Electronic, Raman and vibrational properties of Ag\textsubscript{m}Cu\textsubscript{n} (m + n = 3-6) clusters: First principles study

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Abstract. The electronic, Raman and vibrational properties of Ag\textsubscript{m}Cu\textsubscript{n} (m + n = 3-6) nanoclusters were investigated using first principles. Results indicate that the electronegativity, hardness, softness, electrophilicity index, and energy gap vary with copper atom adding. Ag\textsubscript{5}Cu\textsubscript{1} cluster has the maximum energy gap and hardness, Ag\textsubscript{1}Cu\textsubscript{2} cluster has the maximum electronegativity, Ag\textsubscript{2}Cu\textsubscript{1} cluster has the maximum softness and electrophilicity index. Their Raman and vibrational spectra are related with their compositions, sizes, and geometries. As the amount of copper atom adds, the strongest Raman peaks of 3-6-atom silver-copper move large wavelength, and the strongest vibrational peaks of 3-atom, 5-atom (except Ag\textsubscript{2}Cu\textsubscript{3} ), and 6-atom (except Ag\textsubscript{3}Cu\textsubscript{3} ) silver-copper clusters also have a trend to shift large wavenumber. The wavenumber of the maximum vibrational peak of Ag\textsubscript{3}Cu\textsubscript{1} is the largest and the wavenumber of the maximum vibrational peak of Ag\textsubscript{2}Cu\textsubscript{2} is the smallest among the 4-atom silver-copper clusters.

1. Introduction

Bimetallic clusters have particular optical [1, 2], and magnetic properties, so they are potentially applied in the field of solar cell [3, 4], catalysis [5, 6] and so on. Their physical and chemical properties usually are different from their the bulk and may be mediated by their composition and size and so on [7-9]. The bimetallic noble clusters such as silver-copper are very hot due to their large scale potential applications. However, the relationships between structure and physical and chemical properties of silver-copper clusters are not substantially investigated.

There are some complexities in experimental production of silver-copper cluster and there are wide size and shape distributions, therefore, their characterization become difficult. Generally speaking, the sizes and shapes of most clusters are related to their optical, vibrational and Raman spectra. Conversely, the size and shape of the clusters can be characterized by their optical, vibrational and Raman spectra, and even their structures can be predicted by their optical, vibrational and Raman spectra. Bishea et al. [10, 11] obtained the silver-copper binding energy and vibrational bands of AgCu\textsubscript{2} cluster using resonant two-photon ionisation spectrometry, and they analyzed four band systems in the range of 20,000-27,000 cm\textsuperscript{-1}. Cazayous et al. [12] investigated vibrational types of silver-copper nanoparticles using micro-Raman spectroscopy, they found that the silver-copper and...
pure silver nanoparticles have two distinct contributions in the same Raman spectroscopy. James et al. [13] studied adiabatic ionization potential of neutral bimetallic CuAg, and dissociation energy and frequency of cationic CuAg+ clusters using photoionization spectroscopy technique. Ranjan et al. [14-16] studied electronic and optical properties of mixed and impurity-doped bimetallic CuAg, AgAu, and CuAu clusters using density functional theory (DFT) methodology. Recently, we systematically calculated the electronic, Raman and vibrational properties of seven, eight and thirteen-atom silver-copper nanoclusters [17-24]. Therefore, there is an important role for vibrational and Raman models of silver-copper clusters using the theoretical prediction. Some studies have concentrated on structural and absorption spectra of pure silver and copper nanoclusters, but the systematic investigations on electronic properties, vibrational and Raman spectra of silver-copper nanoclusters are extremely limited till date.

Consequently, this paper systematically study on electronic properties, Raman and vibrational spectra of Ag\textsubscript{m}Cu\textsubscript{n} (m + n = 3-6) clusters by means of DFT. Their Raman and vibrational spectra would be conducive to confirming the sizes, structures, and compositions of these nanoclusters.

