1. INTRODUCTION

Hydrogen is the most promising energy source as an environmentally friendly alternative to fossil fuels because it does not contribute to the carbon emission as fossil fuels when it is burnt, and it produces water. But the major problem is the storage of hydrogen to use it as an energy source. At the current state of technology, hydrogen must be compressed, liquefied, and stored in bulk tanks. In a bare system, because of its low boiling point (20.39 K), at least 1000 bar pressure is required to liquefy gaseous hydrogen at room temperature. Research on different chemical entities has been of growing interest in the search for novel storage materials. Metal–organic frameworks (MOFs), a class of highly porous crystalline materials, after the first promising results reported by the Yaghi group,1,2 are being extensively studied.3–5 The development of liquid hydrogen carriers such as liquid organic hydrogen carriers (LOHC) and ammonia is also considered to be a method of hydrogen storage, especially in renewable energy (wind, solar, etc.)-rich areas.6–8 Different classes of metal–hydrogen complexes are being paid continuous attention in the search for potential storage materials.9–13 Though there are several methods for hydrogen storage, other than compressing the gas, only that in which a material adsorbs hydrogen due to physisorption is a winning method to store hydrogen because of the absence of chemical bonds with the adsorbent and the reversibility of the process; hence, physisorption by porous solid-state materials and metal hybrids offers a solution to store hydrogen gas, but still, there are few materials that meet industrial requirements. Therefore, the search for hydrogen storage materials is a challenge in the early stage of the century for both experimentalists and theorists.

In parallel to experimental approaches, a considerable amount of theoretical work has been carried out in designing and characterizing storage materials. H2 adsorption on a porous nanotube network,14 as well as on oxygen-functionalized carbon slit pores,15 was studied by the Froudakis group. They also reported the improved hydrogen storage abilities of...
potential heterogeneous system within the recommended species in each series of di... potential heterogeneity, chemical hardness, and highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) gap (HLG). The hydrogen adsorption was characterized using similar parameters, such as hydrogen adsorption energy, bond distance analysis, vibrational frequency analysis, orbital occupancy analysis, and frontier molecular orbital (FMO) analysis.

The average binding energies of a CuₙAgₙ cluster and those of a hydrogen-adsorbed cluster are calculated as follows

\[
\text{ABE(CuₙAgₙH)} = \left[ mE(Cu) + nE(Ag) - E(CuₙAgₙ) \right] / (m + n)
\]

(1)

\[
\text{ABE(CuₙAgₙH₂)} = \left[ mE(Cu) + nE(Ag) + 2E(H) \right] - E(CuₙAgₙH₂) / (m + n + 2)
\]

(2)

Adiabatic ionization potential (AIP) and adiabatic electron affinity (AEA) of both CuₙAgₙ and CuₙAgₙH₂ clusters are calculated using the following expressions

\[
\text{AIP(CuₙAgₙ)} = E(CuₙAgₙ)^+ - E(CuₙAgₙ)
\]

(3)

\[
\text{AEA(CuₙAgₙ)} = E(CuₙAgₙ) - E(CuₙAgₙ)^-
\]

(4)

\[
\text{AIP(CuₙAgₙH₂)} = E(CuₙAgₙH₂)^+ - E(CuₙAgₙH₂)
\]

(5)

\[
\text{AEA(CuₙAgₙH₂)} = E(CuₙAgₙH₂) - E(CuₙAgₙH₂)^-
\]

(6)

In addition, chemical hardness (\(\eta\)), which is also a measure of the relative stability of an electronic system, can be estimated as half the difference between the adiabatic ionization potential and adiabatic electron affinity through the electronic chemical potential of the system.35–38

\[
\eta = \frac{\text{AIP} - \text{AEA}}{2}
\]

(7)

The hydrogen adsorption energy is given by the equation

\[
E_{\text{Ad}} = E(CuₙAgₙH₂) + E(H₂) - E(CuₙAgₙH₂)
\]

(8)

### 2. CALCULATION DETAILS

We used Kohn–Sham density functional theory (DFT) in all of the calculations of the bare cluster and H₂ adsorption using the Gaussian 16 software package.33 In this study, we used the Becke 3 parameter Lee–Yang–Parr (B3LYP) correlation functional and the Los Alamos relativistic effective core potential for core electrons with double-\(\zeta\) basis set for valence electrons (LanL2DZ) for Cu and Ag of the CuₙAgₙ system.34

In the case of H₂ adsorption, we mixed the LanL2DZ basis set with Dunning’s correlation-consistent basis set, aug-cc-pVQZ, for Cu and Ag, and H₂ of the CuₙAgₙH₂ system, respectively. We will compare our results with the literature and rationalize the selection of the functional and basis set in Section 3.1.

### 3. RESULTS AND DISCUSSION

All of the possible geometries of CuₙAgₙ \((m + n \leq 8)\) clusters were designed, and their global minimum was located by applying extensive optimization procedures at different special arrangements of copper and silver atoms including all possible spin arrangements and by the absence of the imaginary modes in the calculated Hessian. Then, the most stable neutral cluster species in each series of different cluster sizes were subjected to H₂ molecule adsorption. The H₂ adsorption on all of the different positions for each cluster was studied. The stability of the cluster series was compared utilizing the average binding energy (BE), adiabatic ionization and electron affinity, chemical hardness, and highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) gap (HLG). The hydrogen adsorption was characterized using similar parameters, such as hydrogen adsorption energy, bond distance analysis, vibrational frequency analysis, orbital occupancy analysis, and frontier molecular orbital (FMO) analysis.

### Table 1. Comparison of the Calculated Binding Energies (BE/eV per Atom) and the Average First Neighbor Bond Distances ((\(r\))/Å) of Cuₙ \((n = 2–8)\) Clusters with Some of the Major Literature Data and Available Experimental Data

| cluster | PG symmetry and multiplicity | PW91\(^b\) | TB-LMTO\(^c\) | LSDA\(^d\) | TBMD\(^e\) present | exp\(^f\) | LSDA\(^d\) | TBMD\(^e\) | PW91\(^b\) present |
|---------|-----------------------------|-----------|--------------|---------|-------------------|------|---------|----------|------------------|
| Cu₂     | \(D_{2h}\) 1                | 1.055     | 0.23         | 1.36    | 1.01              | 1.02 | 2.18    | 2.52     | 2.26             |
| Cu₃     | \(C_{2v}\) 2                | 1.187     | 0.68 (C₃h)  | 1.52 (1.63) | 1.43              | 1.00 | 1.07 ± 0.12 | 2.27     | 2.25  | 2.54 | 3.33 |
| Cu₄     | \(D_{3h}\) 1                | 1.580     | 1.28 (T₂)   | 1.97 (2.09) | 2.00              | 1.31 | 1.48 ± 0.14 | 2.30     | 2.23  | 2.52 | 2.43 |
| Cu₅     | \(C_{2v}\) 2                | 1.724     | 1.43 (C₃h)  | 2.01    | 2.24              | 1.41 | 1.56 ± 0.15 | 2.29     | 2.25  | 2.50 | 2.44 |
| Cu₆     | \(D_{3h}\) 1                | 1.909     | 1.56 (C₃h)  | (2.49)  | 2.54 (C₃h)        | 1.59 | 1.73 ± 0.18 | 2.40     | 2.47  | 2.44 |
| Cu₇     | \(D_{3h}\) 2                | 2.032     | 1.81(C₃h)   | (−)     | 2.65              | 1.63 | 1.86 ± 0.22 | 2.41     | 2.48  | 2.52 |
| Cu₈     | \(Tₜ\) 1                    | 2.105     | 2.15 (D₁₂h) | (−2.84) | 2.87 (C₃h)        | 1.73 | 2.00 ± 0.23 | 2.41     | 2.47  | 2.51 |

