The study on characteristics of mercury cluster ions from sputtering ion source

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Abstract

The electronic structure of mercury atom is $5d^{10}6s^2$ closed shell, which is isoelectronic with helium. Therefore the diatomic molecule and smaller clusters are bounded by van der Waals force. For intermediated cluster size, the 6*s* and 6*p* orbitals broaden. The overlapping of 6*s* and 6*p* bands gives the metallic behavior of bulk Hg. The non-metal to metal transition of mercury cluster was studied by various methods such as recording the autoionization lines (5d = 6p) excited by synchrotron radiation, measuring the ionization potential and binding energy. Every experiment showed the non-metal to metal transition occurred at cluster size around 15. Furthermore, the nonmetal to metal transition was also observed about the mercury-alkali metal binary cluster ions at cluster size n = 30.

This thesis consists of the three following subjects.

(1) The size distribution of mercury-silver binary cluster ions, Hg_nAg^+ and $Hg_nAg_2^+$. The structure of Hg_nAg^+ was interpreted by electronic shell model rather than geometric. On the other hand, the stable $Hg_{18}Ag_2^+$ was considered to be geometrical double icosahedron structure. In order to know more accurate character of mercury-silver binary cluster ions, the fragmentation pattern was also investigated.

(2) Determination of appearance sizes of doubly and triply charged mercury cluster ions from direct observation of fission and evaporation. They were decided to $N_a^{2+} = 20$ and $N_a^{3+} = 46$ for doubly and triply charged cases, respectively. The fission channels were also investigated and estimated by calculation of Q values. The symmetric fission of doubly charged cluster ions was caused by van der Waals bonding of small mercury clusters. The fission channels of triply charged were asymmetric since the metallic character came into prominence for both precursor and large one of fission fragment.

(3) Estimation of lifetime distribution of cluster ions from sputtering ion source using fragmentation rate obtained from experimental data. The one atom evaporation of singly charged silver and mercury-silver binary cluster ions were investigated. The lifetime distributions of both samples were widely broadened and resembled each other where dissociation energies, which were related to lifetime, were quite different. From the size dependence of lifetime distribution, $Hg_{12}Ag^+$, which could understand by geometrical icosahedron structure, was turn out to be rather stable.

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1. Introduction

1.1 Cluster

The cluster is an aggregate consisting of 2 - 1000 atoms (or molecules) and its radius is in the order of 10 . It is in one of the phase between a atom (or molecule) and bulk as shown in Fig. 1. 1. It shows quantum-mechanical properties depending on its shape and size like atoms and molecules. The characteristic point of the cluster is most of containing atoms are on the surface, and so the surface phenomena take a significant part for its stabilities. It also exhibits, at finite temperatures, physical properties often encountered in macroscopic systems like liquids. This is due to the presence of large number of low-lying metastable states.

There are mainly two methods for producing cluster. One is cohering the atoms or molecules



Fig. 1. 1. Classification of the fragments according to their sizes obtained by successive division of material.

by adiabatic expansion method. The clusters produced by this method have relatively low internal energy (low temperature). The other way is subdividing the bulk into clusters by bombarding with neutral atoms (FAB: Fast Atom Bombardment) or ions (SIMS: Secondary Ion Mass Spectrometry). The clusters having relatively high internal energy (high temperature) clusters are produced using this method. They cause the spontaneous fragmentation and are qualified for studying fragmentation processes. The later production method was used in this experiment.

The stabilities and characters of clusters are very sensitive to their sizes (consisting atoms). Therefore, mass spectrometer, which can separate the cluster ions by their sizes, is available for cluster analyses. Usually, the discontinuous variations are observed in size distributions obtained from mass spectra. These anomalous sizes are called "magic number" that are clues to understand the structures of the clusters.

The clusters, which the consisting atoms (or molecules) are bound by different kind of binding forces, were investigated. The characteristic magic numbers were observed for each kind of the cluster.

The magic numbers of noble gas clusters (e.g. Xe_n^+) observed in the mass spectrum were n = 13, 19, 23, 25, 55, 71, 81, 101, 135 and 147 [1.1]. These numbers are coincided with the numbers of constituent atoms of the icosahedron or the double icosahedron structures. The geometrically packed structures are well known for van der Waals clusters.

The alkali-halide cluster [1.2] (e.g. (CsI)_nCs⁺), which the binding force of bulks are ionic, have the magic numbers of, n = 13, 22, 31, 37 and 52 consisted with 27, 45, 63, 75 and 105 atoms, respectively. The structures of these cluster ions are understood to be rock-salt structures such as $(3 \times 3 \times 3), (3 \times 3 \times 5), (3 \times 3 \times 7), (3 \times 5 \times 5)$ and $(3 \times 5 \times 7)$, respectively.

