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Reaction of Silver Sulfide Cluster Anions with Bromine Atoms

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Using a laser double ablation reactor built on the basis of a tandem time-of-flight mass spectrometer (TOF MS), we studied the reaction of clusters produced by laser ablation of silver (potassium) bromide and silver sulfur powder mixture. The results showed that reactions took place and that Ag/S/Br ternary cluster anions were produced. The formation of Ag/S/Br clusters is considered to occur by the addition of bromine atom to the silver sulfide cluster anions. The results provide grounds for the argument we proposed that silver sulfide cluster anions can act as positive hole traps during the exposure of photosensitive silver bromide microcrystals.

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Introduction

In the photographic process, two photogenerated charge carriers: a photoelectron and a positive hole (equivalent to a bromine atom) are generated when photosensitive silver halide emulsions are exposed to light. The fate of the two carriers is the most fundamental problem of photographic theory. With regard to the electron, it is commonly considered that Ag_2S specks, that are formed during the sulfur sensitization of photographic emulsion, are traps where latent images are formed by repeat interaction of electrons with interstitial silver ions.[1a,b] With respect to the positive hole (Br), Mitchell[2a,b] pointed out that it should be trapped by Ag_2S specks. Subsequently, Sonoike[3] thought S^{2-}-interstitial silver ion complexes were traps for positive holes by observing infrared quenching of luminescence peaks in S-doped silver bromide crystals. Sahyun[4] analyzed the recombination behavior of photogenerated charge carriers in micrystalline powders of II–VI semiconductors. He also thought it possible that $(Ag_2S)_n$ centers could act as hole-trapping centers. Using a photostimulated desorption (PSD) technique, Kaneda[5] studied the properties of chemical sensitization centers in AgBr emulsion grains. He found that sulfur sensitization centers were hole traps. Tani[6] pointed out that Ag_2S monomers were hole traps. Gradually, people have begun to take note to the phenomenon that sulfur sensitization centers trap positive holes. But there are different viewpoints on the nature and composition of the hole traps. At present, very little is known about the charge of silver sulfide clusters, which is of prime importance for the element process of latent image formation. The reason for this gap in our knowledge has been the lack of experimental methods to investigate this property.

Today the advancement of experimental methodologies of cluster physics and chemistry offers an obvious hope for gaining insight into positively or negatively charged clusters of silver sulfide. We have studied formation of silver sulfide cluster ions by laser ablation tandem time-of-flight mass spectrometry.[7] We obtained $Ag(Ag_2)^+_n$, $[Ag_3(Ag_2S)_n]^+$ and other similar cationic cluster series and a large number of anionic clusters such as $AgS(Ag_2)^-_n$, $[AgS_2(Ag_2S)_n]^-$, and the like by laser ablation of pressed disks of a mixture of silver and sulfur powders. By correlating these clusters with sulfur-sensitization centers of photographic emulsions, we consider the cationic clusters to be electron traps; correspondingly, the anionic clusters trap holes. But do the silver sulfide cluster anions have reactivity towards atomic bromine? If so, what products may be generated upon reaction? In this work, we report the results of silver sulfide cluster anions reacting with bromine atom using a laser double-ablation reactor.

Experimental

Equipment. To study the reactivity of clusters, a very complicated apparatus must be applied. Only a few laboratories carry out cluster reactivity research.[8–11] On the basis of a tandem time-of-flight mass spectrometer in our lab, with a modified sample holder, we designed a laser double-ablation reactor to study the reactivity of clusters.[12] The following is a brief description of the equipment.