"Column 2 presents the point group symmetry of each species from the current study. Binding energies in parenthesis under the column LSDA are from ref 42. The experimental binding energy (1.02 eV per atom) is taken from ref 44. The calculated binding energies and the average bond distances in this study with the theory level of B3LYP/LanL2DZ are given in the columns "present"."
3.1. Structures and Relative Stability of Bare Cu$_m$Ag$_n$ Clusters. The binding energies and spatial arrangements of atoms (point group symmetry) in the optimized structures with spin multiplicity given in Table 1 are compared with data of previous studies on Cu clusters obtained by different techniques, especially in generalized gradient approximation.

Table 2. Comparison of Calculated Binding Energies (BE/eV per Atom) and the Average First Neighbor Bond Distances ($\langle r \rangle$/Å) of Ag$_n$ (n = 2−8) Clusters$^a$

| cluster | PG symmetry and multiplicity | cohesive energy (BE)/eV per atom | average bond distance ($\langle r \rangle$/Å) | present | expet |
|---------|-----------------------------|----------------------------------|------------------------------------------|--------|-------|
| Ag$_2$  | $D_{\infty h}$ 1            | 0.83 0.76 0.75 1.01 0.92 1.10   | 0.78 0.74 0.93 1.09 0.74 0.87       | 2.61   | 2.48  (2.53)$^g$ |
| Ag$_3$  | $C_{2v}$ 2                | 0.82 0.74 0.71 0.99 0.88 1.09   | 0.74 0.71 0.93 1.09 0.74 0.87       | 2.63   | 2.78  |
| Ag$_4$  | $D_{4h}$ 1                | 1.09 0.96 0.93 1.09 0.93 1.09   | 0.95 0.93 0.93 1.09 0.93 1.09       | 2.80   | 2.80  |
| Ag$_5$  | $C_{2v}$ 2                | 1.19 1.05 1.02 1.20 1.09 1.19   | 1.04 1.02 1.02 1.20 1.09 1.19       | 2.87   | 2.87  |
| Ag$_6$  | $D_{4d}$ 2                | 1.36 1.20 1.18 1.20 1.18 1.20   | 1.17 1.18 1.18 1.20 1.18 1.20       | 2.87   | 2.87  |
| Ag$_7$  | $T_d$ 1                   | 1.46 2.28 2.12 1.28 2.28 2.12   | 1.26 2.28 2.12 1.28 2.28 2.12       | 2.87   | 2.87  |

$^a$Column 2 presents the point group symmetry of each species with the spin multiplicity in this study. Calculated binding energies under the functionals of BP86, revPBE, and B3LYP are from ref 45, those corresponding to the BPW91, B3LYP, and PB86 are from ref 47, and experimental values are from refs 46 and 48−50. The calculated binding energies and the average bond distances in this study with the theory level of B3LYP/LanL2DZ are given in the columns "present". $^b$Liao et al. $^c$Srinivas et al. $^d$Beutel et al. $^e$Hilpert et al. $^f$Morse et al. $^g$Simard et al.
Figure 2. continued
(GGA) at the PW91 level, parameterized tight-binding linear muffin-tin orbital (TB-LMTO), local-spin-density approximation (LSDA), and tight-binding molecular dynamics (TBMD) with parameters fitted to first-principles calculations by Kuang et al., Lammers et al., Jackson and Massobrio et al., and Kabir et al., respectively. The binding energies derived from both the local-spin-density approximation and from the tight-binding molecular dynamics showed overestimated figures compared to the experimental values and those derived from generalized gradient approximation were relatively in agreement with the experimental values. Similarly, the binding energies calculated using the parameterized tight-binding linear muffin-tin orbital were also in good agreement with the experimental values for the clusters larger than $n = 3$ though cluster symmetries were inconsistent. The calculated values in this study using DFT with the B3LYP correlation functional and the basis set of LanL2DZ showed excellent agreement with the experimental values. In the case of the dimer, the calculated binding energy (1.01 eV per atom) and the bond distance (2.26 Å) showed excellent agreement with those of experimental values (1.02 eV per atom and 2.22 Å, respectively).

Similarly, Table 2 compares the binding energies of neat Ag clusters reported in two different studies and obtained in the present study with the available experimental data of the Ag dimer and trimer. Liao et al. compared the binding energies per atom of the Ag clusters calculated by three density functionals, generalized gradient approximation (GGA) at BP86 and revPBE, and B3LYP with the experimental binding energy of the Ag dimer. In this comparison, STO basis functions with triple zeta frozen core plus 1 polarization function (TZP fc) were used and BP86 was considered as the best suit on their study of oxygen adsorption on both neutral and anionic silver and gold clusters. On the other hand, Srinivas et al. reported the performance of three DFT functionals, BPW91, B3LYP, and BP86, separately against two different 28-electron ECPs and an all-electron basis for the atomic orbital treatments by calculating and comparing the binding energy per atom of the dimer and trimer with those of experimental data. Their study concluded that the performance depends on the choice of the specific functional within DFT and the basis set used in combination; in general, B3LYP showed better agreement with the binding energy. With these extensive comparisons, we selected the B3LYP/LanL2DZ combination for the calculation in our study, especially considering the copper clusters.

Minimum energy structures of both neat copper and silver motifs are shown in Figure 1. The dimension transitions (from 1-D to 3-D) of both copper and silver cluster structures occur when the cluster size increases. The dimer is a 1-D structure, the trimer to the hexamer possess planar 2-D structure patterns, and the clusters above the hexamer are in 3-D arrangements aligning with previous observations. The clusters of both pure Cu and Ag have the shapes of an isosceles triangle for the trimer, rhombus for the tetramer, trapezoid for the pentamer, triangle for the hexamer, pentagonal bipyramid for the heptamer, and tetracapped tetrahedron for the octamer.