As compared with the geometrical stabilities of noble gas and alkali-halide clusters, the stabilities of alkali metal [1.3] and noble metal [1.4] clusters are interpreted by the valence electrons shell model. This model is on the basis of a one-electron shell model in which the valence electrons are bound in a spherically symmetric potential well. The cluster would be rather stable when the number of total valence electrons is a shell closed number such as 2, 8, 18, 20, 34, 58, 92 $\cdot \cdot$.

1. 2 Mercury cluster

The electronic shell structure of mercury atom is $5d^{10}6s^2$ closed shell, which is isoelectronic with helium. Therefore the diatomic molecule and smaller clusters are bound by the van der Waals force. For intermediated cluster size, the 6*s* and 6*p* orbitals broaden as indicated in Fig. 1. 2. For bulk Hg, the overlapping of 6*s* and 6*p* bands gives the metallic behaviors.



Fig. 1. 2. Electoric configurations of the Hg atom, cluster, and bulk.

The non-metal to metal transition of mercury clusters was studied by various methods. BrJchingac *et al.* [1.5] recorded the autoionization lines ($5d \quad 6p$) excited by synchrotron radiation. The transition to metallic bonding occurs gradually from $n \sim 15$. Rademann *et al.* [1.6] measured the ionization potentials of mercury cluster ions and found that the van der Waals behavior deviated at $n \sim 15$. Kaiser *et al.* [1.7] showed that large mercury clusters of approximately 100 atoms already possess a high density of p states near Fermi level. Harberland *et al.* [1.8] measured the ionization potentials and binding energies of Hg_n, and deduced that the bonding force first changes from van der Waals to covalent between n = 20 and n = 70, and then becomes metallic above n = 100.

1. 3 The outline of this thesis

The experimental conditions are described in chapter 2. The production of cluster ions, the mass spectrometer used in this experiment, and the determination of fragmentation pattern of singly charged cluster ions are described.

The characters of mercury-silver binary cluster ions, Hg_nAg^+ and $Hg_nAg_2^+$, are discussed from size distributions and fragmentation pattern in chapter 3.

The fragmentation pattern of doubly and triply charged cluster ions were argued in chapter 4. The fragmentation channel of multiply charged cluster ion is roughly classified into fission and evaporation,

 X_n^{i+} $X_m^{j+} + X_{n-m}^{(i+j)+}$ (i = j: evaporation, i > j: fission).

The fission and the evaporation processes are competed. The size which the fission and the evaporation occurred with same probability is called appearance size. The evaporation are prior to the fission at cluster size larger than the appearance size. The appearance sizes of doubly and triply charged mercury and mercury-silver cluster ions were determined by direct observation of evaporation and fission processes. Furthermore, the Q values, which is the total energy difference between initial and final states, of doubly and triply charged mercury clusters were calculated using both the metallic droplet model and the experimental data reported in ref. [1.8]. The asymmetric fission channels were expected for the metallic droplet model, however, the van der waals bonding of small cluster ions leaded to the symmetric fission channels of doubly charged cluster ions.

The lifetime and internal energy distributions of cluster ions produced by the sputtering method are discussed in chapter 5. The fragmentation channels of Ag_{n+1}^+ $Ag_n^+ + Ag$ (n = 12, 14) and $Hg_{n+1}Ag^+$ $Hg_nAg^+ + Hg$ (n = 8 - 14) were investigated. At first, the fragmentation rates of each channels was obtained from experimental data. The fragmentation rates were rather power function than exponential one. The lifetime distributions were calculated using the experimental fragmentation rates. It was carried out based on the consideration that the non-exponential nature was originated by superposition of different lifetime according to the different internal energy. The stabilities of cluster mercury-silver cluster ions were also discussed by the size dependence of lifetime distribution. The characteristic cluster, $Hg_{12}Ag^+$, which could understand by icosahedron structure, turned out to be rather stable.

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2. Experimental

2. 1 Production of cluster ions

The cluster ions were produced by Xe ions bombardment on a sample material. The silver plate was used as the sample to produce silver clusters, and silver amalgam in case mercury and mercury-silver binary clusters. The primary ions (Xenon ions) were produced by a discharged type of a compact ion gun [2.1] and were accelerated up to several keV. The discharge current was kept constant at 0.3 - 0.4 mA in order to obtain the stable ion beam intensity by controlling the discharge voltage and the Xe gas pressure. The secondary ions were extracted and accelerated toward the mass spectrometer by the potential applied to the electrostatic lens system. The schematic diagrams of the primary ion gun and the electrostatic lens system are shown in Fig. 2. 1.

2. 2 Double focussing mass spectrometer, GEMMY

The cluster ions were mass analyzed by the sector type mass spectrometer "GEMMY" [2.2] shown in Fig. 2. 2. The field arrangement is QQHQC (Q denotes a electric quadropole, H; a homogeneous magnetic sector, C; a cylindrical electric sector). The radii of magnetic sector and electric sector were 1.25 m and 0.90 m, respectively. The maximum flux density of the magnet was 1.8 T. The flight path from the main slit to the detector slit was 7.635 m. The vacuum pressure of mass analyzer was about 10⁻⁷ Torr.



