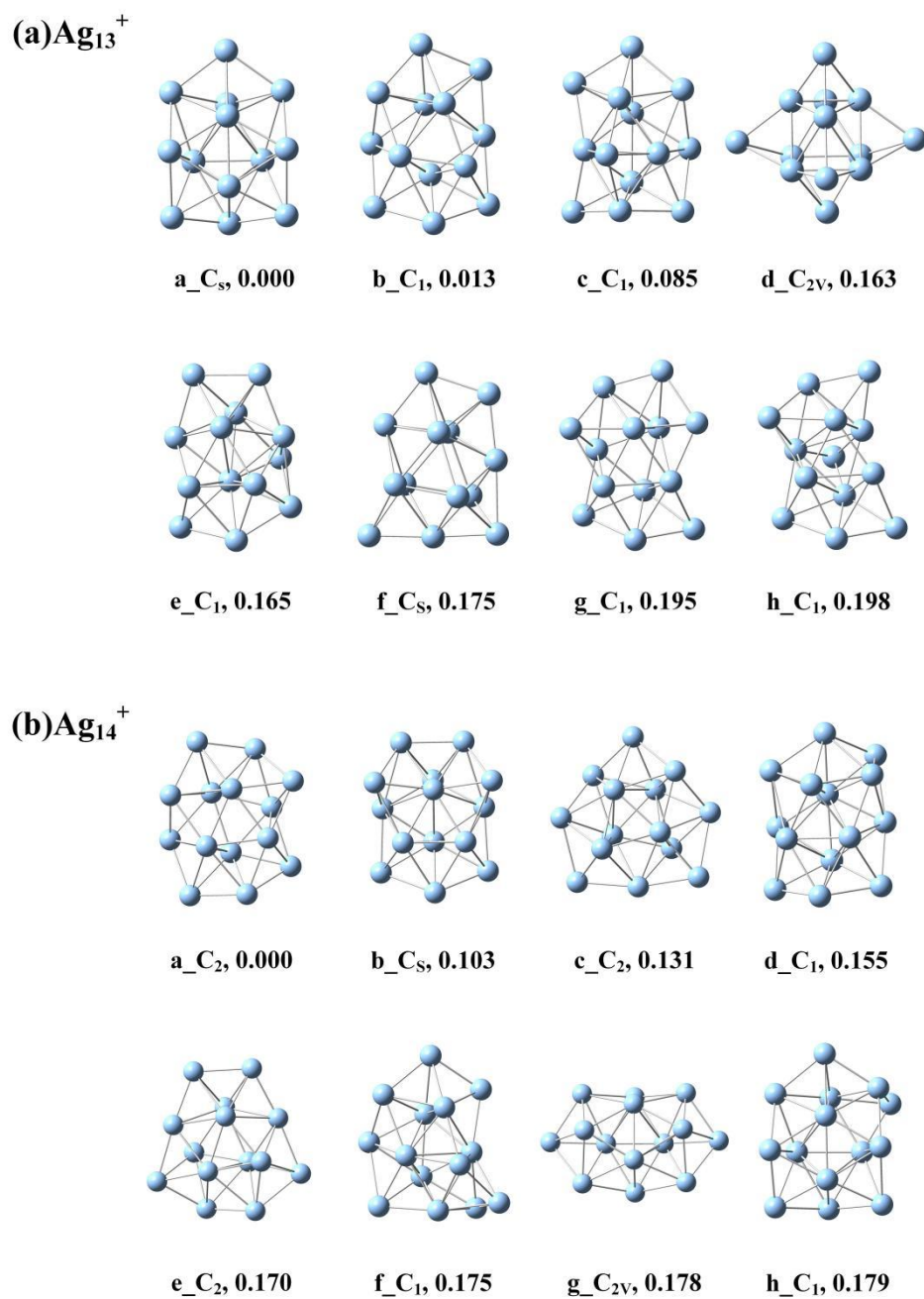
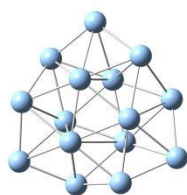
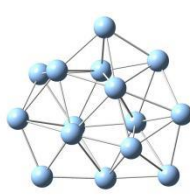