Both Cu and Ag belong to the coinage group (group 11) in the periodic table. The optimized structures of the mixed clusters given in Figure 2a,b show that the copper atoms always tend to occupy the middle position when it is available due to the smaller size of the Cu atom ($3d^{10}4s^1$) compared to the Ag atom ($4d^{10}5s^1$) and reduced electronegativity of Cu (1.9) compared to that of Ag (1.93) according to the general fact that atoms with the most positive charges favor the middle positions (nuclei) of the clusters, where an atom can have the optimal coordination number. The mixed clusters of each stoichiometric ratio of copper and silver were designed using the stable configurations of Cu$_n$ clusters as the precursors. In this process, Cu atoms were systematically replaced by Ag atoms one by one accounting for all of the possible positions, and the most stable structure of each mixed cluster was obtained by energy optimization. The deviation from the
original monometallic cluster morphology with heterogeneity is also noticed. Different structural shapes for the different stoichiometry of copper and silver in a particular cluster size can be observed, and Cu atoms reside in such a way that they can possess the optimal coordination number. As shown in Figure 2a, the mixed clusters follow similar structural patterns of Ag₆ and Cu₆ clusters observed in this study as well as in previous work. The dimer of the Cu₆Ag₆ cluster is a 1-D structure, whereas the trimers to the hexamer of Cu₆Ag₆ clusters possess planar 2-D structure patterns except for the 3-D structure of CuAg₆. Cu₆Ag₆ clusters above the hexamer are in 3-D arrangements (Figure 2b). The hexamers consist of triangular and capped spatial arrangements lying in a broad energy spectrum instead of pursuing the original triangular shape of Cu₆ and Ag₆. In contrast to the low symmetric (C₃ᵥ) triangular structure of CuAg₆ observed by Wei-Yin et al. (with four coordinated Cu), we observed high symmetric (Cᵥ) capped spatial arrangements of the atoms with the maximum of five coordination for Cu following the observation made by Zhou and co-workers. Though the Cu₄Ag₅ cluster possesses a capped shape, all of the other candidates in the hexamer are triangular including the Cu₄Ag₅ cluster, whose single Ag atom is not favorable to be in the middle forming a capped shape structure because of comparatively high positive charge and small size of the Cu atom compared to Ag. All of the heptamers, except Cu₅Ag₅, possess the original pentagonal bipyramid structural shape of Cu₅ and Ag₅. Cu₄Ag₅ is a tricapped tetrahedron with the Cᵥ symmetry that consists of three layers of packing. The first layer is an equilateral triangle of three Cu atoms, the next layer is an equilateral triangle of three Ag atoms, and then the fourth Cu atom is above the center of the triangles. The minimum energy structures of single Cu atom-substituted cluster series, AgₙCuₙ for n = 1−8, reported by Ding et al. using the meta-GGA functional were in accordance exactly with the structures observed in this study for the corresponding entities.

In addition to these minimum energy structures, we examined the other higher energy structures (low-lying isomers) of CuₙAgₙ clusters for m + n = 3−8, and the structures of those isomers with energies relative to the lowest energy geometry are given in Figure S2a−f in the Supporting Information. A detailed comparison of low-lying energy structures is beyond the scope of this article and interested readers can find a detailed comparison in the literature.

The average bond distance of a cluster is also an important parameter to understand the cohesiveness of the cluster with its size. Figure 3 depicts the change of the average bond distances of Cuₙ and Agₙ clusters with the number of atoms in the cluster. In addition, the variation of the average first neighbor bond distance of the CuₙAgₙ cluster for n = 1−7 with the silver substitution is also shown in the same graph. This shows that the cluster expansion with the consecutive addition of an atom to both neat copper and silver systems shows a uniform parallel behavior keeping the difference between the two at about 0.36 Å, which is approximately the difference of the equilibrium bond distances of the Ag dimer (2.61 Å) and the Cu dimer (2.26 Å). This reveals that the atomic radii (size of the atoms) play a major role in the cluster size expansion but not the electronic structure due to the same valence electronic configuration of Cu and Ag (3d¹⁰4s¹ and 4d¹⁰5s¹, respectively). Similarly, the stepwise replacement of a copper atom in a cluster, CuₙAgₙ for example, by a silver atom shows a gradual increase of the average bond distance, resulting in the expansion of the cluster size with the same number of atoms. In contrast to this gradual increase of the average bond distance for n = 1−7, as shown in Table 4, the abrupt change of the average bond distances occurs in the transition from Cu₄ to Cu₅Ag (from n = 0 to 1) and from Cu₅Ag to Ag₆ (from n = 7 to 8). In the first case, the addition of a Ag atom to high symmetric Cu₄ causes symmetry loss from Tₐ to Cᵥ (Figures 1 and 2a,b), which increases the average bond distance compared to the addition of a Ag atom to the already symmetry lost clusters for n ≥ 1. In the second case, the relaxation of low symmetric Cu₅Ag occurs when the Ag atom is added to gain the high symmetry from Cᵥ to Tₐ.

Similarly, we can observe a rapid increase in the binding energy per atom compared to the slower rate of cluster expansion with the number of atoms in the cluster except for the slight decrease for n = 3 and 7 as shown in Figure 4.

Interestingly, n = 3 and 7 are the points where we observed the dimensional transition from 1-D to 2-D and from 2-D to 3-D, respectively. Cuₙ clusters have higher binding energies than corresponding Agₙ clusters and the energy gap (difference) increases with the number of atoms in the cluster; at the lower end, it accounts for 0.23 Å, which is the difference in two dimers, while at the higher end, it is about 0.47 Å. The cluster expansion and binding energy lowering with the replacement

Figure 3. Variation in the average bond distance of neat copper clusters (Cuₙ: orange) and silver clusters (Agₙ: blue) with the number of atoms in the cluster from n = 2 to 8. The black color plot shows the expansion of the CuₙAgₙ cluster with the substitution of a Ag atom in place of the Cu atom.

Figure 4. Variation in the binding energy of neat copper clusters (Cuₙ: orange) and silver clusters (Agₙ: blue) with the number of atoms in the cluster from n = 2 to 8. The black color solid line shows the binding energy lowering of the CuₙAgₙ cluster with the substitution of a Ag atom in place of the Cu atom.
have the opposite trend as shown in Cu(m+n)Ag(n), for example, in Figures 3 and 4, for a given size of a cluster. The average rates of the cluster expansion and binding energy lowering are about 0.043 Å and 0.059 eV per Ag atom substitution, respectively.