2. Computing methods

The structures of silver-copper clusters were displayed in the Ref. [25]. During DFT calculations, the exchange-correlation functional is Perdew–Burke–Ernzerhof (PBE) [26]. A global cutoff of grid integration is 5.5 Å. The wavelength of incident light for Raman spectra were simulated at 514.5 nm and 10 K. All computations used Dmol\textsuperscript{3} package [27, 28]. According to Koopmans’ approximation [29], electron affinity (EA) and ionization energy (IE) of all the nanoalloys are as following:

\[ EA = -\varepsilon_{LUMO} \]  
\[ IE = -\varepsilon_{HOMO} \]

where, HOMO is the highest occupied molecular orbital energy of nanoalloys, LUMO is the lowest unoccupied molecular orbital of nanoalloys.

The energy gap (\( E_{\text{gap}} \)) between HOMO and LUMO is as following:

\[ E_{\text{gap}} = \text{LUMO-HOMO} \]

Therefore, the electronegativity (\( \chi \)), molecular softness (\( S \)), global hardness (\( \eta \)), and electrophilicity index (\( \omega \)) were computed using \( I \) and \( A \). The equations are as following:

\[ \chi = -\mu = \left( IE + EA \right)/2 \]  
\[ \eta = \left( IE - EA \right)/2 \]  
\[ S = 1/2\eta \]  
\[ \omega = \mu^2S \]

where, \( \mu \) is the chemical potential of the nanoalloys.

3. Results and discussions

The calculated electronegativity, molecular softness, global hardness, and electrophilicity index on the basis of electronic structure theory, and energy gap of 3-6-atom silver-copper clusters are given in Figure 1. For 3-atom silver-copper clusters, when the amount of copper atom increases, \( E_{\text{gap}} \) and hardness values increase; electrophilicity index values decrease; electronegativity values fluctuate; the softness of the 3-atom cluster reaches its maximum when the composition of the cluster is Ag\textsubscript{2}Cu\textsubscript{1} cluster. For the 4- and 5-atom silver-copper clusters, the \( E_{\text{gap}} \), \( \eta \) and \( \chi \) values increase, while \( S \) and \( \omega \) values reduce when the amount of copper atom adds. For the 6-atom silver-copper nanoclusters, with the amount of copper atom increasing, \( E_{\text{gap}} \) and \( \eta \) values firstly decrease, then increase; \( \chi \) values firstly decrease, then increase, and then decrease; \( S \) and \( \omega \) values have maximum values at the compositions of Ag\textsubscript{2}Cu\textsubscript{4} and Ag\textsubscript{3}Cu\textsubscript{3} cluster, respectively.
Figure 1. The energy gap, electronegativity, global hardness, molecular softness, and electrophilicity index of 3-6-atom silver-copper clusters.

Figure 2 exhibits Raman and vibrational spectra for 3-atom silver-copper nanoclusters. The Raman spectra of Ag$_2$Cu$_1$ and Ag$_1$Cu$_2$ show three peaks. The wavelengths of the most intense peaks of Ag$_2$Cu$_1$ and Ag$_1$Cu$_2$ clusters are smaller than those of the pure Ag$_3$ and Cu$_3$. The intensities of the strongest peaks of Ag$_2$Cu$_1$ and Ag$_1$Cu$_2$ are weaker than that of Ag$_3$ cluster, but are stronger than that of the Cu$_3$ cluster. There is a shift in the Raman spectra and a decrease in the main peak intensity when cluster composition changes from Ag$_2$Cu$_1$ to Ag$_1$Cu$_2$, and (Figure 2a-d). The vibrational spectra of Ag$_2$Cu$_1$ and Ag$_1$Cu$_2$ also show three peaks. The hybrid clusters show larger wavenumbers compare to pure Ag$_3$ cluster, while the strongest peak wavenumber of pure Cu$_3$ cluster is located between the Ag$_2$Cu$_1$ and Ag$_1$Cu$_2$ clusters. As the amount of copper atom increases, the intensities of the strongest vibrational peaks become strong. The wavenumber of Ag$_2$Cu$_1$ is smaller than that of Ag$_1$Cu$_2$ cluster (Figure 2e-h).