Fig. 2. 1. Schematic diagram of ion source and electrostatic lens system.



Fig. 2. 2. Grand scale sector type of mass spectrometer, GEMMY



Fig. 2. 3. Schematic diagrams of detector and signal to AD board.

In order to increase the detection efficiency, the ions passing through a detector slit were post accelerated up to about 15 keV and exchanged to electrons using conversion dinode. The converted electrons were detected by a conventional sixteen-stage electron multiplier. Mass spectra were obtained by scanning the magnet current in a linear mode and were recorded using a 486 PC with an analog to digital converter. The schematic diagram of the detector and recorder are shown in Fig. 2. 3.

2. 3 Determination of fragmentation pattern of cluster ions

The cluster ions produced by the sputtering ion source have high internal energy enough to cause the spontaneous fragmentations. The contour map modification method and the acceleration voltage scan method are used in this study in order to determine the fragmentation pattern of singly charged cluster ions. The concept of two methods are same. The kinetic energy of product ions which could path through the cylindric electric sector, E_0 (eV / charge), was fixed, and changed the acceleration voltage, V_a (V), related to kinetic energy of precursor ion. The mass ratio of M_{pre}/M_{pro} are equal to V_a/E_0 for singly charged cluster ion, where M_{pre} and M_{pro} are the mass of precursor and product ion, because the kinetic energy of precursor ion is approximately equally divided into products in proportional to each of their mass.

The most advantageous point of the contour map modification method is that the fragmentation occurred at entire region of mass spectrometer can be observed. This makes it possible to discuss lifetime distributions (Chapter 5). On the other hand, the relatively narrow limitation of M_{pre}/M_{pro} is disadvantage point. It was supplemented by the acceleration voltage scan method which mainly investigated the fragmentations occurred between ion source and magnetic sector. The acceleration voltage scan method is useful to determine the fragmentation channels yielding small product ions.

2. 3. 1 Contour map modification method

The procedure of the contour map modification method was is as follows. (1) The potential of the cylindrical electric sector and the width of energy slit were kept constant so that the ions of $E_0 \pm E$ (eV / charge) could path through the sector. (2) The acceleration voltage was changed within the certain limitation by V (V) step. The value of V was decided to satisfy the relation, V = 2E . (3) Mass spectra were obtained by scanning the magnetic field in a linear mode (B scanning) for each acceleration voltage. (4) The obtained mass spectra were modified as a form of a contour map for visual understanding. Microcal Origin. ver. 4.1 (Microcal Software, Inc.) was used for modification.

The appearance positions in a contour map or appearance mass in mass spectra were different according to the occurring places in spite of the same fragmentation channel. For convenience, the mass spectrometer is divided into five regions and named as (see Fig. 2. 4)

region1: electrostatic lens in ion source

region2: field free region between ion source and magnetic sector

region3: magnetic sector

region4: field free region between magnetic sector and electric sector region5: electric sector.

The mass spectra at acceleration voltages of 5100V and 5430V are shown in Fig. 2. 5. These mass spectra were the parts of a series of the mass spectra acquired to study the fragmentation of mercury-silver cluster ions by the contour map modification method. The experimental conditions,



Fig. 2. 4. Five regions of GEMMY.

region1: electrostatic lens in ion source
region2: field free region between ion source and magnetic sector
region3: magnetic sector
region4: field free region between magnetic sector and electric sector
region5: electric sector



Fig. 2. 5. The mass spectra at acceleration volteges of (a) 5100 V and (b) 5430V. The figures labeled each fragmentaion peaks indicated the fragmentaion channel and region. For instance, symbol n(r) corresponded to Hg_{n+1}Ag⁺ Hg_nAg⁺ + Hg occurred in region r.

the potential of cylindrical electric sector and the width of energy slit, were fixed so that the ions of 5000 ± 5 (eV / charge) could path through.

It is difficult to assign the corresponding fragmentation channel and region of fragment peaks or plateau observed in mass spectra from only one mass spectrum. One must investigate several mass spectra of adjacent acceleration voltages to assign accurate fragmentation channel and region. However, it is not rational to see over 50 - mass spectra one by one. The contour map modification method is, therefore, very useful for visual understanding of fragmentation channels and region as a whole. The symbols n(r) shown in Fig. 2. 5 are the assigned fragmentation channels and regions.

Now, let us discuss the correlation between the positions in a contour map and regions1-5 in which fragmentation occurred. Here, fragmentation channel is $A^+ = B^+ + C$, where A^+ denote the precursor ion, B^+ : the product ion and C: the neutral loss. The mass of the precursor and the product ion are M_{pre} and M_{pro} , respectively. The potential of cylindrical electric sector was fixed so that the ions of 5 (keV / charge) could path through.