### 3.2. Hydrogen Adsorption on Clusters

We explored the hydrogen adsorption on Cu(m)Ag(n) clusters extensively using the effect of the adsorption on the binding energy, average bond distances, hardness, HOMO–LUMO gap, properties of electronic energy states, and the vibrational frequencies of bare and adsorbed bimetallic clusters. The adsorption of a hydrogen molecule on each atom in a particular cluster was examined and then one that had the most favorable adsorption was reported. Tables 3 and 4 present all of the energy parameters and selected vibrational frequencies with corresponding bond lengths for both bare and H2-adsorbed Cu(m)Ag(n) clusters, respectively. The average binding energies of hydrogen-adsorbed copper-rich clusters are comparatively higher than those of silver-rich clusters of the same size (decrease in the binding energy with Ag substitution), indicating the higher stability of copper-rich systems over the silver-rich systems similar to the trend observed in bare Cu(m)Ag(n) systems (Figure 4). The rate of the decrease in the average binding energy of a particular cluster

| Cluster | BE(eV) | E_ads(kJ mol⁻¹) | HLG(eV) | AIP(eV) | AE(eV) | VIP(eV) | VEA(eV) |
|---------|--------|----------------|---------|---------|--------|--------|--------|
| Cu2    | 1.01   | 1.78           | -30.37  | 5.23   | 3.89   | 0.64   | 7.93    |
| CuAg   | 0.89   | 1.72           | -29.42  | 3.08   | 3.72   | 0.64   | 7.83    |
| Ag2    | 0.78   | 1.59           | -31.91  | 2.91   | 3.10   | 0.19   | 7.73    |
| Cu10   | 1.00   | 1.67           | -54.92  | 1.40   | 1.42   | 0.02   | 5.74    |
| Cu2Ag  | 0.93   | 1.62           | -50.11  | 1.34   | 1.36   | 0.02   | 5.79    |
| Ag12   | 0.86   | 1.56           | -40.53  | 1.28   | 1.30   | 0.02   | 5.88    |
| Ag3    | 0.74   | 1.41           | -5.91   | 1.26   | 1.28   | 0.02   | 5.80    |
| Cu4    | 1.31   | 1.78           | -66.60  | 1.91   | 2.85   | 0.94   | 6.59    |
| Cu3Ag  | 1.24   | 1.74           | -63.05  | 1.92   | 2.84   | 0.92   | 6.58    |
| Cu2Ag12| 1.18   | 1.69           | -56.02  | 1.76   | 2.55   | 0.79   | 6.50    |
| Ag27   | 0.95   | 1.47           | -19.31  | 1.61   | 2.22   | 0.61   | 6.42    |
| Cu5    | 1.41   | 1.73           | -26.40  | 1.34   | 1.37   | 0.03   | 5.99    |
| Cu3Ag  | 1.35   | 1.69           | -27.61  | 1.32   | 1.31   | 0.01   | 6.02    |
| Cu2Ag2 | 1.29   | 1.65           | -25.39  | 1.30   | 1.30   | 0.01   | 6.05    |
| Cu2Ag12| 1.22   | 1.59           | -24.67  | 1.24   | 1.27   | 0.03   | 5.99    |
| Cu14   | 1.14   | 1.51           | -8.55   | 1.20   | 1.20   | 0.00   | 5.92    |
| Ag28   | 1.04   | 1.43           | -5.13   | 1.18   | 1.18   | 0.00   | 5.82    |
| Cu50   | 1.59   | 1.81           | -16.71  | 3.24   | 3.24   | 0.00   | 7.11    |
| Cu4Ag  | 1.54   | 1.78           | -15.89  | 3.14   | 3.20   | 0.06   | 7.12    |
| Cu2Ag12| 1.49   | 1.74           | -15.45  | 3.06   | 3.15   | 0.09   | 7.04    |
| Cu2Ag2 | 1.44   | 1.70           | -12.89  | 3.01   | 3.00   | 0.00   | 7.04    |
| Cu2Ag12| 1.36   | 1.63           | -10.41  | 2.98   | 2.98   | 0.00   | 7.00    |
| Cu51   | 1.28   | 1.59           | -22.70  | 3.01   | 3.03   | 0.03   | 6.68    |
| Ag30   | 1.50   | 1.50           | -7.51   | 3.00  | -0.99  | 0.01   | 6.95    |
| Cu6    | 1.63   | 1.82           | -22.21  | 1.27   | 1.27   | 0.00   | 5.89    |
| Cu5Ag  | 1.57   | 1.77           | -22.51  | 1.27   | 1.27   | 0.00   | 5.82    |
| Cu2Ag2 | 1.51   | 1.73           | -22.36  | 1.27   | 1.27   | 0.00   | 5.76    |
| Cu2Ag12| 1.45   | 1.69           | -23.53  | 1.24   | 1.25   | 0.01   | 5.74    |
| Cu2Ag2 | 1.38   | 1.63           | -19.29  | 1.25   | 1.25   | 0.00   | 5.63    |
| Cu2Ag12| 1.32   | 1.56           | -5.42   | 1.25   | 1.25   | -0.07  | 5.56    |
| Cu2Ag2 | 1.25   | 1.51           | -7.45   | 1.21   | 1.23   | 0.02   | 5.67    |
| Ag31   | 1.17   | 1.44           | -1.80   | 1.17   | 1.17   | 0.00   | 5.76    |
| Cu7    | 1.73   | 1.88           | -20.46  | 3.30   | 3.03  | -0.27  | 6.41    |
| Cu6Ag  | 1.69   | 1.85           | -21.94  | 3.20   | 2.98  | -0.22  | 6.38    |
| Cu2Ag2 | 1.64   | 1.81           | -19.74  | 3.16   | 2.90  | -0.26  | 6.47    |
| Cu2Ag2 | 1.60   | 1.78           | -18.14  | 3.13   | 2.85  | -0.28  | 6.78    |
| Cu2Ag2 | 1.56   | 1.74           | -15.73  | 3.10   | 2.80  | -0.30  | 6.54    |
| Cu2Ag2 | 1.48   | 1.68           | -12.73  | 3.10   | 2.82  | -0.28  | 6.44    |
| Cu2Ag2 | 1.41   | 1.61           | -10.41  | 3.09   | 2.83  | -0.26  | 6.32    |
| Cu2Ag2 | 1.33   | 1.55           | -7.12   | 3.08   | 2.82  | -0.26  | 6.19    |
| Ag32   | 1.26   | 1.49           | -1.83   | 3.08   | 3.08  | 0.00   | 6.34    |

| Clusters, which show perpendicular H₂ adsorption, are highlighted in red, and those whose adsorption energies fall into the energy range between -6 and -18 kJ mol⁻¹ are highlighted in green. Δ symbolizes the HLG difference between the bare and H₂-adsorbed clusters.
size with silver composition is higher for the bare clusters than for hydrogen-adsorbed clusters, and also, this decrease in the rate decreases with the cluster size (Figure S3: 0.095 eV for \( m + n = 2 \) while 0.05 eV for \( m + n = 8 \) per substitution). On the