Figure 3 shows the Raman and vibrational spectra of 4-atom silver-copper nanoclusters. There are three peaks in Raman spectrum of Ag$_3$Cu$_1$ cluster and two peaks in the spectra of Ag$_2$Cu$_2$ and Ag$_1$Cu$_3$ clusters. As the amount of copper atom adds, the wavelengths of the strongest peaks become larger, the intensities of the strongest peaks become weaker (Figure 3a-e). The vibrational spectra of Ag$_3$Cu$_1$, Ag$_2$Cu$_2$ and Ag$_1$Cu$_3$ clusters show four, two and three peaks, respectively (Figure 3g-i). The wavenumber of the strongest peak of Ag$_3$Cu$_1$ cluster is the largest among the three silver-copper clusters, however, its peak intensity is the weakest(Figure 3g). The wavenumber of the strongest peak of Ag$_2$Cu$_2$ is less than Ag$_1$Cu$_3$ and Cu$_4$, while its intensity is the strongest (Figure 3h). The wavenumber of the strongest peak of Ag$_1$Cu$_3$ is bigger than Ag$_2$Cu$_2$ but is less than Cu$_4$ (Figure 3i).

Figure 4 shows the Raman and vibrational spectra of 5-atom silver-copper clusters, their Raman and vibrational spectra become complicated and have many peaks. For their Raman spectra, wavelengths of the strongest peaks of four silver-copper nanoclusters are bigger than Ag$_5$ and less than Cu$_5$, however, their intensities are weaker than Ag$_5$ and stronger than Cu$_5$ (Figure 4a-f). Among their Raman spectra, Ag$_1$Cu$_4$ has the largest wavelength, Ag$_4$Cu$_1$ has the smallest wavelength,
Ag₂Cu₃ has the strongest intensity, Ag₁Cu₄ has the weakest intensity (Figure 4b-e). For the strongest peaks of vibrational spectra of 5-atom silver-copper nanoclusters, their wavenumbers are larger than Ag₅ and smaller than Cu₅, the intensity of Ag₅ is stronger than Ag₁Cu₄, Ag₂Cu₃ and Ag₃Cu₂ and is weaker than Ag₄Cu₁, the intensity of Cu₅ is stronger than Ag₁Cu₄ and Ag₂Cu₃ and is weaker than Ag₄Cu₁ and Ag₃Cu₂ (Figure 4g-l). For the strongest peak of vibrational spectra of four silver-copper nanoclusters, Ag₁Cu₄ has the largest wavenumber, Ag₄Cu₁ has the smallest wavenumber, the wavenumber of Ag₂Cu₃ is slightly larger than Ag₃Cu₂, Ag₄Cu₁ has the strongest intensity, Ag₂Cu₃ has the weakest intensity, the intensity of Ag₃Cu₂ is stronger than Ag₁Cu₄ (Figure 4h-k).

**Figure 2.** Raman and vibrational spectra of Ag₃ (a, e), Ag₂Cu₁ (b, f), Ag₁Cu₂ (c, g) and Cu₃ (d, h) clusters. Left row is Raman spectrum, right row is vibrational spectrum.

**Figure 3.** Raman and vibrational spectra of Ag₄ (a, f), Ag₃Cu₁ (b, g), Ag₂Cu₂ (c, h), Ag₁Cu₃ (d, i) and Cu₄ (e, j) clusters. Left row is Raman spectrum, right row is vibrational spectrum.
Figure 4. Raman and vibrational spectra of pure Ag<sub>5</sub> (a, g), Ag<sub>4</sub>Cu<sub>1</sub> (b, h), Ag<sub>3</sub>Cu<sub>2</sub> (c, i), Ag<sub>5</sub>Cu<sub>3</sub> (d, j), Ag<sub>1</sub>Cu<sub>4</sub> (e, k) and Cu<sub>5</sub> (f, l) clusters. Left row is Raman spectrum, right row is vibrational spectrum.