Figure S6. The low-lying eight structures of Ag_{13}^+ and Ag_{14}^+ determined by the calculations at the PBE/def2-SVP level of theory. The Ag_{13}^+ is in its singlet state and the Ag_{14}^+ is in its doublet state. The geometry of each structure and its energy (in eV) relative to the lowest-lying one was indicated.

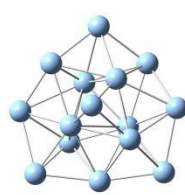
(a) Ag₁₅⁺



a_C₂, 0.000



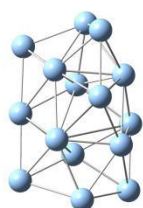
b_C₁, 0.224



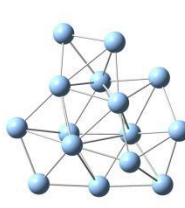
c_C₁, 0.245



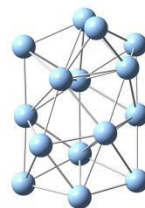
d_C_s, 0.321



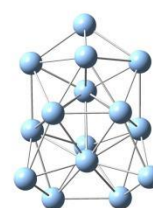
e_C₁, 0.334



f_C₁, 0.374

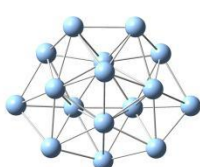


g_C₁, 0.381

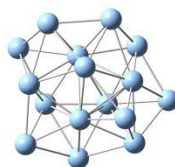


h_C_s, 0.401

(b) Ag₁₆⁺



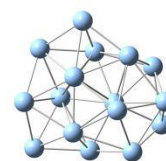
a_C_s, 0.000



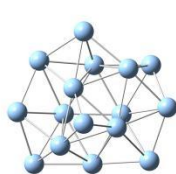
b_C₁, 0.071



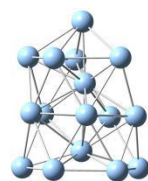
c_C_s, 0.087



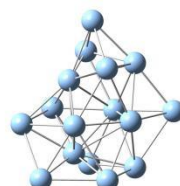
d_C₁, 0.093



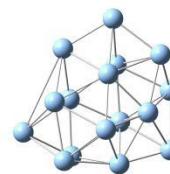
e_C₁, 0.114



f_C₁, 0.126



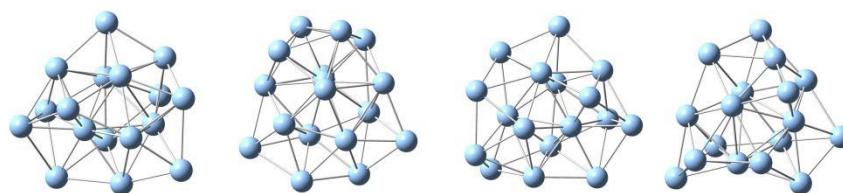
g_C₁, 0.134



h_C₁, 0.150

Figure S7. The low-lying eight structures of Ag₁₅⁺ and Ag₁₆⁺ determined by the calculations at the PBE/def2-SVP level of theory. The Ag₁₅⁺ is in its singlet state and the Ag₁₆⁺ is in its doublet state. The geometry of each structure and its energy (in eV) relative to the lowest-lying one was indicated.