### Table 4. Comparison of Calculated Average Nearest Neighbor Bond Distances (\( <r> \)/Å and the Minimum and Maximum Vibrational Frequencies (\( \nu \))/cm\(^{-1} \) of Both Bare and H\(_2\)-Adsorbed Clusters of Cu\(_m\)Ag\(_n\) (\( m + n = 2 − 8 \)) with Hydrogen–Hydrogen Bond Distances, and Frequencies (\( \nu \))/cm\(^{-1} \) Corresponding to Those Hydrogen and Metal–Hydrogen Vibrational Modes

| Cluster | Bare | Ads | H-H | M-H1 | M-H2 | H-H | M-H | M-M\(_{\min}\) | M-M\(_{\min}\) | M-M\(_{\max}\) | M-M\(_{\max}\) |
|---------|------|-----|-----|------|------|-----|-----|-----------|-----------|-----------|-----------|
| H\(_2\)  | 2.259| 2.279| 0.770| 1.765| 1.766| -   | -   | -         | -         | -         | -         |
| Cu\(_3\) | 2.326| 2.409| 0.792| 1.687| 1.680| -   | -   | -         | -         | -         | -         |
| Cu\(_4\) | 2.492| 2.488| 0.799| 1.666| 1.677| -   | -   | -         | -         | -         | -         |
| Cu\(_5\) | 2.672| 2.668| 0.798| 1.687| 1.678| -   | -   | -         | -         | -         | -         |
| Cu\(_6\) | 2.801| 2.798| 0.742| 2.037| 2.038| -   | -   | -         | -         | -         | -         |
| Cu\(_7\) | 2.314| 2.516| 0.760| 1.700| 1.710| -   | -   | -         | -         | -         | -         |
| Cu\(_8\) | 2.612| 2.611| 0.748| 2.363| 2.647| -   | -   | -         | -         | -         | -         |
| Cu\(_9\) | 2.362| 2.533| 0.780| 1.785| 1.739| -   | -   | -         | -         | -         | -         |
| Cu\(_10\) | 2.612| 2.611| 0.748| 2.363| 2.647| -   | -   | -         | -         | -         | -         |
| Cu\(_11\) | 2.672| 2.668| 0.798| 1.687| 1.678| -   | -   | -         | -         | -         | -         |
| Cu\(_12\) | 2.784| 2.780| 0.768| 2.037| 2.038| -   | -   | -         | -         | -         | -         |
| Cu\(_13\) | 2.801| 2.798| 0.742| 2.037| 2.038| -   | -   | -         | -         | -         | -         |
| Cu\(_14\) | 2.314| 2.516| 0.760| 1.700| 1.710| -   | -   | -         | -         | -         | -         |
| Cu\(_15\) | 2.612| 2.611| 0.748| 2.363| 2.647| -   | -   | -         | -         | -         | -         |
| Cu\(_16\) | 2.672| 2.668| 0.798| 1.687| 1.678| -   | -   | -         | -         | -         | -         |
| Cu\(_17\) | 2.784| 2.780| 0.768| 2.037| 2.038| -   | -   | -         | -         | -         | -         |
| Cu\(_18\) | 2.801| 2.798| 0.742| 2.037| 2.038| -   | -   | -         | -         | -         | -         |
| Cu\(_19\) | 2.314| 2.516| 0.760| 1.700| 1.710| -   | -   | -         | -         | -         | -         |
| Cu\(_20\) | 2.612| 2.611| 0.748| 2.363| 2.647| -   | -   | -         | -         | -         | -         |
| Cu\(_21\) | 2.672| 2.668| 0.798| 1.687| 1.678| -   | -   | -         | -         | -         | -         |
| Cu\(_22\) | 2.784| 2.780| 0.768| 2.037| 2.038| -   | -   | -         | -         | -         | -         |
| Cu\(_23\) | 2.801| 2.798| 0.742| 2.037| 2.038| -   | -   | -         | -         | -         | -         |
| Cu\(_24\) | 2.314| 2.516| 0.760| 1.700| 1.710| -   | -   | -         | -         | -         | -         |
| Cu\(_25\) | 2.612| 2.611| 0.748| 2.363| 2.647| -   | -   | -         | -         | -         | -         |
| Cu\(_26\) | 2.672| 2.668| 0.798| 1.687| 1.678| -   | -   | -         | -         | -         | -         |
| Cu\(_27\) | 2.784| 2.780| 0.768| 2.037| 2.038| -   | -   | -         | -         | -         | -         |
| Cu\(_28\) | 2.801| 2.798| 0.742| 2.037| 2.038| -   | -   | -         | -         | -         | -         |
| Cu\(_29\) | 2.314| 2.516| 0.760| 1.700| 1.710| -   | -   | -         | -         | -         | -         |
| Cu\(_30\) | 2.612| 2.611| 0.748| 2.363| 2.647| -   | -   | -         | -         | -         | -         |
| Cu\(_31\) | 2.672| 2.668| 0.798| 1.687| 1.678| -   | -   | -         | -         | -         | -         |
| Cu\(_32\) | 2.784| 2.780| 0.768| 2.037| 2.038| -   | -   | -         | -         | -         | -         |
| Cu\(_33\) | 2.801| 2.798| 0.742| 2.037| 2.038| -   | -   | -         | -         | -         | -         |
| Cu\(_34\) | 2.314| 2.516| 0.760| 1.700| 1.710| -   | -   | -         | -         | -         | -         |
| Cu\(_35\) | 2.612| 2.611| 0.748| 2.363| 2.647| -   | -   | -         | -         | -         | -         |
| Cu\(_36\) | 2.672| 2.668| 0.798| 1.687| 1.678| -   | -   | -         | -         | -         | -         |
| Cu\(_37\) | 2.784| 2.780| 0.768| 2.037| 2.038| -   | -   | -         | -         | -         | -         |
| Cu\(_38\) | 2.801| 2.798| 0.742| 2.037| 2.038| -   | -   | -         | -         | -         | -         |
| Cu\(_39\) | 2.314| 2.516| 0.760| 1.700| 1.710| -   | -   | -         | -         | -         | -         |
| Cu\(_40\) | 2.612| 2.611| 0.748| 2.363| 2.647| -   | -   | -         | -         | -         | -         |
| Cu\(_41\) | 2.672| 2.668| 0.798| 1.687| 1.678| -   | -   | -         | -         | -         | -         |
other hand, the binding energy difference given in Table S1, which accounts for the extra binding energy per atom added to the cluster due to the adsorption of a hydrogen molecule (two hydrogen atoms), decreases with the increase of cluster sizes as it is an average over the entire cluster.

Here, we first summarize the best cluster candidates found in this study and then discuss the scientific base pieces of evidence to clarify the result. According to the U.S. Department of Energy Standard,56 physisorption-based materials have been identified as good candidates for a hydrogen storage system. For optimum adsorption capacity of the storage system, the adsorption enthalpy between hydrogen molecules and materials should be less than $-18 \text{ kJ mol}^{-1}$ to meet the lower (3 atm) and upper (100 atm) pressures of the storage tank at the ambient temperature, respectively, and also, it should be higher than $-6 \text{ kJ mol}^{-1}$. The adsorption enthalpies given in Table 3 and their variations with copper composition for each cluster reveal the tunable capacity of bimetallic clusters that meet the above optimum standard. A previous study by Fang et al. on hydrogen molecular adsorption on Pt-doped gold clusters also found similar behavior.30 All Cu$_n$ clusters (except Cu$_6$, discussed below) have larger adsorption enthalpies falling in the range of chemisorption, while Ag$_n$ clusters have much smaller values, which are even below the lower limit of physisorption (except Ag$_4$) at which almost all hydrogen molecules stay unbound to the material. Smaller Cu$_m$Ag$_n$ clusters up to the hexamer, except CuAg$_4$, show much higher adsorption enthalpies than the recommended optimum value of $-18 \text{ kJ mol}^{-1}$ but, interestingly, some of the heterogeneous clusters of the hexamer and above, which are highlighted in green in Table 3, fall in the range of $-6$ to $-18 \text{ kJ mol}^{-1}$, namely, the clusters CuAg$_6$, Cu$_6$, Cu$_5$Ag, Cu$_4$Ag$_2$, Cu$_3$Ag$_3$, Cu$_2$Ag$_4$, Cu$_6$, Cu$_5$Ag$_3$, Cu$_4$Ag$_4$, Cu$_3$Ag$_5$, Cu$_2$Ag$_6$, and Cu$_7$, shown in Figure 5.