Assuming that the electrostatic lens system was a pair of parallel plates for simplicity, product ions yielded at distance x (x = 0 to be start of lens system) in the electrostatic lens system has kinetic energy:

$$U_{pro} = V_a \left\{ 1 - \frac{M_{pre} - M_{pro}}{M_{pre}} \frac{x}{L} \right\} = 5 \text{ (keV)} \quad (0 < x < L)$$

where V_a is the acceleration voltage, and L is the length of electrostatic lens system. The kinetic energy of product ion, U_{pro} , must be 5 keV in order to reach the detector. Accordingly the acceleration voltage must be set depending on x for 5 kV (x=0) to $5M_{pre}/M_{pro}$ (kV) (x = L). Considered with the fact that the product ions are mass analyzed by the magnetic sector, the fragmentation occurred at region1 expected to appear as lines parallel to the abscissa axis in the contour map, region1: $(V_a, m/z) = (5 < V_a < 5M_{pre} / M_{pro}, M_{pro}).$

Fragmentation occurred at region2 - 4 (from exit of ion source to entrance of cylindrical electric field (C)) appeared at the same acceleration voltage in contour map. In order to pass through the electric sector, precursor ions must be accelerated by $5M_{pre}/M_{pro}$ (keV). The appearing m/z values are different according to the position of fragmentation so that are analyzed ions by magnetic sector. The fragmentation occurred at regin2-4 appeared in contour maps

region2: the peak at $(V_a, m/z) = (5M_{pre} / M_{pro}, M_{pro})$

region3: the line at (V_a , m/z) = ($5M_{pre}/M_{pro}$, $M_{pro} < M < M_{pre}^2/M_{pro}$)

(line connecting region2 and region4 fragmentation peak)

region4: peak at (V_a , m/z) = ($5M_{pre} / M_{pro}$, M_{pre}^2 / M_{pro}).

The precursor ions that have the kinetic energy of 5 - $5M_{pro}/M_{pre}$ decomposed at certain place in the cylindrical electric sector could path through it and are detected. The fragmentation in electronic sector are shown as the line,

region5: $(V_a, m/z) = (5 < V_a < 5M_{pre} / M_{pro}, V_a M_{pre} / 5)$

(connecting peaks of region4 and not fragmented peak of M_{pre}).

In summary, a typical contour map and an appearance positions in the contour map corresponding to fragmentation channel, $A^+ = B^+ + C$, at each region are described in Fig. 2. 6. The lines at acceleration voltages 5100 and 5430 V are corresponding to the mass spectra of Fig. 2. 5. (a) and (b). It is understood that the fragmentation channels and regions of peaks appeared in mass spectra can assign easily. The appearance position of the fragmentation channel, $Hg_{12}Ag^+ = Hg_{11}Ag^+$ + Hg, is shown in the contour map. The values of M_{pre} and M_{pro} are 2515.0 and 2314.4, respectively. The appearance position decomposing in each region are

region1: (V_a (keV), m/z) = ($5 < V_a < 5.43, 2314$), region2: ($V_a, m/z$) = (5.43, 2314) region3: ($V_a, m/z$) = (5.43, 2314 < M < 2733), region4: ($V_a, m/z$) = (5.43, 2733) region5: ($V_a, m/z$) = ($5 < V_a < 5.43, 2515 V_a / 5$).



Fig. 2. 6. The typical contour map (upper) and the appearence position dependence of fragmentation regions in contour map about the channel of which the mass of precursor and product ion are M_{pre} and M_{pro} , respectively (bottom). Two lines parallel to m/z axis were correspond to Fig. 2. 5. (a) and (b). The appearence position dependence of fragmentation regions about the channel, Hg₁₂Ag⁺ Hg₁₁Ag⁺ + Hg, were also described in contour map.

2. 3. 1 Acceleration voltage scan method

Since about one minute was necessary for one magnetic field scan, it took about 2 hours in order to make a contour map consisted with 100 mass spectra. It was difficult to maintain the ion source constant and stable for such a long time. As a result, the contour map modification method was available when the consisting mass spectra were less than 100. In other words, the experiment to investigate the fragmentation channels which mass ratio of precursor ions to product ions were about $M_{pre}/M_{pro} < 3$. An acceleration voltage scan method is available to study the fragmentation channels of $M_{pre}/M_{pro} < 6$. This method was generally applied for the fragmentation yielding small size of the product ion. A acceleration voltage scan spectrum corresponded to trace of the line parallel to a acceleration voltage axis of a contour map. The decompositions occurred at region2, which have higher intensities than others, were mainly investigated.