(a)Ag₁₇⁺

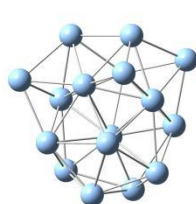


a_C₁, 0.000

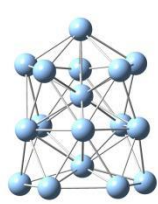
b_C₂, 0.037

c_C₁, 0.044

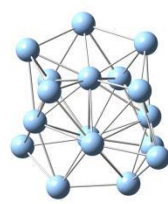
d_C₁, 0.053



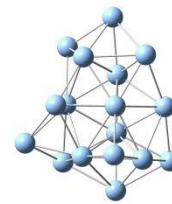
e_C₁, 0.068



f_C_s, 0.123

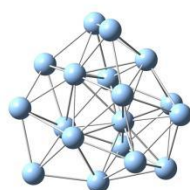


g_C₁, 0.137

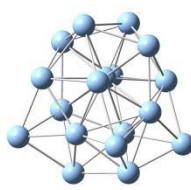


h_C₁, 0.148

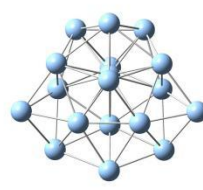
(b)Ag₁₈⁺



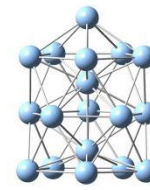
a_C₁, 0.000



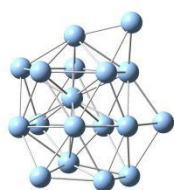
b_C₁, 0.006



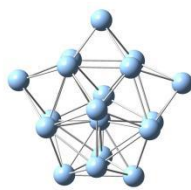
c_C_s, 0.146



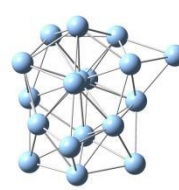
d_C_{5v}, 0.153



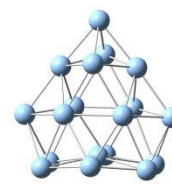
e_C₁, 0.164



f_C_s, 0.169



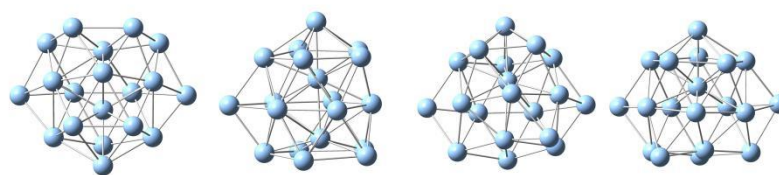
g_C₁, 0.176



h_C_{2v}, 0.221

Figure S8. The low-lying eight structures of Ag₁₇⁺ and Ag₁₈⁺ determined by the calculations at the PBE/def2-SVP level of theory. The Ag₁₇⁺ is in its singlet state and the Ag₁₈⁺ is in its doublet state. The geometry of each structure and its energy (in eV) relative to the lowest-lying one was indicated.