The HOMO–LUMO gap (HLG) and chemical hardness values calculated (eq 7) using both adiabatic ($\eta_a$) and vertical ($\eta_v$) processes of the substance, which have a similar meaning, give information about the chemical reactivity of the clusters; it measures how a substance shows resistance to a change in its electron distribution.57–59 As shown in Table 3, HLG shows an odd–even fluctuation in the series from $n = 2$ to 8 that the clusters with an even number of atoms have higher values than the cluster with an odd number of atoms. As a general trend, HLG decreases with the silver substitution in the same cluster. These trends are common for both bare and hydrogen-adsorbed cluster series.
Some correlation between HLG and the $H_2$ adsorption energy can be observed. The clusters, which have larger adsorption energy over $-55$ kJ mol$^{-1}$, show considerably lower HLG values than the corresponding $H_2$-adsorbed clusters, namely, Cu$_4$, Cu$_5$Ag, Cu$_6$Ag$_2$, and Cu$_5$Ag$_3$. The HLG differences, $\Delta$ shown in Table 3, are as large as 0.8 eV for these clusters. The clusters with moderate hydrogen adsorption energy, generally between $-19$ and $-55$ kJ mol$^{-1}$, except most of the neat silver clusters (Ag$_2$, Ag$_3$, Ag$_5$, Ag$_6$, Ag$_7$, and Ag$_8$) and silver-rich clusters with silver more than 70% (CuAg$_6$, Cu$_2$Ag$_5$, and Cu$_2$Ag$_7$), have HLG values still lower than those of their hydrogen-adsorbed counterparts with the difference (\(\Delta\)) less than 0.7 eV. The most interesting fact is that the clusters that are named good candidates for hydrogen storage materials have HLG values similar to or even greater than their hydrogen-adsorbed counterparts (\(\Delta \leq 0.1\)), indicating the intact electron distribution of the cluster material upon $H_2$ adsorption. Chemical hardness calculated using the vertical processes (\(\eta_v\)) is higher than that calculated using adiabatic processes (\(\eta_a\)), in which the relaxation of ionic clusters after removal and gain of an electron is considered. While observing a similar trend of HLG to the chemical hardness, as expected because of the qualitatively same parameters calculated in different ways, chemical hardness exhibits higher numerical values than the HLG except for the hexamer and the octamer, which show the opposite. The practical use of these parameters, HLG and chemical hardness, one over the other is more substance-specific, and more information can be found elsewhere.$^{53}$

The adsorption strengths were further distinguished using the vibrational frequency and corresponding bond distance analysis. Table 4 summarizes the average bond distances of the clusters before and after the adsorption of the $H_2$ molecule, metal–$H_2$ bond distances, minimum and maximum vibrational frequencies of both bare and hydrogen-adsorbed clusters, hydrogen–$H_2$ frequency, and metal–$H_2$ frequency. The orientation or the approach of the $H_2$ molecule upon adsorption to the cluster occurs in two different ways: either by perpendicular (only one of two hydrogen atoms interacts with the cluster) or by parallel (both hydrogen atoms interact with the cluster) to the cluster. Perpendicular orientation is defined using MH$_1$ and MH$_2$ bond lengths that the MH$_1$ bond length is the sum of the MH$_2$ bond length plus the approximate bond distance of a free $H_2$ molecule (\(\approx 0.7\)Å) while parallel adsorption is defined as the adsorption with equal or closer bond lengths of MH$_1$ and MH$_2$. A comparison of Tables 3 and 4 and the structures in Figure S1 reveal that the perpendicular orientation of the $H_2$ molecule (marked red in Tables 3 and 4) has reduced adsorption energy and is predominantly in silver-rich clusters except for Cu$_6$. Among them, the neat silver clusters are almost unbound to the $H_2$ molecules and the mixed systems, CuAg$_6$, Cu$_5$Ag$_2$, and Cu$_2$Ag$_6$, have no vertex Cu atom. Perpendicular orientation in the Cu$_6$ cluster, which has three vertices of Cu atoms, may be due to the geometry of the cluster. The geometry of the original cluster is $D_{3d}$ and perpendicular adsorption reduces it only to $C_{3v}$ while parallel adsorption would reduce it further. This results in lower adsorption energy compared to the other copper neat clusters. Three predominant features from hydrogen adsorption data and structures can be drawn: (1) favorable adsorption on the cluster vertex Cu atom, (2) unfavorable interaction to Ag atoms, and (3) high symmetry adaptation. Up to the pentamer, heterogeneous clusters have at least one vertex Cu atom in the cluster except for CuAg$_4$ and also can adopt some symmetry on parallel adsorption. Therefore, we can observe high adsorption energy. In the case of CuAg$_6$, it favors the perpendicular adsorption to maintain a sort of symmetry. Adsorption on all clusters of the heptamer and octamer, except on Ag$_5$- and Ag$_6$ on which no adsorption was observed, is parallel. They all have at least one vertex Cu atom and reduced symmetry, which would not be affected effectively on adsorption. These observations can be summarized as the adsorption of the $H_2$ molecule noticeably favors the sites, where the most positively charged environment persists. $H_2$ molecule adsorbs onto either the most positively charged copper atoms (or reaches onto the most positive silver atom in Ag$_n$ monometallic clusters) at the vertices of the cluster or the site which has the most positive charge environment avoiding the negatively charged atoms in the vicinity as also observed in previous studies, especially that the $H_2$ adsorption occurred on top of the most positively charged three-coordinated Cu atom in the small diagonal of Cu$_4$ rhombus.$^{31,32}$ With the adsorption, the positive charge density of the adsorbed atom or the atom closer to the adsorbed site decreases, acquiring more negative charge density. We will discuss the electron distributions further in the natural bond orbital (NBO) analysis below.

