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Fragmentation of Chalcogen Microclusters

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ABSTRACT

S, Se and Te microclusters were produced in free space by a supersonic jet expansion method. The neutral cluster beam were ionized by electron impact and analyzed by a Wiley-Mclaren type Time-of-Flight mass spectrometer. The mass spectrum near the appearance potential revealed that S_8 is dominant species in the sulfur cluster beam, and Se_5 is dominant in the selenium cluster beam. As the electron impact energy (E_e) increases, the relative intensity of small clusters increases due to fragmentation. The E_e dependence of the relative intensities may suggest that the neutral dimers are emitted from the clusters in the fragmentation process. In the case of selenium cluster, other process such as evaporation of dimer ion should be considered in addition to the evaporation of neutral dimer.

1.INTRODUCTION

Much efforts have been devoted to study the fragmentation process of the covalently bonded clusters such as C[1-5], Si[6-7] and Ge[7]. In these clusters, the small clusters are evaporated in dominant fragmentation pathway. For example, the fragmentation of C_n^+ clusters is dominated by loss of neutral C_3 when $n<30$, while for large carbon clusters the dominant fragmentation process is loss of neutral dimer.

For chalcogen clusters, mass spectroscopy[8-14] and photoelectron spectroscopy[15] are done by several authors. However, not much is known about the fragmentation process of chalcogen microclusters, except for tellurium clusters, for which the evaporation of Te_2^+, Te_5^+ and Te_4 is dominant in the fragmentation process.[16]

In the present study, we have produced chalcogen microclusters by means of supersonic expansion method, and carried out mass spectroscopic measurements as a function of an electron impact energy. From the energy dependence of the relative intensity of cluster, we discuss on the fragmentation process of the sulfur and selenium clusters.

2.EXPERIMENTAL PROCEDURE

The experimental apparatus consists of an expansion chamber and an analyzing chamber. The former was evacuated with pumping speed of 1200l/s and the latter with 400l/s. A cluster source was made of a quartz glass tube. The glass tube had a converging nozzle with about 0.1 mm in diameter at the end, and a sample reservoir was connected to the middle part of the glass tube. We used S with 99.999%, Se with 99.999% and Te with 99.999% purity as starting materials and Ar gas with 99.99% purity as carrier gas whose pressure was controlled at about 10 torr. A conical skimmer with an aperture of 2 mm was located at about 10 mm apart from the nozzle. We used a Wiley-Mclaren type time-of-flight mass spectrometer [17], for which the clusters were ionized by electron impact. Further details of experimental procedure are described elsewhere.[18-19]

3.RESULT

Figure 1 shows the mass spectrum for S, Se and Te clusters ionized with an electron energy E_e of 16 eV. The mass spectrum shown in Fig.1 were taken

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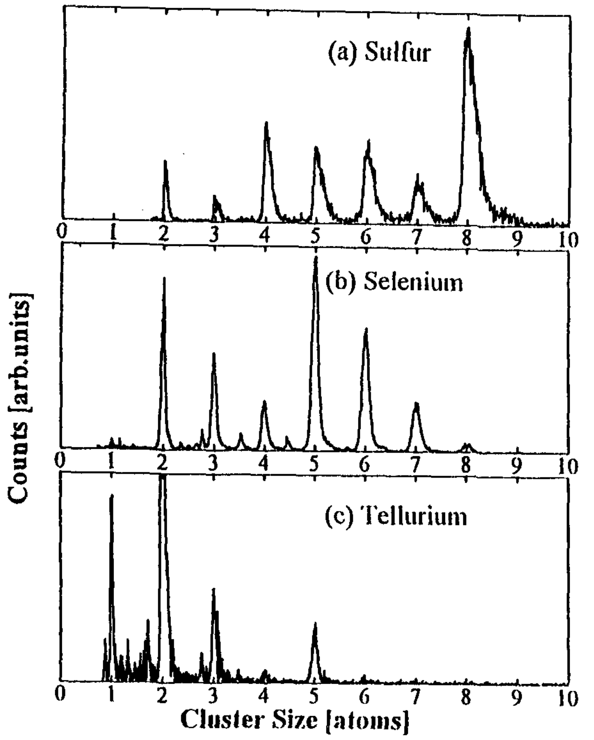

Fig. 1 Mass spectrum of chalcogen clusters ionized with an electron energy of 16eV. (a) Sulfur clusters. The nozzle temperature is 200°C (b) Selenium clusters. The nozzle temperature is 400°C. (c) Tellurium clusters.The nozzle temperature is 500°C.

under condition that nozzle temperature was 200°C for S, 400°C for Se and 500°C for Te. Positively charged clusters, X_n^+ (X=S,Se,Te), are seen up to n=8 for S and Se, up to n=6 for Te.

