Structure of Ag-Cu clusters resolved by absorption, Raman and vibrational spectroscopy

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Abstract. The structures of Ag9, Ag10, Ag8Cu1, and Ag6Cu3 clusters and their optical, Raman and vibrational spectra are calculated by GGA/PBE. The results display that the structures of the Ag9, Ag10 and Ag8Cu1 (three isomers) clusters can be distinguished by comparing their energies and optical, Raman and vibrational spectra. The difference between the two isomers of the Ag6Cu3 clusters cannot be distinguished by comparing their energies and cannot be directly observed, with their uniform shapes proved by their optical, Raman and vibrational spectra.

1. Introduction
Clusters are microscopic or submicroscopic aggregates of several to thousands of atoms, molecules or ions, and their properties vary with size and differ from those of bulk. Nanoclusters, such as noble metal clusters, are gradually growing in interest because they can be applied in catalysis [1], electronics [2], optics [3] and so on. Therefore, a large number of theoretical and experimental studies on noble metal clusters have been carried out. Some difficulties have been encountered in the study of noble metal clusters, for example, their preparation and the determination of their composition and structure in the preparation process, because most experiments involve the measurement of the optical spectra of a collection of noble metal nanoparticles.

In order to study their properties, suitable structures of the clusters must first be established by methods such as genetic algorithms and annealing, and then their structural stabilities are studied by first principles. When increasing the sizes of clusters, the structures of clusters can become complex and a series of structures may be obtained by genetic algorithm and annealing methods. Similar structures appear in these structures and the question of how to distinguish these similar structures is important. Predicting the structures of bimetallic clusters composed of two elements, such as silver and copper, is also challenging.

The structural properties of silver and copper clusters have been widely studied. For instance, Agrawal et al. investigated the structural and electronic properties of Agₙ (n = 1–10) clusters by DFT/LDA [4]. Chen et al. studied neutral silver clusters using DFT and determined the low energy isomers for each cluster size [5]. Massobrio et al. determined the equilibrium geometries and electronic properties of neutral copper clusters via first principles calculations [6]. Jug et al. studied the structure and stability of neutral and ionic small copper clusters with DFT [7]. The structural and electronic properties of small gas-phase AgₙCuₙ clusters are investigated using spin-polarized DFT [8].
The structures and chemical ordering of 34-, 38- and 98-atom Cu-Ag clusters are studied using a genetic algorithm global optimization with the Gupta semiempirical many-body potential [9]. The optical spectra of pure silver and copper clusters have also been investigated. Baishya et al. investigated optical absorption spectra of the three lowest-energy isomers of 10-20-atom Ag within the TDDFT. Rao et al. investigated the optical properties of Ag13, Ag12Cu1 and Cu13 clusters using DFT [10]. Weissker and Mottet investigated the optical absorption spectra of magic number Ag-Cu clusters using pseudopotential TDDFT [11]. Ogut et al. studied optical absorption spectra of 2-8-atom Ag clusters using static and TDDFT [12]. Bosnick et al. determined the structure of a Ag7 cluster by resonance Raman spectroscopy and DFT [13]. The vibrational and Raman of pure silver and copper clusters were also studied by DFT and experiments. Cazayous et al. measured the vibration modes of Cu-Ag and pure Ag clusters by confocal micro-Raman spectroscopy and calculated the nanoparticle sizes [14]. In our previous work, the structural, optical, vibrational and Raman properties of 2–9-, 13- and 55-atom Ag-Cu clusters are investigated by the DFT, the results show that their spectra are determined by their structures [15–26]. Therefore, we can use spectra to distinguish similar cluster structures.

The appearance of bimetallic clusters makes the prediction of clusters more complicated. In the process of predicting cluster structure, many isomers appear and while the differences between some are obvious, the differences of others cannot be easily distinguished. In this study, we distinguish similar structures of Ag-Cu clusters using optical, vibrational and Raman spectra.