As we mentioned above, there is no change in the bond distance of the $H_2$ molecule in the perpendicular adsorption, while the elongation of the $H_2$ bond distance can be observed in the parallel adsorption. Stronger metal–$H_2$ interactions cause the MH$_1$ and MH$_2$ distances shorter with the $H_2$ bond elongation. Among the cluster species selected as candidates for the hydrogen storage system, the interactions between $H_2$ and CuAg$_4$, Cu$_6$, Cu$_5$Ag$_2$, and Cu$_2$Ag$_4$ species do not affect the $H$–$H$ bond distance, and the metal–$H_2$ distance is comparatively longer, while the rest, Cu$_5$Ag, Cu$_5$Ag$_2$, CuAg$_6$, Cu$_5$Ag$_5$, Cu$_3$Ag$_4$, Cu$_3$Ag$_5$, Cu$_3$Ag$_6$, and Cu$_2$Ag$_4$, make interactions with both hydrogen atoms of the molecule causing a longer $H$–$H$ distance and metal–$H_2$ distance is about 1 Å shorter than the former. The frequencies of $H$–$H$ and the $M$–$H$ modes show the same observations as expected relevant to the bond distance change (marked green in Table 4) upon adsorption. The effect of hydrogen adsorption on metal–metal interactions can also be understood by comparing the minimum and maximum frequencies of the metal–metal vibrational modes before and after the adsorption since all of the other modes are within these two extremes. At the lower end of the cluster series (especially, $m + n = 2$ and 3 clusters), there are observable changes in vibrational modes, but when the cluster size increases, in general, the differences are not in a smooth pattern and become smaller. The minimum frequency modes show a red shift (lower frequency) in $m + n = 2$ clusters, while $m + n = 3$ clusters show a blue shift (lager frequency) upon $H_2$ adsorption, reflecting the differences in adsorption energies of two species. In the clusters of $m + n = 4$, both minimum and maximum frequency modes are red-shifted as the observation made for the Cu$_m$Pt$_{(4-n)}$ ($n = 0–4$) clusters by Gálvez-González et al.$^{32}$ In contrast to the literature on dissociative hydrogen adsorption on some of Au$_m$Pt clusters reported by Gálvez-González et al.$^{13}$ and Fang and Kuang,$^{30}$ some cationic Pt clusters reported by Kerpal et al.$^{16}$ and some Au$_m$ clusters reported by Fang and Kuang$^{39}$ and Molina et al.$^{41}$ nondissociative adsorptions of $H_2$ on the entire series of Cu$_m$Ag$_n$ for ($m + n \leq 8$) clusters were observed.
3.3. Electronic Structure Change and Charge Transfer Processes. The natural bond orbital (NBO) analysis for those 12 clusters was performed to understand their electron redistributions and charge transfer process at the formation of the cluster and also on H₂ adsorption. Both intra- and interatomic charge transfer within the cluster and adsorbed H₂ molecules could be observed. For each cluster, spatial distributions of HOMO and LUMO frontier orbitals and the natural electron configurations of constituent elements, which give the occupancies of atomic orbitals, with their natural charge distribution are given in Figure 6 and Table S2 in the Supporting Information, respectively. The electron configuration of free atoms, Cu, Ag, and H, is [Ar]3d¹⁰4s¹, [Kr]4d¹⁰5s¹, and 1s¹, respectively. Inner core notations, [Ar] and [Kr], will be dropped hereon for easy presentation.

Cu₆: It has a planar triangle structure consisting of copper atoms with two different electron configurations, 3d⁹4s⁰4p⁰ for the three atoms at the vertices and 3d⁹24s²4p⁴ for the three atoms along the sides of the triangle. All six Cu atoms in the cluster molecule show spd hybridization with intra-atomic charge transfer from 4s and 3d to 4p in contrast to the charge transfer process reported in this study and literature for Cu₄.⁴¹ In Cu₆, the two Cu atoms on the short diagonal promoted electrons from 4s and 3d to 4p, while those of the long diagonal promoted electrons from 3d to 4s. In addition, these electron configurations give further insight into interatomic charge transfer between the atoms in the cluster. Each atom at the vertices lost 0.143 electrons, leaving it positively charged, while each atom along the sides gained 0.143 electrons and hence became negatively charged. The spd hybridization and then the intra- and interatomic charge transfer give stability to the cluster.⁶³ Moving onto the H₂-adsorbed Cu₆, there is no accountable intermolecule charge transfer between the H₂ molecule and Cu₆ cluster but an induced dipole moment on the H₂ molecule by the Cu₆−dipole can be observed. With the hydrogen adsorption, while there is no further intra-atomic charge transfer taking place, interatomic charge transfer from the 4s orbital of the Cu atoms at the vertices to 4p orbitals of the Cu atoms on the sides of the triangle takes place; each Cu atom at the vertices loses 0.03 electrons with the result of 0.03 electrons gained by each Cu atom on three sides. This process has further enhanced the already existing charge separation on the cluster. In parallel to this process, the H₂ molecule also becomes polarized in