The schematic diagram of the acceleration voltage scan method is shown in Fig. 2. 7. At first, the strength of the magnetic and the electric field were fixed so that the product ions of given kinetic energy and mass could path through to detector. When the function generator received the start signal (TTL signal) from the PC for scanning, then outputs the signal shown in Fig. 2. 8, which was used as the reference signal of acceleration voltage power source. Two acceleration voltage spectra could obtain for one scan because the reference signal was going up and down. The acceleration voltage power supply output the voltage multiplied the reference signal by 5000.

A typical acceleration voltage scan spectrum is shown in Fig. 2. 9, where the selected product ion is Ag_{13}^+ of 1 keV. Three peaks observed in the spectrum were determined as Ag_{13}^+ of (a) nonfragmented, (b) in fragmentation channels Ag_{14}^+ $Ag_{13}^+ + Ag$, and (c) Ag_{15}^+ $Ag_{13}^+ + Ag_2$. These were calculated from the observed acceleration voltages. The peak (a) had wide-based tail toward to the peak (b). This was the product ions in Ag_{14}^+ $Ag_{13}^+ + Ag$ at region 1.



Fig. 2. 7 Schematic diagram of acceleration voltage scan method.



Fig. 2. 8. Reference voltage transmitted from function generator to acceleration voltage power supply.



Fig. 2. 9. Acceleration voltage scan spectrum that the selected product ions was Ag_{13}^{+} of 1 keV.

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3. Size distribution and fragmentation pattern of mercury-silver binarycluster ions

3.1 Introduction

The size distributions of mercury-alkali metal binary cluster ions (Hg_nK^+ , Hg_nCs^+ , Hg_nRb^+) produced by the sputter ion source were already investigated [3.1,2]. The magic numbers, n = 8, 12, 14, 18, 22, 25 and 31, were observed at small size region. These were independent of including alkali metal, and were quite similar to those of van der Waals cluster ions. This fact indicated that the bonding force of mercury-alkali metal binary cluster ions were also van der Waals force at n < 30. The structures of stable mercury-alkali metal cluster ions believed to be icosahedral or double icosahedral structures, where alkali metal ions were at the center of the cluster.

The size distribution of large Hg_nCs^+ (n < 1000) clusters was also investigated [3.2]. It showed the wave like variation where the cluster sizes at bottom of valleys were roughly consistent with those of predicted electronic shell closed numbers. The authors concluded that this was originated from the metallic structure of neutral Hg_n . Two kinds of clusters, Hg_n and Hg_nCs^+ were created in the ion source, and the wave like variation was the results of former.

In this section, the size distribution and fragmentation pattern of mercury-silver binary cluster ions were reported. Silver atom has the one s valence electron (5s electron) as well as alkali metals.

3.2 Results

3. 2. 1 Size distribution of mercury-silver binary cluster ion

The mass spectrum, m/z = 350 - 4250, is shown in Fig. 3. 1. (a). Each peak of the same size seen as like one peak had own peak pattern, because both mercury and silver were not monoisotope elements. At m/z < 1500, the mass resolution was enough to separate each peak. Thus, I could assign composition of each cluster peak by comparing with calculated peak pattern. The peak patterns of cluster ions were calculated from the IUPAC isotopic compositions of the elements [3.3] and the 1983 atomic mass table [3.4]. For example, enlarged mass spectrum of Fig. 3. 1. (a) between m/z = 895 - 925, and calculated peak pattern of Hg₄Ag⁺ under the condition that mass resolution 1000 are shown in Fig. 3. 1. (b) and (c).

As for the m/z > 1500, however, insufficient mass resolution prevented from assigning the composition of cluster ions by comparing with calculated peak patterns. Accordingly, the peaks were assigned by appeared masses and extrapolation from the composition of smaller size cluster ions. The dominant peaks shown in Fig. 3. 1. (a) had the m/z values of 200.6 n + 107.9, thus they were assigned to Hg_nAg⁺.

The enlarged mass spectrum of Fig. 3. 1. (a) is shown in Fig. 3. 2. There were two smaller peaks between Hg_nAg^+ and $Hg_{n+1}Ag^+$ peaks. They were assigned to be Hg_n^+ and $Hg_{n-1}Ag_2^+$, because their appeared masses were m/z values of 200.6 *n* and 200.6 (n - 1) + 215.8, respectively. These two peaks could not resolve at the n > 15, however, $Hg_{n-1}Ag_2^+$ were dominant considering the appeared m/z values.

The size distribution of Hg_nAg^+ (n = 1 - 45) is shown in Fig. 3. 3. Generally, the size distributions of cluster ions produced by a sputtering ion source are well known to logarithmically decreased as the size increased. On the contrary, the suddenly intensity decrease was observed at n



Fig. 3. 1. (a). Mass spectrum of cluster ions made by 10 keV Xe ions bombardment on silver mercury amalgam.