Figure 1 schematically shows the tandem time-of-flight mass spectrometer (TOF MS) we built for cluster study. Cluster ions are produced by laser ablation. A disk of powder mixture is ablated with the focused second harmonic of an Nd:YAG laser (532-nm). In Chamber 1, the cluster ions produced are extracted and accelerated with a pulsed voltage of 1200-V; they drift in a field-free region for 3.5 m where deflector and focus systems are installed to decrease the dispersion of cluster ions

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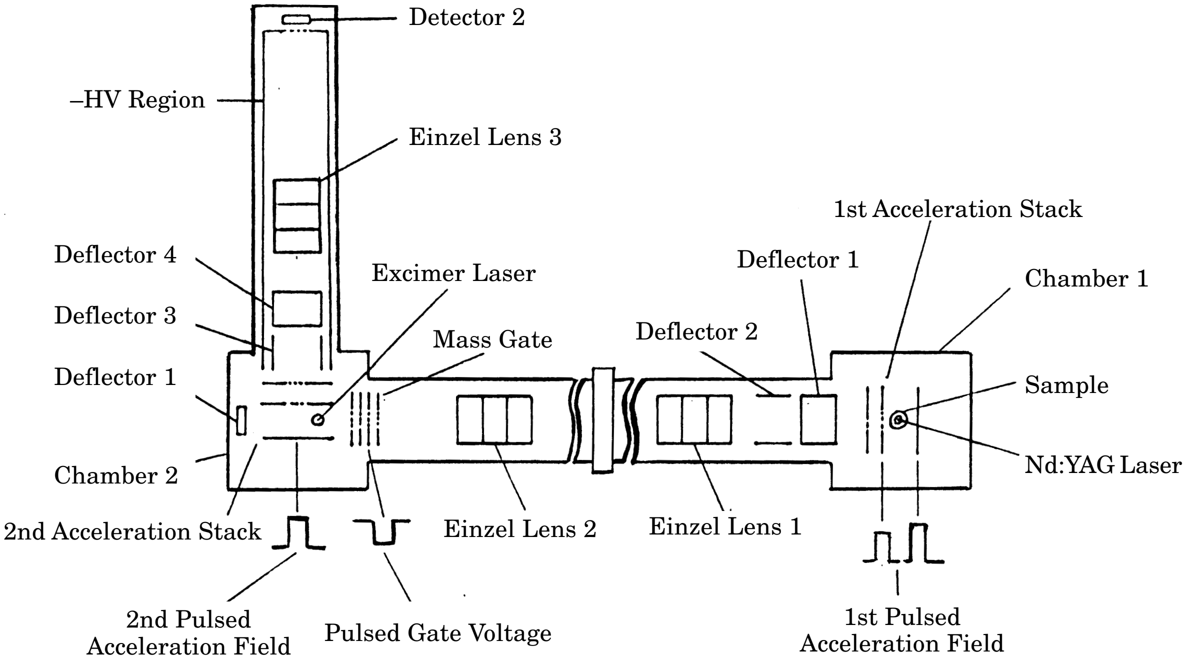

Figure 1. Schematic diagram of a tandem TOF MS.

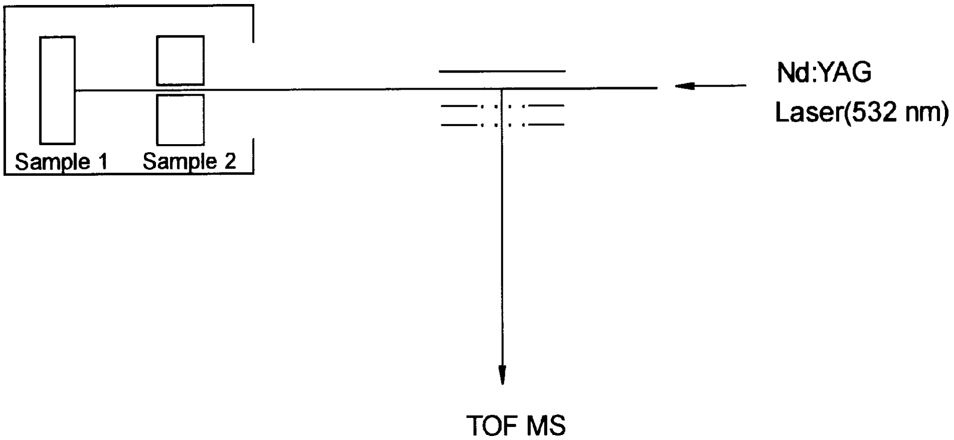

Figure 2. Schematic diagram of a laser double-ablation reactor.