Figure 6. Spatial distributions of HOMO and LUMO frontier molecular orbitals of 12 clusters identified as candidates for hydrogen storage materials; red and blue color lobes correspond to the two different phases of the orbital wave function with positive and negative signs, respectively.
H2 molecule interaction can be considered as a weak ionic
(Tab. S2 in the Supporting Information). Then, the cluster
rounding analysis.
previous section based on the bond distance and vibrational frequency analysis, the H2 reaching out to Cu6 as perpendicular adsorption (Figure 5) is further confirmed by this charge transfer analysis. Therefore, the hydrogen adsorption arises only due to the induced dipole interaction, which results in physisorption (−16.71 kJ mol−1, Tab. 3) but not due to the charge transfer between the H2 molecule and the cluster.
Cu6Ag: All atoms in the cluster show spd hybridizations similar to Cu6 with intra-atomic charge transfer from 4s and 3d to 4p in the five Cu atoms and from 5s and 4d to 5p in the Ag atom. Interatomic charge transfer is unsymmetrical compared to that of Cu6 as a result of Ag substitution (Tab. S2 in the Supporting Information). The Ag atom has been substituted to one of three vertices as discussed in Section 3.2 due to its larger size and enhanced electron negativity. All three atoms at the vertices (2 Cu, Ag) donated electrons to the three atoms on the sides. The transfer of electrons from Ag (4d0.965s0.931p0) is less compared to the transfer from the two Cu atoms (3d9.934s0.924p0.02); this is in accordance with the higher electron negativity of Ag compared to Cu. The two Cu atoms (3d0.924s0.834p0.41) on two sides bonded to the Ag atom gained fewer electrons for the same reason. Therefore, accumulations of the electrons are more predominant on the Cu atom on the side connecting two vertex Cu atoms (3d0.924s0.834p0.41).
In the case of H2 adsorption, the H2 molecule lost 0.04 electrons (0.02 from each hydrogen: 1s0.98), which were gained by the cluster. The total charge of the cluster becomes negative (−0.027) equally to the positive charge of the H2 molecule (+0.028); this slight difference arises from the error due to the round-off of the charge values to the third decimal point (Tab. S2 in the Supporting Information). Then, the cluster−H2 molecule interaction can be considered as a weak ionic interaction with −15.89 kJ mol−1 physisorption energy. This charge transfer upon H2 adsorption caused the redistribution of electrons in the cluster while the electron-deficient H2 molecule remains unpolarized. Three atoms at the vertices now become less positive as a result of the rearranging of both the interatomic charge transfer and also with the electron promotion from 4s and 3d to 4p, and its electronic state was rearranged from 3d9.934s0.894p0.02 to 3d9.904s0.854p0.15. The other vertex Cu atom gained 0.04 electrons only by the interatomic charge transfer during the adsorption with the enhanced enrollment of 4s orbital and 5s orbital, [(3d9.934s0.894p0.02) → (3d9.954s0.924p0.025s0.01)], which changed the atomic charge from 0.148 to 0.123. Similarly, in the third vertex atom, Ag, only the 5s orbital gained 0.03 electrons to reduce the charge from 0.148 to 0.091. In addition, one of three Cu atoms on sides also gained 0.01 electrons to its 4s atomic orbital while only two vertex Cu atoms donated 0.09 electrons to the entire system. This charge transfer analysis and hence the weak ionic interaction between the cluster and the H2 molecule justify the identified parallel adsorption of the H2 molecule in the previous section based on the bond distance and vibrational analysis.
HOMO−LUMO frontier orbital diagrams (Figure 6) also depict the induced dipole interaction of the H2 molecule with the Cu6 cluster as perpendicular adsorption and weak ionic interaction of the H2 molecule to the Cu6Ag cluster as parallel adsorption. In Cu6, the FMO shapes of the HOMO and LUMO of H2-adsorbed clusters are similar to those of the HOMO and LUMO before the adsorption. Two phases (opposite phases of the orbital donated by red and blue) of the HOMO concentrated around the two vertex Cu atoms (blue and red color in the diagram), leaving the Cu atom on the side connecting these two vertexes and the Cu atom remaining at the third vertex. These two opposite phases have created a narrow hollow region inside the triangle. In contrast, the LUMO, which is responsible for attracting electrons from the HOMO of another molecule, has no hollow region; instead, one of the two phases (blue) resides at the center of the cluster (inside the triangle) and the other phase (red) is concentrated separately at three vertices as three separate lobes. This shape of the LUMO influences the H2 molecule reaching perpendicularly toward the center of the triangle and induced the electron density of the H2 molecules to be polarized. The same shapes of HOMO and LUMO frontier molecular orbitals after the adsorption of H2 molecules revealed that there is no charge transfer between the H2 molecule and the cluster, and hence, the induced dipole interaction takes place as discussed before.
But in the case of Cu6Ag, where we identified H2 adsorption to the cluster due to a weak ionic interaction and as parallel adsorption, the FMO shapes of the HOMO and LUMO before and after the H2 adsorption are different. In the bare cluster, two vertex atoms, Cu and Ag, and the Cu atom on the side connecting these two atoms are clouded by one lobe of two opposite phases of the FMO (blue) and the remaining lobe (red) resides at the remaining vertex, leaving the vicinity of two Cu atoms on the other two sides and the center of the triangle free of electron density. The LUMO appears to be the same as the LUMO of Cu6, indicating good electron acceptance capacity. In Cu6AgH2 (after the H2 adsorption), the HOMO and LUMO are completely different from those of the bare cluster, confirming the electron transfer from the H2 molecule to the cluster and also the redistributions of electrons. In the HOMO, electrons are localized on the atoms away from the Ag atom, and in the LUMO, they are lobed on the vertex atoms including Ag.
Continuation of the discussion on atomic orbital occupancy and FMO analysis for the remaining 10 clusters, CuAg6, Cu4Ag2, Cu3Ag6, Cu2Ag6, CuAg6, Cu4Ag, Cu3Ag6, CuAg6, Cu6Ag6, and CuAg7, will find the same pattern of behavior, confirming the hydrogen adsorption characteristic identified in Section 3.2. The clusters identified with perpendicular adsorptions, CuAgH2, CuH2, Cu4AgH2, and Cu6AgH2, have no charge transfer between the H2 molecule and the cluster and polarize the H2 molecule; hence, their H2 adsorptions are due to the induced dipole interactions. On the other hand, the remaining six clusters, CuAgH2, Cu4AgH2, Cu3AgH2, Cu2AgH2, Cu4AgH2, Cu3AgH2, and CuAgH2, identified with parallel adsorption, have charge transfer between the H2 molecule and the cluster and pull the electrons from the H2 molecule; hence, their H2 adsorptions are due to the ionic interactions.
4. CONCLUSIONS
In the search for potential candidates for hydrogen storage, Cu₉Ag₆ clusters for m + n ≤ 8 were explored. The dimension transitions of both copper and silver cluster structures occur when the cluster size increases. The dimer is a 1-D structure, whereas the trimers to the hexamer possess planar 2-D structure patterns and the clusters above the hexamer are in 3-D arrangements. The clusters of both pure Cuₙ and Agₙ have the shapes of an isosceles triangle for the trimers, rhombus for the tetramer, trapezoid for the pentamer, triangle for the hexamer, pentagonal bipyramid for the heptamer, and tetracapped tetrahedron for the octamer. With the heterogeneity, the Cu atoms tend to have maximum coordination within the cluster and the stability of copper clusters is relatively higher than that of the silver clusters. Hydrogen adsorptions to the clusters are observed with two general mechanisms, hydrogen is either parallel or perpendicular to the clusters. In the perpendicular reach, clusters polarized the H₂ molecule and there is no charge transfer process between the cluster and H₂ molecule and hence the adsorption is due to an induced dipole interaction. On the other hand, in parallel reach, the charge transfer between the H₂ molecule and cluster takes place and hydrogen donates electrons to the cluster. The cluster becomes negatively charged and the H₂ molecule becomes positively charged, resulting in weak ionic interactions between two entities. The adsorption is due to this ionic interaction. The H₂ adsorption energies of the entire series reveal that out of all of the candidates, only Cu₉Ag₆, Cu₈Ag₃, Cu₈Ag₄, Cu₆Ag₄, Cu₅Ag₃, Cu₄Ag₄, Cu₃Ag₅, Cu₂Ag₆, and CuAg₇ fall within the recommended energy range of −6 to −18 kJ mol⁻¹ for hydrogen storage materials. The H₂ adsorption on the first four of 12 entities is due to the induced dipole interactions, while that on the remaining eight entities is due to the ionic interactions.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c06146.

Structures of hydrogen-adsorbed CuₙAgₙ clusters; average binding energy of bare and H₂-adsorbed CuₙAgₙ clusters; lowest energy and low-lying isomers of CuₙAgₙ clusters; variation of binding energy of H₂-adsorbed CuₙAgₙ clusters with silver substitution; and valence-shell electron configurations and the natural atomic charge on constituent elements of bare and hydrogen-adsorbed CuₙAgₙ clusters (PDF)

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Notes
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