Figure 5 shows the Raman and vibrational spectra of 6-atom silver-copper nanoclusters. Their Raman and vibrational spectra are complex and have many peaks. For the strongest peaks of their Raman spectra, the wavelengths of five silver-copper clusters are larger than Ag<sub>6</sub> and are smaller than Cu<sub>6</sub>, their intensities are weaker than Ag<sub>6</sub> and are stronger than Cu<sub>6</sub> (Figure 5a-g). For the strongest peaks of Raman spectra of five silver-copper nanoclusters, the wavelengths and intensities enlarge with the amount of copper atom increasing (Figure 5b-f). For the strongest peaks of their vibrational spectra, the wavenumbers of five silver-copper clusters are bigger than Ag<sub>6</sub> and are smaller than Cu<sub>6</sub>, their intensities (except Ag<sub>3</sub>Cu<sub>3</sub>) are weaker than Ag<sub>6</sub> and Cu<sub>6</sub>, the intensity of Ag<sub>5</sub>Cu<sub>3</sub> is stronger than Ag<sub>6</sub> and Cu<sub>6</sub> (Figure 5h-n). In the strongest peak of vibrational spectra of five silver-copper nanoclusters, Ag<sub>5</sub>Cu<sub>3</sub> has the largest wavenumber, Ag<sub>2</sub>Cu<sub>4</sub> has the smallest wavenumber, the wavenumber of Ag<sub>4</sub>Cu<sub>2</sub> is slightly less than Ag<sub>5</sub>Cu<sub>1</sub> and is slightly bigger than Ag<sub>3</sub>Cu<sub>3</sub>, Ag<sub>5</sub>Cu<sub>3</sub> has the strongest intensity, Ag<sub>1</sub>Cu<sub>5</sub> has the weakest intensity, the intensity of Ag<sub>5</sub>Cu<sub>1</sub> is slightly stronger than Ag<sub>2</sub>Cu<sub>4</sub> but is a bit smaller than Ag<sub>4</sub>Cu<sub>2</sub> (Figure 5i-m).
4. Conclusion

The electronic, Raman and vibrational properties of $\text{Ag}_n\text{Cu}_m$ ($m + n = 3-6$) clusters were calculated using DFT. As the amount of copper atom increases, $E_{\text{gap}}$ and hardness values of the 3-5-atom silver-copper nanoclusters add, $E_{\text{gap}}$ and hardness values of the 6-atom silver-copper nanoclusters firstly reduce, then add; electrophilicity index values of the 3-5-atom silver-copper nanoclusters decrease, electrophilicity index values of the 6-atom silver-copper nanoclusters firstly add, then reduce; electronegativity values of 3- and 6-atom silver-copper nanoclusters firstly decrease, then add, and then reduce, electronegativity values of 4- and 5-atom silver-copper increase; softness values of 3- and 6-atom silver-copper nanoclusters firstly add, then reduce, softness values of 4- and 5-atom silver-copper nanoclusters decrease. All Raman and vibrational models of silver-copper nanoclusters are related with their compositions, sizes, and geometries. As the amount of copper atom increases, the strongest Raman peak wavelengths of 3-6-atom silver-copper nanoclusters become large, and wavenumbers of the strongest vibrational peaks of 3-atom, 5-atom (except $\text{Ag}_2\text{Cu}_3$), and 6-atom (except $\text{Ag}_3\text{Cu}_3$) silver-copper almost become large. The wavenumber of the strongest vibrational peak of $\text{Ag}_3\text{Cu}_1$ cluster is the largest and the wavenumber of the strongest vibrational peak of $\text{Ag}_2\text{Cu}_2$ cluster is the smallest of 4-atom silver-copper.

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