and intensify the detected signals. The detector of the first-stage signal, that consists of two microchannel plates in series, is set up at the end of the first-stage flight region (at the side of Chamber 2). In Chamber 2, a mass gate selects cluster ions of specific mass number. The mass-selected cluster ions are decelerated (<100-eV) and photolyzed with an ultraviolet (UV) laser beam (248-nm) so further studies can be performed. The fragmented and parent ions are detected and analyzed with the second-stage TOF MS whose accelerating voltage is 4100 V with a field-free flight length of 1.5 m. The second-stage TOF MS is perpendicular to the first-stage TOF MS, its detector is another dual microchannel plate, fixed at the end of the second-stage flight region. The signals are preamplified and recorded with a transient recorder (10-MHz), then stored in an IBM PC. The vacuum of the system is maintained at about 6×10^{-4} Pa. The repetition rate is 10-Hz.

Figure 2 schematically shows the laser double-ablation reactor sample holder, which comprises two samples, 1 and 2. In the center of Sample 2, a small hole (Φ=1.0 to 1.5 mm) is drilled. When Sample 2 is ablated by the laser (532-nm, 5 to 20 mJ/pulse, 10 pulses/s), Sample 1 is also ablated at almost the same time after the laser beam passes through the hole in Sample 2. Maintaining the distance of the two samples at 5 to 10 mm can ensure that the two samples evaporate and form clusters seperately. The clusters formed from Sample 1 are ejected from it. Part of the clusters encounter and collide and react with the clusters formed from Sample 2. Finally, all the clusters diffuse away from the samples and are detected with the first -stage TOM MS.

Samples. The reagents included silver powder, silver bromide powder, sulfur powder, and sodium bromide. According to requirements, the reagents were mixed in different molar ratios and pressed to form disks.

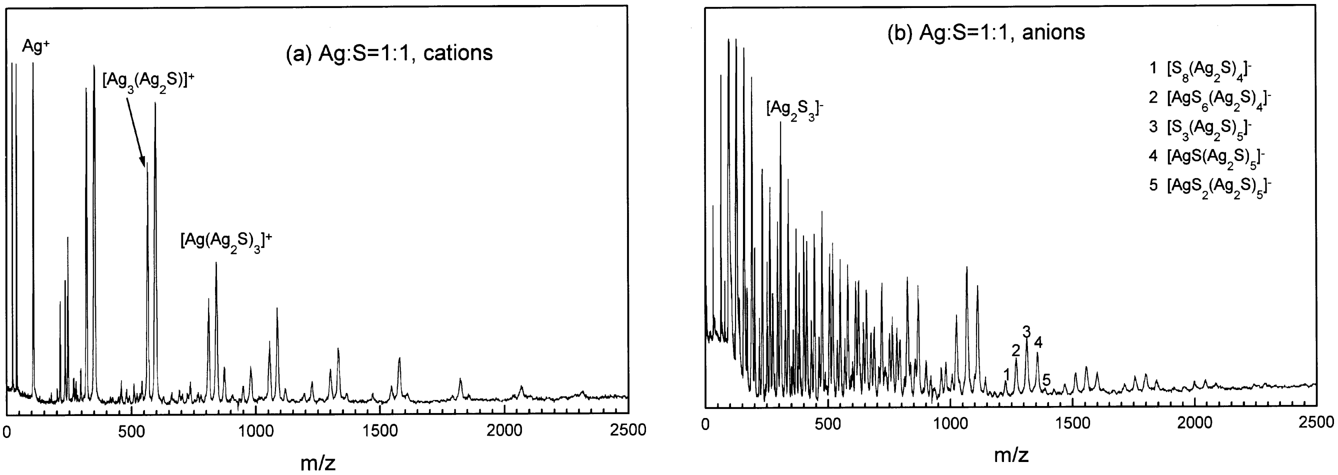

Figure 3. TOF mass spectrum of cluster (a) cations and (b) anions produced by laser ablation of a sample of molar Ag:S=1:1.

