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STUDIES ON LASER PLASMA REACTION OF SILVER AND SULFUR

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It is well known that under the ordinary conditions the product of the reaction of silver and sulphur is Ag_2S. However, it seems to be an interesting attempt to carry out such a reaction under extreme conditions, for example, in the plasma. the reaction is carried out only between silver and sulfur in no solvent. Since there is quite a part of reactants in the excited electronic states, reactions involving these states will possibly take place while that under moderate conditions will not. The TOF mass spectrometry makes it feasible to observe these products *in situ*. Since the time that takes the produced ions to get to the detector is fairly long (about 10^{-5} s), the produced ions of higher energy and lower stability, will decompose before they get to the detector because there is no medium for the ions to release their excessive energy. Thus, the detected ions are those of higher stability. Such an experiment was performed on a "home-made" laser-probe TOF mass spectrometer in our laboratory.

I. EXPERIMENTAL

The experimental apparatus has been previously described in detail[1, 2]. Powder of pure silver and sulfur was thoroughly ground and then pressed into a disk. The surface of the solid sample, which was set 8 cm outside from the extraction region, was irradiated on a spot of about 0.5 mm in diameter by the focused output (532 nm, 30 mJ per laser pulse, 7 ns pulse width) from a double-frequency Nd^{3+}: YAG laser (Spectro-Physics DCR-11) operated at a repetition rate of 10 Hz. The produced plasma was expanded into the vacuum (about 10^{-6} torr). Both the positive and negative ions in the plasma were extracted simultaneously by the pulsed voltage into two opposite field-free flight tube of mass spectrometer. The ions were detected by two channeltron electron multipliers at the end of each tube. The signals were amplified externally, averaged, and collected by an IBM-PC/XT computer.

A mass spectrum of negative ions is shown in Fig. 1. The spectrum represents an average of 100 laser shots. Mass spectra of positive ions were also taken, on which only Ag^+ ion was observed. The Ag/S ratios of the samples used in the experiments were changed

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(i.e. 1 :4, 1 :2, 1 :1, 2 :1, 4 :1). However, no distinct variation was observed in the mass spectra.

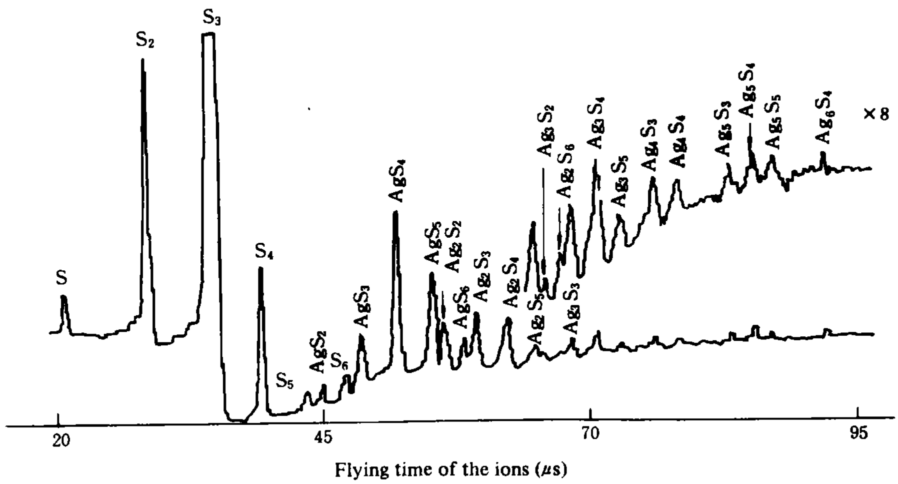

Fig. 1. A mass spectrum of negative ions.

II. Results

From the analyses of Fig. 1 and the experimental conditions, we can get:

1. In the plasma produced from the sample, there are sufficient collisions between silver and sulfur atoms and/or ions. Thus, the observed products and their relative abundance mainly depend on their stability. Since the magnitude of the delay time between the laser pulse and the ion extraction pulse is on the order of 10^{-5} s, the detected ions are only those that can exist for such a long time.

2. Most species in the mass spectra (both positive and negative) are Ag^+ and S_n^- ($1 \leqslant n \leqslant 6$). The relative abundance of S_n^- cluster ions is quite similar to that of the pure sulfur sample, which indicates a small cross-section for silver and sulfur in the plasma. Various S_n^+ ions can be observed in the positive mass spectra of pure sulfur sample, but after Ag is added, only Ag^+ ion is found in this experiment. This is attributed to the low ionization potential(IP) of silver.

3. The produced ions of the reaction between silver and sulfur are all of negative charges , which shows that the ion-molecule reactions only take place between Ag and S_n^- cluster ions, not between Ag^+ ion and Sn clusters. The produced ions have plentiful species though they are of lower yields compared with S_3^- ions. All the AgS_n^- species ($1 \leqslant n \leqslant 6$) can be observed in the spectrum while none of the Ag_nS^- species are observed. Besides, with the increase of the m value in the observed $Ag_mS_n^-$, the n value does not increase. Accordingly, we suggest that sulfur in the plasma are inclined to form S_n^- cluster ions first, and then the cluster ions react with the silver atoms. This argument is supported by that the $Ag_nS_{3-5}^-$ ($1 \leqslant n \leqslant 6$) peaks are comparatively stronger, in accordance with the

abundance of S_{3-5}^- cluster ions. It helps explain why the n value in Ag_mSn^- ions is not larger than that in the observed Sn^- cluster ions.

Assuming the above argument, it is easy to get that the AgS_3^- peak is quite strong. In fact, it is AgS_4^-, but not AgS_3^-, which is of the largest abundance in the silver-sulfur reaction products. The fact suggests that AgS_4^-, either is formed by adding an S to AgS_3^- or by decomposition of other Ag_mSn^-, is the most stable species among the products. Though the structure of AgS_4^- is still unknown, that the number of sulfur atoms in AgS_4^- is four is consistent with the coordination number in most silver complex.

The reaction products do not variate much in their yields when the Ag/S ratio of the samples changes. It suggests that the stability of these products depends more on the thermodynamical than on dynamical factors.

References

[1] Zheng Lansun et al., *Analytical Instrumentation*, 1990, 2:12.
[2] Zheng Lansun et al., *ibid.*, 1991, 3:27.