

Study of Reactions of Silver and Sulfur Clusters

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The reactions between silver and sulfur clusters are studied with a laser double ablation reactor. The main reaction products are $[\text{AgS}_4]^+$, $[\text{AgS}_8]^+$, $[\text{AgS}_{12}]^+$, and $[\text{AgS}_{16}]^+$, which have different compositions from those of Ag/S clusters produced from Ag/S mixed sample by laser ablation. The photolysis of the products with a 193 nm excimer laser indicates that $[\text{AgS}_{12}]^+$ and $[\text{AgS}_{16}]^+$ have a photodissociation efficiency much higher than that of $[\text{AgS}_4]^+$ and $[\text{AgS}_8]^+$. The structure of the products and the mechanism of the reactions to form products $[\text{AgS}_{12}]^+$ and $[\text{AgS}_{16}]^+$ are discussed.

Introduction

The compounds composed of silver and sulfur elements exist in nature with the composition of Ag_2S and three polymorphs: monoclinic at room temperature, body-centered cubic (bcc) at 176 °C, and face-centered cubic (fcc) at 576 °C.¹ These kinds of compounds have important applications in optics and electronics.^{2–6} It has been known that the compounds can be used to prepare superionic conductive materials because of their attractive ionic conduction properties.² It was also reported that by the doping of Ag_2S in CdS on Pt electrodes the efficiency of splitting H_2S into H_2 and S could be much improved.³ Sulfur sensitization is one of the most important stages for the formation of latent images composed of Ag in the photographic emulsion-making process,⁴ and it is attributed to the Ag/S cluster sensitization center. Applications of Ag_2S compound as photovoltaic cells and infrared detectors have also been reported.^{5,6}

Molecular sulfur can be reduced to S_2^- by most metals in condensed phase chemistry,⁷ although sulfur does not react with metal ions in solution.^{8,9} However, the reactions in the condensed phase are influenced strongly by the environment; therefore, the reactions in the gas phase are preferred to better understand the chemical reaction mechanisms.

The reactions of clusters were performed in the gas phase using various experimental conditions.^{8–18} With a high-intensity focused laser beam, a solid sample can be vaporized. The vaporized species collide with each other, emit with speed of sound, and cool in the gas phase to form cluster ions by ion–molecule reactions or neutral clusters by atom–molecule reactions.^{10–15} This kind of reaction is a clustering reaction. We have studied clustering reactions of silver and sulfur elements by laser ablation of a sample made of silver and sulfur.¹⁰ The mass spectrum indicated that the binary Ag/S clusters were related by an incremental unit of Ag_2S . The most abundant cluster series in the mass spectrum had the composition of $[\text{Ag}(\text{Ag}_2\text{S})_n]^+$ ($n = 1, 2, 3, \dots$). It should be noted that the composition of Ag/S clusters with the unit, Ag_2S , was coincident with that of silver sulfide compounds in nature. The mass spectrum also indicated that the regularity of composition for small clusters was not marked, and when the clusters became larger, it appeared prominently. This feature might display the

transition of the composition from the gas phase to the condensed phase.

Another kind of reaction is a chemical reaction between clusters or between clusters and atoms or molecules,^{8,9,17,18} which have been performed in the gas phase by Fourier-transform ion-cyclotron resonance (FTICR) spectrometer¹⁹ and a flow tube reactor (FTR).²⁰ The reactions of all the transition metal ions, $[\text{M}^+]$, with sulfur have been reported,⁸ and the study with Ag^+ was highlighted.⁹ The reaction between silver ion Ag^+ and S_8 studied in a FTICR gave the products $[\text{AgS}_4]^+$, $[\text{AgS}_8]^+$, and $[\text{AgS}_{16}]^+$. The compositions of these products are totally different from that of condensed phase compounds or that of Ag/S clusters produced from a Ag/S mixed sample,¹¹ without composition of a Ag_2S unit. Herein, we report on a study of the reactions between silver and sulfur clusters by a new apparatus called a laser double ablation reactor (LDAR). LDAR has a simple construction with only two solid samples. Thus the clusters are produced by laser ablation of the two samples, forming ions, and the ions collide to react with each other. The experiments show that the reaction products obtained by LDAR are similar to that obtained by FTICR,^{8,9} indicating that this new technique is very effective for study of the reactions between clusters. In this paper, we also present the study of the photodissociation of the reaction products.

Experiment

Figure 1 shows the construction of an LDAR, which is attached to the homemade tandem time-of-flight mass spectrometer (TOF MS)²¹ for detection. The details of the LDAR were reported in our previous work.²² Herein, only a brief description is presented.