Results and Discussion

Mass Spectra Obtained from Laser Ablation on Ag:S=1:1 (Molar Ratio) Mixture. Figure 3(a) shows the TOF mass spectra of cationic clusters. From the increasing trends of silver sulfide binary clusters of different series we can see that cluster growth is increased by incremental addition of the Ag_2S unit. Of all the series, the signals from the $[Ag(Ag_2S)_n]^+$ series are the strongest, these from the $[Ag_3(Ag_2S)_{n-1}]^+$ series are weaker and those from the other series, $[(Ag_2S)_n]^+$ and $[Ag_2(Ag_2S)_n]^+$, weaker still. Further analysis of the mass spectra of the first series shows that the strongest peak is $Ag_3S^+ (n = 1)$, then $Ag_5S_2^+ (n = 2)$. The abundance of these two peaks is much greater than of the other peaks, which indicates that they have high-stability structures. The fact that Ag_3S^+ has a high-stability structure is also confirmed in the photolysis experiment. When the 248 nm UV laser is used to photolyze the Ag_3S^+ cluster, we find that no product fragment is formed, that is, Ag_3S^+ is not dissociated, indicating its high stability.

Figure 3(b) shows the TOF mass spectra of anionic clusters obtained from a molar Ag:S=1:1 sample. We can see that the distribution of peaks is distinctively different in the lower and higher mass regions. In higher mass region, the peak groups appear at equal distance, that corresponds to 248 amu, that is, a single Ag_2S unit. We can conclude that these cluster groups progress by incremental addition of Ag_2S. In the lower mass region, the peak distribution is disordered. After analyzing it, we found that there were S_n^- (n = 2 to 8) and $Ag_pS_m^-$ cluster anions. All the cluster anions and their peak intensities in Fig. 3 are indicated in Fig. 4. By identifying these clusters with sulfur-sensitization centers of photographic emulsions, we propose that the cationic clusters act as electron traps; correspondingly, the anionic clusters trap holes.

Reaction of Cluster Anions with Bromine Atoms. Using the laser double-ablation reactor shown in Fig. 2, taking Ag : S = 1:1 as Sample 2 and the AgBr sample as Sample 1, all the while maintaining the distance of the two samples at 6 mm, we obtain the reaction results shown in Fig. 5. In the higher mass region, there is no difference between Figs. 3(b) and 5. But in lower mass region, two kinds of new clusters emerge [Figs. 6(a) and 6(b)]: one corresponds to a $[Br(AgBr)_n]^-$ series, the other to $[Ag_xS_yBr]^-$ ternary clusters. The ternary clusters, characterized by containing only one bromine atom in each, include (1)

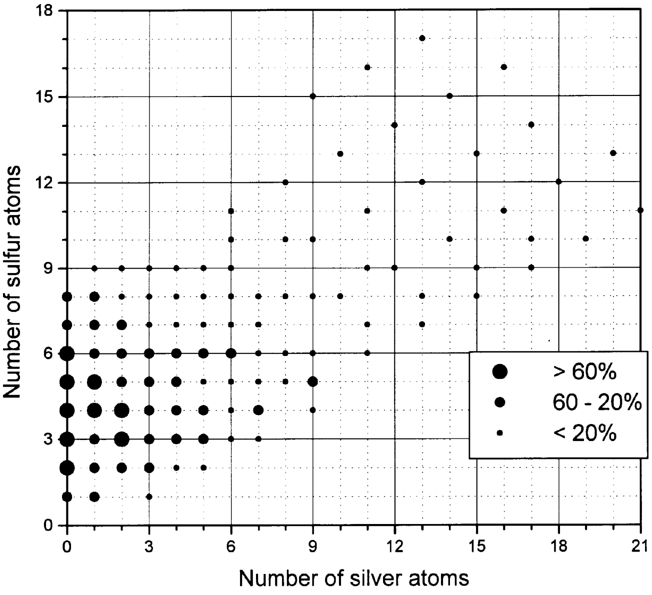

Figure 4. Map of the compositions of $[Ag_nS_m]^-$ anions in Fig. 3(b). The sizes of the circles indicate relative intensity (the percentages refer to mass peak abundance).