Fig. 3. 1. (b) Enlarged mass spectrum of Fig. 3. 1. (a). The observed peak pattern of Hg_4Ag^+ . (c) Calcurated peak pattern of Hg_4Ag^+ .



Fig. 3. 2. Enlarged mass spectrum of Fig. 3. 1. (a). Two peaks between the Hg_nAg^+ (saturated peaks) were Hg_n^+ and $Hg_{n-1}Ag_2^+$.



Fig. 3. 3. Size distribution of Hg_nAg^+ (n = 1 - 45). The figures are the predicted shell closed sizes and number of total valence electron (in parentheses) based on electronic shell model.

< 10. Whether such intensity reduction at small size was caused by characters of mercury-silver clusters or by the creation mechanism was very interesting. It would be argued in later text taking account of fragmentation patterns, too.

Several variations were appeared in size distribution at n < 40. The conspicuous step like variations were observed at cluster size n = 10, 22 and the less were observed at n = 17, 26. The size distribution of Hg_nAg⁺ was quite different from Hg_nM⁺ (M : alkali metals). The observed characteristic numbers, n = 10, 17, could not be interpreted by icosahedron or double icosahedron structures. Moreover, the magic numbers indicating geometrical stabilities (n = 12, 18) were not observed. The total number of valence electrons in Hg_nAg⁺ was 2*n*. Considering the electronic shell structures of Hg_nAg⁺, the predicted magic number would be n = 4, 9, 10, 17, 20 and 29 (total valence electrons were 8, 18, 20, 34, 40 and 58, respectively), which relatively consistent with my experimental result. It is well known that the internal energy of cluster (or temperature) is greatly contributed to variety of stability whether geometrical or electronic. The internal energy of clusters made by sputtering method were widly distributed (see chapter 5) so that the geometrical and electronic shell structure than geometric one, which was differed from the mercury-alkali metal binary cluster ions. It was believed that the delocalization of the charge at silver atom of Hg_nAg⁺ caused the metalic structure in the size distribution of Hg_nAg⁺.

The mass spectrum of m/z = 10000 - 68200 is shown in Fig. 3. 4. The abscissa is expressed in number of Hg atoms in cluster size of Hg_nAg⁺. Each peaks were resolved up to n = 250. Taking account the energy window of the cylindrical electric sector, the product ions, Hg_nAg⁺ (n > 200), yielded by a Hg atom evaporation at region2 could also reach to the detector and would appear at cluster size about (n - 2). The wave like variation was appeared in size distributions at the cluster size lager than n > 30. The cluster size of n = 46, 74, 100, 133, 176, 225, 284 were the bottom of



Fig. 3. 4. Mass spectrum of Hg_nAg^+ (n = 50-340). The wave like variations were appeared. The cluster size at the bottom of valley and total number of valence electrons (in parentheses) were shown.



Fig. 3. 5. The size distribution of $Hg_nAg_2^+$ (n = 4 - 39).

valleys. This wave like variation and sizes at bottom of valleys were quite similar to those of Hg_nCs^+ that already reported [3.2].

The shell closing numbers predicted by a shell model based on Woods-Saxon potential were 58, 92, 138, 198, 254, 268, 338, 440, 562 [3.5]. The number of valence electrons at bottoms of valleys were roughly equal calculated shell closing numbers. Taking the total valence electrons of Hg_nAg^+ was 2n into account, there were agreement between the total number of valence electrons at local minima and the shell closing numbers. This agreement was interpreted as well as Hg_nCs^+ [3.2]. The production of mercury-silver cluster ions was competed with neutral mercury clusters, Hg_n , where neutral species were believed to be a major yield. Size distributions of neutral species would seriously influence on the ions. It is considered that weak intensities of Hg_nAg^+ at valley were indicating the strong intensities of Hg_n , since the number of valence electrons in Hg_n and Hg_nAg^+ were the same (= 2n) as illustrated in Fig. 3. 4.

The size distribution of $Hg_nAg_2^+$ (n = 4 - 39) is shown in Fig. 3. 5. The suddenly discontinuous was observed at n = 18, however, it was hard to understand its stability by electronic shell model because $Hg_{18}Ag_2^+$ has 37 total valence electrons. It is believed that the stable $Hg_{18}Ag_2^+$ cluster ion has geometric double icosahedron structure (see the picture in Fig. 3. 5). The silver dimmer ion, Ag_2^+ , considered to be behaved like an atom at the center of these complex cluster.

The interpretations of mass spectra, whether geometrical or elecrical, were changed according to the number of silver atom in the mercury clusters. The same phenomenon was also observed for $Hg_nK_i^+$ [3.1], where size distributions were interpreted geometrically for i = 1, 2 and 3, on the other hand, electrically for i = 4.