2. Models and calculation method
The original Ag-Cu cluster configuration was obtained by a genetic algorithm [24]. The obtained Ag-Cu clusters are further optimized using the Dmol³ software [27,28]. During optimizations of structures and their binding energy, Raman and vibration spectra using the PBE/GGA, the exchange-correlation functional is PBE [29], core treatment is DFT-based semi-core pseudopotentials [28], the basis set is the double numerical plus polarization function [30]. The calculations of their absorption spectra are the PBE/GGA with TDDFT [31]. The simulated Raman spectra are at 514.5 nm of the wavelength of incident light and 10 K. The convergence criterion of self-consistent field procedures is 10⁻⁶ Ha.

3. Results and discussion
The structure, optical, Raman and vibrational spectra of Ag9 cluster are described in a previous article [24], to compare the effects of size on the optical, Raman and vibrational spectra, we also draw the structure and optical, Raman and vibrational spectra of Ag9 on Figure 1. Figure 1 displays the structures of the pure Ag9 and Ag10 clusters, and also lists their optical, Raman and vibrational spectra. The configuration of the optimized Ag10 cluster is composed of four tetrahedra and one triprism. Though Ag10 is only Ag9 with an additional Ag atom, their structures are significantly different. We explain the differences between their structures using their optical, Raman and vibrational spectra because their performance is determined by their structure.

There are six and five strong peaks in the absorption spectra of the Ag9 and Ag10 clusters, respectively. The energy and intensity of strongest optical peak of Ag10 are stronger than that of the Ag9 cluster. Therefore, there is a blueshift is observed compared to their absorption spectra. There are two peaks in Raman spectra of the Ag9 and Ag10 clusters, respectively. Although the positions of their strongest Raman peaks are close, their intensity is different, the intensity of the Ag10 cluster is weaker. The positions of the other Raman peaks have a slight difference in wavelength of ~4 cm⁻¹. There are many strong peaks in the vibrational spectra of the Ag9 and Ag10 clusters, with the strongest peaks located at 77.7 and 149.1 cm⁻¹, respectively. The intensities of all the vibrational peaks of the Ag9 cluster are stronger than those of the Ag10 cluster. Although the difference in Raman spectra between the Ag9 and Ag10 clusters is very slight, the differences in the optical and vibrational spectra of the Ag9 and Ag10 clusters are obvious. Therefore, the structures of the Ag9 and Ag10 clusters are not determined by only one spectrum (optical, Raman or vibrational spectrum) and instead are determined by taking into account all their optical, Raman, and vibrational spectra.
When the global minimum energy structures of the cluster are predicted using a genetic algorithm and first principles, the most stable structure can be determined by comparing their differences in energy, but some very similar structures sometimes cannot be excluded through only this method. Thus, we can effectively distinguish the similarities and differences in these structures using their optical, Raman and vibrational spectra. When the Ag9 cluster are doped with an Cu atom, the possible isomers are predicted by the genetic algorithm and first principles. In the isomers, the three clusters with the smallest energy are selected as the research object, Ag8Cu1-I, Ag8Cu1-II and Ag8Cu1-III. The difference in structure between the three clusters can be distinguished by comparing the energy; however, the structure of the Ag8Cu1-I cluster could not be distinguished from that of the Ag8Cu1-III cluster, because the energy difference between them is very small at only 0.0036 eV. Here, we can distinguish the structure of the Ag8Cu1-I cluster from that of the Ag8Cu1-III cluster using their optical, Raman and vibrational spectra.

Figure 2 displays the structures and optical, Raman, and vibrational spectra of the three isomers of the Ag8Cu1 cluster, among them, structures, optical, Raman and vibrational spectra of the two isomers (Ag8Cu1-I and Ag8Cu1-II) are also described in a previous article [24]. For clear comparison, all shown in Figure 2. The three isomer structures are similar to structure of the Ag9 cluster. The copper atom of the Ag8Cu1-I cluster sits at the center of one pentahedron and is located at the bottom of the structure, the copper atom of the Ag8Cu1-II cluster sits at the edge of one pentahedron. Their energy are different, about 0.061 eV. The copper atom of the Ag8Cu1-III cluster sits at the center of the other pentahedron and is located on the top of structure with C1 point group symmetry. Therefore, the difference in structure between these two clusters can be easily distinguished by comparing their energies, while the structure of the Ag8Cu1-I cluster cannot be distinguished from that of the Ag8Cu1-III cluster.