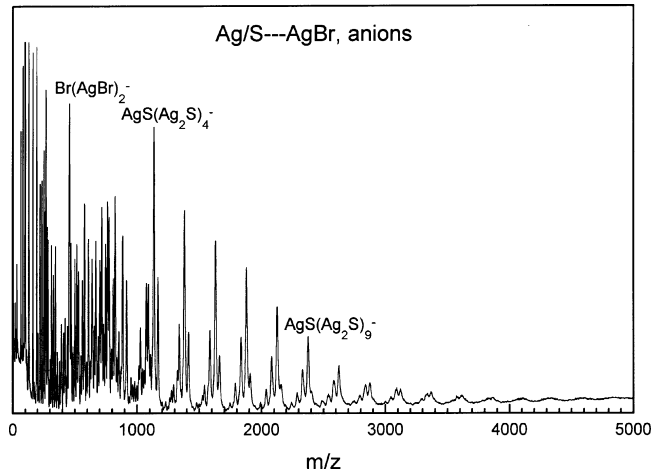

Figure 5. TOF mass spectrum of cluster anions produced by laser double-ablation of samples Ag/S (1:1) and AgBr fixed in the reactor.

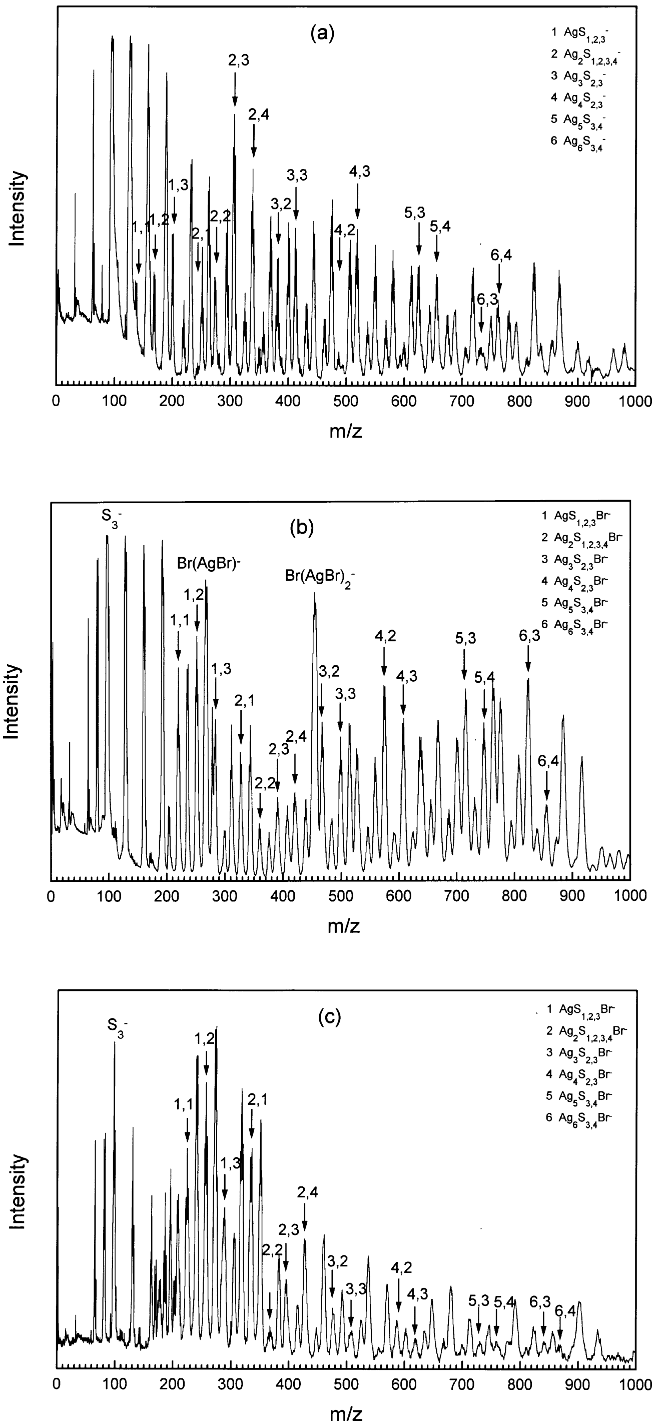

Figure 6. TOF mass spectra (mass number < 1000 ma) of cluster anions produced by laser ablation of samples fixed in the reactor. Samples are (a) Ag/S (1:1), (b) Ag/S (1:1) and AgBr, and (c) Ag/S (1:1) and NaBr. Number pairs refer to the composition of cluster anions indicated in the figure, for example 5,4 means $Ag_5S_4^-$ or $Ag_5S_4Br^-$.

$[AgSBr]^-$, $[AgS_2Br]^-$, and $[AgS_3Br]^-$; (2) $[Ag_2SBr]^-$, $[Ag_2S_2Br]^-$, $[Ag_2S_3Br]^-$, and $[Ag_2S_4Br]^-$; (3) $[Ag_3S_2Br]^-$ and $[Ag_3S_3Br]^-$; (4) $[Ag_4S_2Br]^-$ and $[Ag_4S_3Br]^-$; (5) $[Ag_5S_3Br]^-$ and $[Ag_5S_4Br]^-$; (6) $[Ag_6S_3Br]^-$ and $[Ag_6S_4Br]^-$. On removal of the Br atom, the above ternary clusters would become binary clusters, all of which are generated in Fig. 3(b). Furthermore, we have found only $[AgSBr]^-$, $[AgS_2Br]^-$, and $[AgS_3Br]^-$ clusters using AgBr/S samples. From Fig. 5 we can conclude that, Ag/S and AgBr samples form clusters seperately as they are laser ablated.

After the samples are laser ablated, charged and neutral species are generated simultaneously. The possible pathways for the formation of Ag/S/Br ternary clusters are as follows:

$$[Ag_xS_y]^- + Br \longrightarrow [Ag_xS_yBr]^- \qquad (1)$$

$$Ag_xS_y + Br^- \longrightarrow [Ag_xS_yBr]^- \qquad (2)$$

$$[Ag_{x-1}S_y]^- + AgBr \longrightarrow [Ag_xS_yBr]^- \qquad (3)$$