As shown in Figure 1, the LDAR contains two solid samples, sample 1 and sample 2, separated from each other. In the present experiments, sample 1 is made of silver and sample 2 is made of sulfur. The two samples are shaped as disks (thickness is 5 mm, radius is 5 mm), and a hole is drilled in sample 2. The double frequency beam of a Nd:YAG laser (532 nm) is directed through the hole of sample 2 so as to be normal to the surface of sample 1. The laser beam diameter is larger than the hole in sample 2 so that the central part of laser beam ablates the surface of sample 1 through the hole of sample 2 and the outer part of laser beam ablates the surface of sample 2. Because the energy of the central part of the laser beam is stronger than that of the

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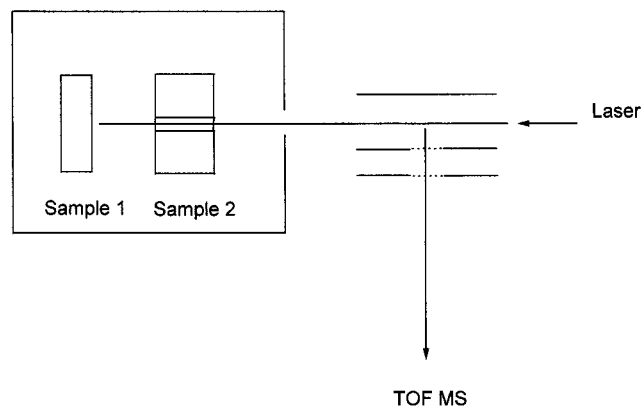


Figure 1. Laser double ablation reactor.

outer part, we used a sulfur sample with lower melting and boiling points than silver. Neutral atoms, molecules, and ions were simultaneously emitted with the speed of sound from each sample using ablation with a laser beam, and clustering had occurred. The clusters produced from sample 1 were passed through the hole of sample 2 and reacted with the clusters produced from sample 2.

The independent clustering of the emitted species from each sample is very important to study the reactions between clusters produced from samples 1 and 2, and it should be completed prior to the reactions between clusters. This condition is called clustering first and reacting second (CFRS).²² To satisfy the condition of CFRS, the value of the distance between samples 1 and 2 plays an important role. If the distance is too short, then the emitted species from the two samples meet first, and clustering occurs. This process is similar to that produced with one sample that contains all elements in samples 1 and 2 without reaction between clusters. On the other hand, the distance between samples 1 and 2 cannot be too long. If it is, then the amount of the reaction products greatly decreases and detection might be difficult. The experiments indicate that with a laser fluence of 100 mJ/cm² and a 1 mm diameter hole in sample 2, the distances in the range of 5–10 mm between samples 1 and 2 are effective. In the present experiments, the distance between sample 1 (silver) and sample 2 (sulfur) was set to 6 mm. The laser beam was focused with a lens ($f = 545$ mm), and the energy of laser beam on the surface of sample 1 was about 10⁸ W/cm². The reaction products were detected by the first stage of the tandem TOF MS.²² In the second stage of the tandem TOF MS,²² photodissociation of the reaction products was performed with a 193 nm laser beam. The ion detections were all performed with dual microchannel plate detectors, and the signals (mass spectrum) were recorded with a transient recorder (10 MHz bandwidth). Typically, the signals with 1000–10 000 laser shots were accumulated and stored in an IBM-PC computer.

Results and Discussion

The mass spectrum of the reaction products is shown in Figure 2. The mass peaks presented in the mass spectrum mainly have the composition of $[\text{AgS}_n]^+$ ($n = 0-16$). It is evident that the mass peaks $[\text{AgS}_4]^+$, $[\text{AgS}_8]^+$, $[\text{AgS}_{12}]^+$, and $[\text{AgS}_{16}]^+$ are very distinct as magic numbers, indicating that these products have more stable structures than the others. For comparison, the mass spectrum of positive cluster ions produced from one Ag/S mixed sample by laser ablation is presented in Figure 3. The mass spectrum mainly consists of two series, $[\text{Ag}(\text{Ag}_2\text{S})_n]^+$ ($n = 1, 2, 3, \dots$) and $[\text{Ag}_3(\text{Ag}_2\text{S})_n]^+$ ($n = 1, 2, 3, \dots$), and the former

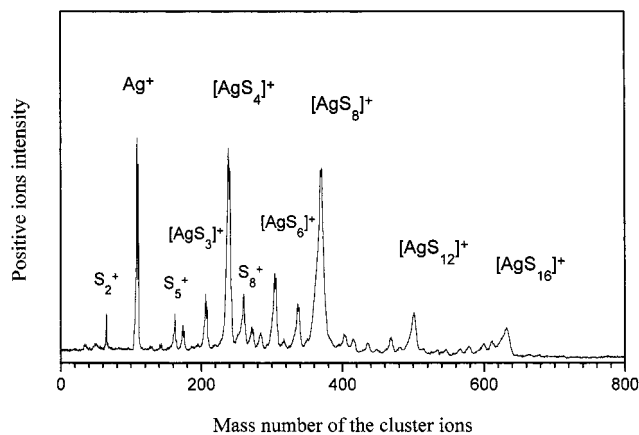


Figure 2. Mass spectrum of positive ions produced from a silver sample and a sulfur sample separated by 6 mm.