The absorption spectrum of the Ag8Cu1-I is exactly same as the Ag8Cu1-III, with five strong peaks located at 2.573, 2.785, 3.415, 4.242 and 4.827 eV. Although the Ag8Cu1-II has five strong optical peaks, their energy positions are different from those of the Ag8Cu1-I and Ag8Cu1-III clusters and are located at 2.742, 3.014, 3.378, 4.191 and 4.757 (0.711) eV. Thus, the optical spectrum of the Ag8Cu1-II cluster has a small redshift compared with another two clusters. The Raman spectrum of the Ag8Cu1-I is almost the same as that of the Ag8Cu1-III, with two strong peaks at 83.0 and 154.5
The Raman spectrum of the Ag8Cu1-II cluster is similar to another two isomers, but the positions and number of the Raman peaks of the Ag8Cu1-II differ from another two isomers, it has three Raman peaks and locates at 44.2, 75.9 and 137.1 cm⁻¹, respectively. The Raman peaks of the Ag8Cu1-I and Ag8Cu1-III shift to a large wavelength compared with the Ag8Cu1-II. The vibrational spectrum of the Ag8Cu1-I is nearly the same as that of the Ag8Cu1-III. There are several important strong peaks in their vibrational spectra, which are obviously different from Ag8Cu1-II. The intensities of the strongest peaks of the Ag8Cu1-I and Ag8Cu1-III are larger than the Ag8Cu1-II.

The shapes of the Ag6Cu3 two isomers are similar to the Ag9 cluster. The linked three copper atoms are located in the same pentahedron in both Ag6Cu3 clusters. However, it is difficult to distinguish directly whether their structures are the same, because they have different shapes and a very small energy difference (0.004 eV). The three Cu atoms locate on the side of the Ag6Cu3-I cluster, while the Cu atoms lie on the bottom of the Ag6Cu3-II cluster. Thus, the uniform shapes of both Ag6Cu3 clusters are proved by their optical, Raman and vibrational spectra.
Surprisingly, the absorption spectra of these clusters completely coincide. There is a weak peak and four strong peaks in the optical spectra of both Ag6Cu3 isomers, with their strongest optical peak at 4.856 eV. The Raman spectra of the two Ag6Cu3 clusters are almost the same. There is a slight difference in the strength of their Raman peaks at 39 cm$^{-1}$. The differences in the positions of the another three Raman peaks are within 3 cm$^{-1}$. Overall, the vibrational spectrum of the Ag6Cu3-I is basically the same as the Ag6Cu3-II cluster, but there are some nuances. The differences of the positions of these vibrational peaks are in the range of 4 cm$^{-1}$.

In summary, the structures of Ag-Cu clusters can be distinguished by their optical, Raman and vibrational spectra. In particular, clusters that are difficult to distinguish according to their shape can be effectively distinguished by their optical, Raman, and vibrational spectra.

4. Conclusions
The structures of Ag-Cu clusters were calculated by a genetic algorithm and GGA/PBE, and their optical, Raman and vibrational spectra were calculated using GGA/PBE. The structures of the Ag9 and Ag10 clusters are not determined by only one spectrum (optical, Raman or vibrational spectrum) and instead are determined by considering their optical, Raman and vibrational spectra. The differences in the structures between the Ag8Cu1 clusters can be distinguished by comparing their energies. The structure of the Ag8Cu1-I cluster could be distinguished from its optical, Raman and vibrational spectra. The shapes of the two isomers of the Ag6Cu3 clusters are similar and it is difficult to distinguish them directly when their structures are the same. Their uniform shapes are proved by their optical, Raman and vibrational spectra.

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