We varied the electron impact energy E_e with keeping the expansion condition as in Fig. 1. In S cluster, S_8^+ is dominant near the threshold energy. As E_e increases, the abundance of S_8^+ is substantially reduced, and that of smaller species increases. In Se cluster, dominant species is Se_5^+ near the threshold, but similar trend is observed when E_e is increased.

In Figure 2, the relative intensity of S_n^+ clusters, $I(S_n^+)$, of even membered clusters and the sum of $I(S_n^+)$ of even membered clusters, are plotted as a function of E_e. Here $I(S_n^+)$ is normalized as

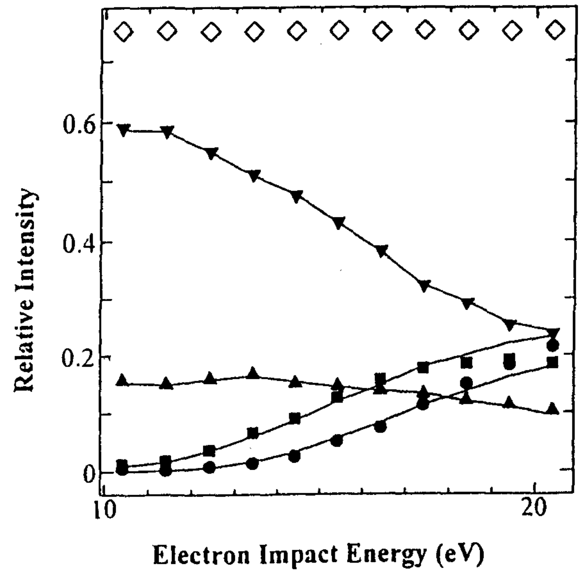

Fig.2 Relative intensities of even membered S_n^+ are plotted as a function of electron energy. Expansion condition is same as Fig. 1(a). ● :n=2, ■ :n=4, ▲ :n=6, ▼ :n=8, ◇ :sum of even membered clusters. Lines denote the results of fitting. (see text)

$$\sum_{n=1}^{8} I(S_n^+)=1 . \qquad (1)$$

The present $I(S_n^+)$ data agree qualitatively with the previous data by Arnold et al.[11]. $I(S_8^+)$ and $I(S_7^+)$ are high at low E_e and decrease rapidly with increasing E_e. $I(S_6^+)$ and $I(S_5^+)$ increase with E_e and show a maximum around 15 eV, where the intensity of smaller clusters starts to rise. It should be noticed that the sum of $I(S_n^+)$ of even membered clusters is nearly preserved when E_e is changed.

The relative intensity of Se_n^+ clusters, $I(Se_n^+)$, are shown as a function of E_e in Fig. 3. In the present experiment $I(Se_n^+)$ shows the following trend at low E_e (around 10eV):

$$I(Se_5^+) > I(Se_6^+) > I(Se_7^+) \geqq I(Se_2^+). \qquad (2)$$

This result is in good agreement with the result by Becker et al.[15], who measured the mass spectrum with keeping the cluster source at 520°C. On the other hand, Tribollet et al.[10] and other authors

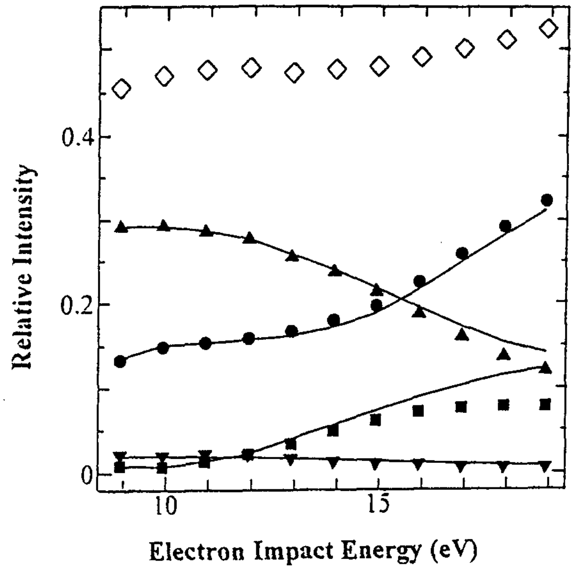

Fig.3 Relative intensities of even membered Se_n^+ are plotted as a function of electron energy. Expansion condition is same as Fig. 1(b). ● :n=2, ■ :n=4, ▲ :n=6, ▼ :n=8, ◇ :sum of even membered clusters. Lines denote the results of fitting. (see text)

[13], who kept the vapor temperature around 220°C, reported that $I(Se_5^+) < I(Se_6^+)$.