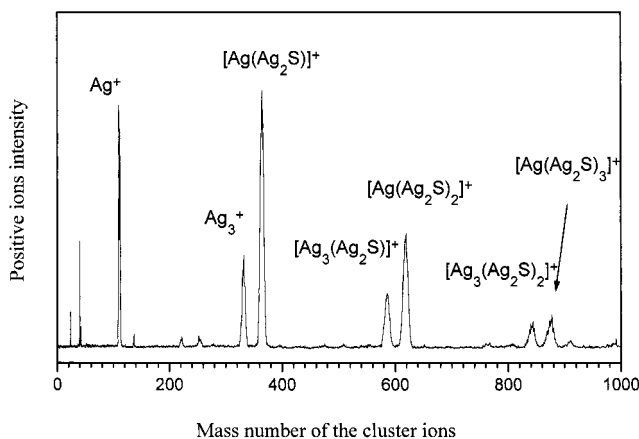
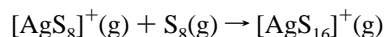
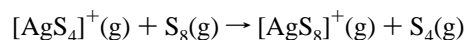
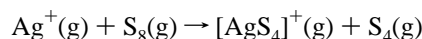


Figure 3. Mass spectrum of positive ions produced from a mixed sample of silver/sulfur (AgS = 1:1).

having ions of greater intensity than the latter. This result shows that the Ag/S cluster positive ions grow by the incremental unit of Ag_2S .

Willett et al. studied the reactions between Ag^+ and S_8 by FTICR^{8,9} and obtained the following results:



It is clear that the reaction products shown above are similar to those obtained with LDAR except for the reaction product $[\text{AgS}_{12}]^+$.

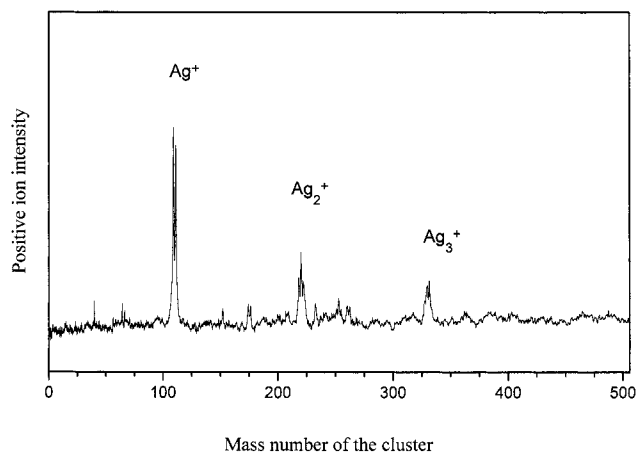
These results indicate that the products from LDAR are different from those produced from a Ag/S mixed sample. The former is produced by reactions between silver and sulfur clusters, while the latter is produced by a clustering process of silver and sulfur elements vaporized by laser ablation.

The reaction products $[\text{AgS}_n]^+$ ($n = 4, 8, 12, 16$) were photodissociated with a 193 nm laser. The photofragments are listed in Table 1. It is known from Table 1 that for $[\text{AgS}_4]^+$ no conspicuous fragment is detected except for a small Ag^+ , while the $[\text{AgS}_8]^+$ is photodissociated to Ag^+ , $[\text{AgS}_2]^+$, and $[\text{AgS}_4]^+$. $[\text{AgS}_{12}]^+$ and $[\text{AgS}_{16}]^+$ have photofragments mainly as $[\text{AgS}_4]^+$ and $[\text{AgS}_8]^+$, respectively. Table 1 also shows that the photodissociation efficiency of $[\text{AgS}_{12}]^+$ and $[\text{AgS}_{16}]^+$ is much higher than that of $[\text{AgS}_4]^+$ and $[\text{AgS}_8]^+$.