3. 2. 2 Fragmentation pattern of mercury-silver binary cluster ion

A typical contour map is shown in Fig. 3. 6 indicating the fragmentation in the flight of the mass spectrometer. The electric field was kept constant so that the ions having $2000 \pm 10 \text{ eV}$ could path through while the acceleration voltage was varied from 2 kV to 3 kV by 20 V step. The mass spectra were obtained at each acceleration voltage by a magnetic field scan. The observed mass range was m/z = 195 - 4975; Hg_nAg⁺ (n = 1 - 24) could be observed. The curved lines on the contour map show predicted positions when precursor cluster ions emitted neutral atoms or cluster in region2. The labeled figures at the upside are corresponding to the number of emitted mercury atoms. Basically, the fragmentation channels which emitted more than two mercury atoms could not be distinguished whether cluster emission or successive atoms emissions. Considering the flight time in region2 ($10^{-6} - 10^{-4} \sec$), however, the large cases of mercury atoms losses believed to be cluster emissions.

The possible fragmentation channels of Hg_nAg^+ (n = 1 - 10) were investigated for discussing the sudden intensity decrease at small cluster size n < 10. In this case, we used the acceleration voltage scan method because the mass ratios of M_{pre}/M_{pro} (M_{pre} denotes the mass of precursor ion and M_{pro} ; mass of product ion) were too large to use the contour map modification method as mentioned in section 2. 3. 1. In the acceleration voltage scan method, the product ions of Hg_n^+ (n =1 - 10) and Hg_nAg^+ (n = 0 - 9) of 1 keV kinetic energy were selected.

A typical acceleration voltage scan spectrum is shown in Fig. 3. 7, where the field strength of the magnet and the electric sector was set to path through Hg_2^+ of 1 keV. The precursor ions were determined from appeared acceleration voltage. The fragment peaks labeled with naked figure *n* were the peaks coming from precursor ions of Hg_nAg^+ and labeled with circled figure were from Hg_n^+ .

The intensities of fragmentation channels from Hg_nAg^+ (n = 1 - 10) are shown in Table. 3. 1.



Fig. 3. 6 Fragmentation patterns shown in a typical contour map. The curved lines showed the predicted positions when precursor clusters emitted neutral atom or cluster in region2. The labeled figures are corresponding to the emitting numbers of mercury atoms.



Fig. 3. 7. The typical acceleration voltage scan spectrum, where the field strength of the magnet and the electric sector was set to path through Hg_2^+ of 1keV.

					Pre	ecursor io	ns (Hg _n A	.g ⁺)			
	п	1	2	3	4	5	6	7	8	9	10
	0	0	0								
	1	0	0	0	0						
Product ions (Hg_nAg^+ , Hg_n^+)	1		20	29	35	20	49	61			
	2		7	8	47	39	45	38	46	52	
	2			272	375	275	347	231	173	146	151
	3			15	16	10	19	27	42	57	81
	3				875	559	703	554	409	291	187
	4				7	0	0	0	0	0	0
	4					836	657	599	551	436	312
	5					7	0	0	0	0	0
	5						1012	337	302	297	275
	6						2	0	0	0	0
	6							988	186	125	171
	7							3	0	0	0
	7								1082	225	171
	8								5	0	0
	8									1116	147
	9									7	0
	9										1115
	10										3

Table. 3. 1. The intensities of fragmentation channels of Hg_nAg^+ . The grayed lines were indicating the fragmentation channels yielding Hg_n^+ as product ions.
The major channel of each precursor ions was an emission of one mercury atom. The fragmentation channels yielding mercury cluster ions were only observed for product ions of Hg_n^+ (n = 2, 3), however, these were considerably minor channels with respect to the channels yielding Hg_nAg^+ .

The cluster ions produced by sputtering method have high internal energy that caused the chain or branch fragmentations from production time. One could only recognize the fragmentation occurred 10^{-7} sec after the production in this experimental conditions. The product ions yeilded by the fragmentations occurred before 10^{-7} sec are not distinguish from non-fragmented ions of same size. The sudden intensity decrease at small size region in mass spectra could be interpreted, if the fragmentation channels, Hg_nAg^+ $Hg_m^+ + Hg_{n-m}Ag$, would occur mainly before 10^{-7} sec. The fragmentation channels during the flight time in mass spectrometer ($10^{-6} - 10^{-4}$ sec) were investigated whether the fragmentation channels, Hg_nAg^+ $Hg_m^+ + Hg_{m-m}Ag$, was dominant at small size. However, the intensity decrease at small size could not interpret by the fragmentation pattern of Hg_nAg^+ (n = 1 - 10). Thus, intensity decrease was believed to be originated from the creation mechanism. It is believed that the low density of Ag atoms in mercury sample caused the production of relatively large mercury-silver binary cluster ions. As a result, the size distribution which the intensities of small cluster ions decreased were observed in this experiment.