To the best of our knowledge, from the view point of electronegativity, we may have to consider that the bromine atom (Br_0) has incomparable higher reactivity than bromide ion (Br^-) and conclude that neither the electron transfer from Br^- to S^{2-} nor the replacement of S^{2-} by Br^- may occur. To test pathway 3, we substitute AgBr for NaBr, still use the equipment shown in Fig. 1, and obtain Fig. 6(c). Comparing Fig. 6(b) and Fig. 6(c), we can find that all reaction products in Fig. 6(b) are present in Fig. 6(c). This result excludes pathway 3. Therefore, the above ternary clusters must have been formed through pathway 1. The results imply that silver sulfide cluster anions have significant reactivity toward atomic bromine and the products of this reaction may still bear negative charge, which implies the possibility that silver sulfide cluster anions can act as positive hole traps during the exposure of photosensitive silver bromide microcrystals.

Conclusions

By applying the methods of cluster science, we observed a great number of positively and negatively charged silver sulfide clusters, many of which can be assigned to different series that progress by incremental addition of a single Ag_2S unit. Among these clusters, the positively and negatively charged clusters were suggested as photoelectron traps and positive hole traps in photographic processes, respectively. To investigate whether the silver sulfide cluster anions have reactivity toward atomic bromide, we carried out experiments using a laser double-ablation reactor. The results show that Ag/S/Br ternary clusters were formed, which we propose to be the addition products of atomic bromine to silver sulfide cluster anions. Although these results were obtained in the gas phase, we believe they have some relevance to the practical silver halide photographic process. ▲

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