TABLE 1: Photodissociation Percentage^a of Reaction Products [AgS_n]⁺ (n = 4, 8, 12, 16)

products	photofragments				
	Ag ⁺	[AgS ₂] ⁺	[AgS ₃] ⁺	[AgS ₄] ⁺	[AgS ₈] ⁺
[AgS ₄] ⁺	0.56				
[AgS ₈] ⁺	0.82	1.05	0.50	0.68	
[AgS ₁₂] ⁺				16.0	
[AgS ₁₆] ⁺					10.5

^a Photodissociation percentage = (intensity of fragments/sum of intensity of fragments and product) × 100.

**Figure 4.** Mass spectrum of positive ions produced from a sample of silver.

From the distribution of photofragments, we can observe that [AgS₄]⁺ and [AgS₈]⁺ are the main photofragments of [AgS₁₂]⁺ and [AgS₁₆]⁺; i.e., they arise from the same dissociation channel in which S₈ is stripped from [AgS₁₂]⁺ and [AgS₁₆]⁺, respectively. So, it might be suggested that in the structure of [AgS₁₂]⁺ and [AgS₁₆]⁺ there are weak combinations between S₈ and [AgS₄]⁺ and [AgS₈]⁺, respectively. For the photodissociation of [AgS₄]⁺ and [AgS₈]⁺, there are few fragments (see Table 1). This means that there may not be such weak interactions in their structure. In the condensed phase, the S–S bond strength (4.40 eV) is stronger than a S–Ag bond (2.25 eV),^{23,24} but all bond strength are lower than the energy of a 193 nm photon (6.42 eV). We can suggest that in [AgS₄]⁺ and [AgS₈]⁺ the silver atom is bonded to the above two sulfur atoms. Fisher et al. studied the reaction between Ag⁺ and HSC₆H₅ in the gas phase and calculated the geometry energy surface of the product [AgHSC₆H₅]⁺.^{8,9} For the geometry-optimized structure of [AgHSC₆H₅]⁺ with the lowest energy, the silver atom is bonded to the sulfur atom. This kind of bond may appear in the structure of [AgS₁₂]⁺ and [AgS₁₆]⁺. So, [AgS₁₂]⁺ and [AgS₁₆]⁺ have different bonding characters from [AgS₄]⁺ and [AgS₈]⁺.

Eyler et al.²⁵ studied the reactions between Ag₂⁺ and diethylaniline (DEAN), and between Ag₂⁺ and dimethylaniline (DMAN). The reaction products of AgL_n⁺ (L = DEAN, DMAN) were obtained. This suggests that Ag⁺ and Ag₂⁺ can both react with some molecules to generate the products in the form of AgL_n⁺. Figure 4 is the mass spectrum of the positive ions produced from the silver sample by 532 nm laser ablation. It is obvious that Ag⁺ is more abundant than Ag₂⁺ and Ag₃⁺. So, we can suggest that the products [AgS_n]⁺ (n = 4, 8, 12, 16) are produced mainly from reactions between Ag⁺ and S_n.

It is possible also that the products [AgS_n]⁺ are formed by the reactions between sulfur cluster ions and silver atoms or molecules. However, the ionization potential of sulfur is much larger than that of silver (IP/S = 10.36 eV, IP/S₂ = 9.356 eV,

IP/Ag = 7.57 eV),²⁶ so the positive sulfur cluster ions are relatively less easy to generate.

The study⁷ of sulfur in the condensed phase shows that sulfur atoms can easily bond to each other to form molecules with undetermined atom numbers. The structure of orthogonal sulfur with 16 S₈ in a unit cell is the most stable at room temperature and atmosphere. The ring S₈ molecule has a structure similar to the skull structure with D_{4d} symmetry. Gas phase sulfur exists mainly in the forms of S₆, S₇, and S₈, while S₈ is the most abundant at the temperature below 673 K. This fact supports our assumption that [AgS₁₂]⁺ and [AgS₁₆]⁺ are produced through the addition of S₈ on [AgS₄]⁺ and [AgS₈]⁺, respectively.

In comparison, we can see that the reaction products and the reaction mechanism by LDAR are different from those by FTICR. The former is of the reactions between the emitted species (atoms, molecules, and clusters) generated by laser ablation. In this case, the product species is more various than that generated by FTICR, and there also exist many possible reaction channels for the product formation.

From the discussion as above, we can describe the process of cluster reactions by LDAR as follows: By laser ablation, silver and sulfur samples are vaporized, and then the clustering occurs. Silver ions from the silver sample react with sulfur atoms or clusters from sulfur sample to produce [AgS₄]⁺ and [AgS₈]⁺, and then [AgS₄]⁺ and [AgS₈]⁺ react with S₈ to form [AgS₁₂]⁺ and [AgS₁₆]⁺, respectively.

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