(a) Ag₁₉⁺

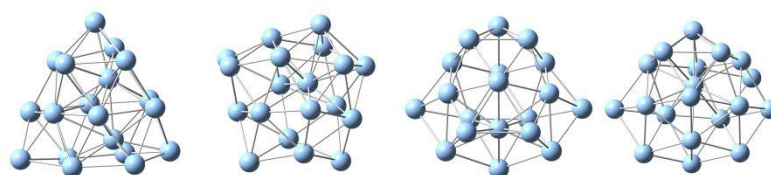


a_C_s, 0.000

b_C_s, 0.065

c_C₁, 0.109

d_C₁, 0.109



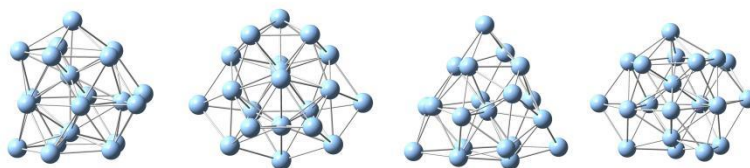
e_C₁, 0.181

f_C₁, 0.201

g_C_s, 0.203

h_C₁, 0.205

(b) Ag₂₀⁺

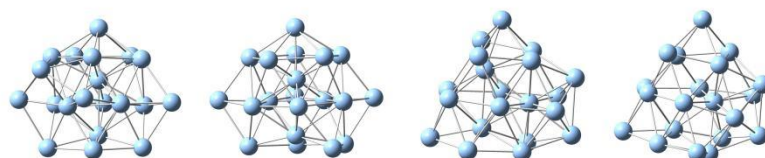


a_C_s, 0.000

b_C_s, 0.016

c_C₃, 0.076

d_C₁, 0.124



e_C₁, 0.133

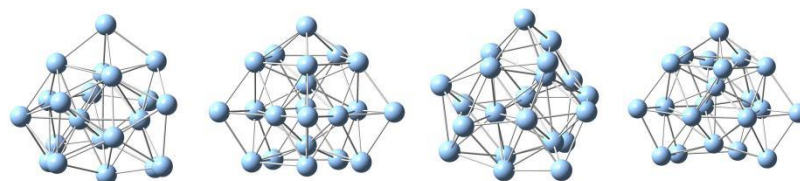
f_C₁, 0.172

g_C₁, 0.183

h_C₁, 0.190

Figure S9. The low-lying eight structures of Ag₁₉⁺ and Ag₂₀⁺ determined by the calculations at the PBE/def2-SVP level of theory. The Ag₁₉⁺ is in its singlet state and the Ag₂₀⁺ is in its doublet state. The geometry of each structure and its energy (in eV) relative to the lowest-lying one was indicated.

(a)Ag₂₁⁺

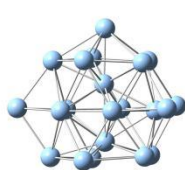


a_C₁, 0.000

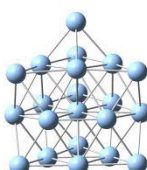
b_C_s, 0.010

c_C₁, 0.037

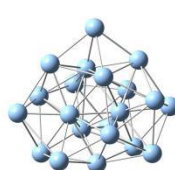
d_C₁, 0.072



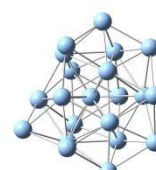
e_C_s, 0.167



f_C_s, 0.174

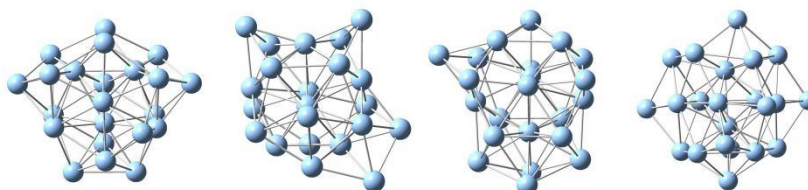


g_C₁, 0.177



h_C₁, 0.183

(b)Ag₂₂⁺

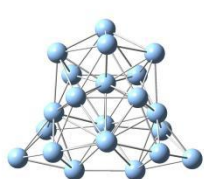


a_C₁, 0.000

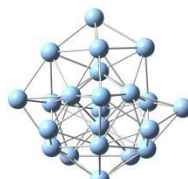
b_C₁, 0.029

c_C₁, 0.041

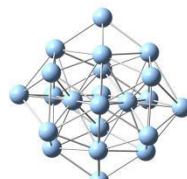
d_C₁, 0.050



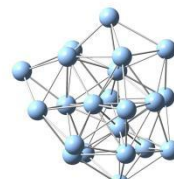
e_C_s, 0.054



f_C₁, 0.075



g_C₂, 0.077



h_C₁, 0.106

Figure S10. The low-lying eight structures of Ag₂₁⁺ and Ag₂₂⁺ determined by the calculations at the PBE/def2-SVP level of theory. The Ag₂₁⁺ is in its singlet state and the Ag₂₂⁺ is in its doublet state. The geometry of each structure and its energy (in eV) relative to the lowest-lying one was indicated.