The observed E_e dependence of $I(Se_n^+)$ is similar to that of $I(S_n^+)$, but the sum of $I(Se_n^+)$ of even membered clusters start to increase around 15eV.

4.DISCUSSION

From the energy dependence of the relative intensities shown in Fig.2, we suggest the following fragmentation processes:

$$S_n^+ \rightarrow S_{n-2}^+ + S_2 \quad \text{for } n=4,5,6,7,8 \qquad (3)$$

These processes involve evaporation of neutral dimer S_2 rather than fission, though the escaping neutral species cannot be detected directly by the mass spectroscopy. The evaporation of stable neutral species is also observed as dominant processes in other covalently bonded clusters such as carbon [1-5]. .

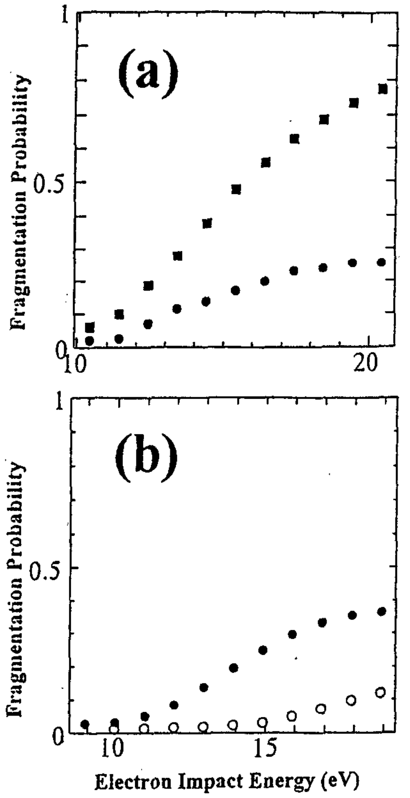

Fig.4 Fragmentation probability of the S_n^+ and Se_n^+. (a) Sulfur cluster. ● :p, ■ :q. p represents the fragmentation probability of S_8^+, and q is fragmentation probability of S_4^+ and S_6^+. (b) Selenium cluster. ● :p, ○ :r. Se_2 emitted with the probability p, and Se_2^+ emitted with the probability r.

In order to describe the fragmentation processes quantitatively, we first tried to fit the observed $I(S_n^+)$ with the simplest model that all even (or odd) membered clusters emits the dimer with the same evaporation probability. However, this model did not reproduce the observed $I(S_n^+)$ of even membered clusters. Then we modified this model, assuming that the fragmentation probability of S_8^+, p, is smaller than that of the S_6^+ and S_4^+ clusters, q, because the S_8^+ cluster is thought to be more stable. This assumption improves the fitting remarkably. In Fig.2 the results of this fitting denoted by lines. The probabilities p and q deduced from this model are plotted as a function of E_e in

Fig.4(a). At low E_e p and q start to rise near the ionization potential and at higher E_e seem to become saturated. This may suggest that S cluster could be thermally excited by excess electron energy (i.e. difference between E_e and the ionization potential) during the ionization process, and that the fragmentation should follow the Arrhenius' equation of chemical kinetics.

For Se cluster, we also tried to fit the observed $I(Se_n^+)$ with the simplest model that all even (or odd) membered clusters have the same evaporation probability. The calculated $I(Se_n^+)$ agrees with the observed $I(Se_n^+)$ at lower E_e. However, the agreement become poor when E_e increases. This is because the sum of $I(Se_n^+)$ of even membered cluster is no more preserved above 15eV. So we should take into account another fragmentation process in which odd membered clusters are converted into even membered clusters. The evaporation of dimer ion is one of the simplest process to achieve such conversion. Assuming that the probability of neutral dimer evaporation is p and that of evaporation of dimer ion is r, we have calculated $I(Se_n^+)$ and shown them by the lines in Fig.3. The calculated $I(Se_n^+)$ reproduce well the experimental values, up to 20eV. We also examined other models, such that neutral trimer would be evaporated from the clusters instead of charged dimer, but they could not explain the observed $I(Se_n^+)$.

5.SUMMARY

We have measured the mass spectrum for S, Se clusters. The dependence of $I(S_n^+)$ on the electron impact energy E_e suggests that neutral S_2 dimer may be evaporated from S_n^+ clusters. The E_e dependence of $I(Se_n^+)$ suggest that other evaporation process such as the dimer ion evaporation should be considered in addition to the evaporation of neutral dimer.

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