The fragmentation pattern of cluster size n = 25 - 100 is shown in Figs. 3. 8 - 10. The consisting mass spectra were obtained under condition that the cylindrical electric field was kept constant so that the ions having 2000 \pm 20 eV could path through and acceleration voltage was varied from 2 to 3 kV by 20 V step. The curved lines on the contour map show predicted positions when precursor cluster ions emitted neutral atom or cluster in region2. The labeled figures at the upside are corresponding to the emitting numbers of mercury atoms. The intensities of fragmentation channels losing large cluster emissions were gradually decreased accompanied with size increase. The mainly observed fragmentation channels were Hg_n (n = 1 - 3) emissions, and priority were



Fig. 3. 9. The framentation pattern of Hg_nAg^+ (n = 25 - 50) modified in contour map.



Fig. 3. 9. The framentation pattern of Hg_nAg^+ (n = 50 - 74) modified in contour map.



Fig. 3. 10. The framentation pattern of Hg_nAg^+ (n = 75 - 100) modified in contour map.

changed from Hg to Hg₂ emission, and furthermore, the Hg₃ emission as the cluster size increased (Fig. 3. 11). As mentioned above, the Hg_n emission and successive *n* mercury atoms emissions were basically indistinguishable, however, the Hg₂ and Hg₃ emission were found out to be mainly two or three successive Hg emission by paying attention to appearance position in counter map for both cases. It would be interpreted in following text.

At the large cluster size region, $Hg_{n+1}Ag^+$ $Hg_nAg^+ + Hg$ (region4) and $Hg_{n+3}Ag^+$ $Hg_{n+2}Ag^+ + Hg$ (region2) were almost superposed. In the same way, $Hg_{n+2}Ag^+$ $Hg_nAg^+ + Hg_2$ (region4) and $Hg_{n+6}Ag^+$ $Hg_{n+4}Ag^+ + Hg_2$ (region2) were also superposed.

The appearance positions of fragmentation channel, $Hg_{n+1}Ag^+$ $Hg_nAg^+ + Hg$, occurred at region5 in the contour map was slant line connecting between non-fragmented peaks $Hg_{n+1}Ag^+$ and fragmentation peaks of channel, $Hg_{n+1}Ag^+$ $Hg_nAg^+ + Hg$ (region4), which was appeared just like the lines between non-fragmented Hg_nAg^+ peak and fragmentation peak of channel, $Hg_{n+3}Ag^+$

 $Hg_{n+2}Ag^+ + Hg$ (region2). These slant lines between non-fragmented peaks and Hg emission peaks were appeared in Fig. 3. 7 at the size region n = 25 - 40 and gradually disappeared as the main



Fig. 3. 11. The size dependence of the observed main fragmentation channels.



Fig. 3. 12. Difference of appearence positions between (a) $Hg_{n+2}Ag^+$ $Hg_nAg^+ + Hg_2$ (region5) and (b) successive fragmentations of $Hg_{n+2}Ag^+$ $Hg_{n+1}Ag^+ + Hg$ (region2) and $Hg_{n+1}Ag^+$ $Hg_nAg^+ + Hg$ (region5). M_n denotes the mass of Hg_nAg^+ .

fragmentation channel proceeded to Hg₂ emission.

There was difference between appearance positions in contour map of dimer emission, $Hg_{n+2}Ag^+$ $Hg_nAg^+ + Hg_2$ (region5) (Fig. 3. 12. (a)), and successive fragmentations of $Hg_{n+2}Ag^+$ $Hg_{n+1}Ag^+ + Hg$ (region2) and $Hg_{n+1}Ag^+$ $Hg_nAg^+ + Hg$ (region5) (Fig.3.12.(b)). The position corresponding with Hg_2 emission was seen at the lines between non-fragmented $Hg_{n+2}Ag^+$ peaks and fragmentation peaks, $Hg_{n+6}Ag^+$ $Hg_{n+4}Ag^+ + Hg_2$ (region2). On the other hand, position for successive Hg emissions were appeared as the slant lines between $Hg_{n+4}Ag^+$ $Hg_{n+3}Ag^+$ + Hg (region2) and $Hg_{n+6}Ag^+$ $Hg_{n+4}Ag^+ + Hg_2$ (region2).

The slant lines between Hg and Hg₂ emission peaks were only seen at the cluster size n > 40. These lines were not indicating the Hg₂ emission at region5 but the successive Hg atom emissions at region2 and region5. The same concept for the cluster size n > 70 may applicable to Hg₃ emission, where successive three Hg atom emission occurred.

3. 3 Conclusions

The size distributions of two type of mercury-silver binary cluster ions, Hg_nAg^+ and $Hg_nAg_2^+$ were investigated. The size distribution of Hg_nAg^+ was quite different from Hg_nM^+ (M: alkali metal) at n < 30 that the magic numbers were rather interpreted in electronic shell model structure. On the other hand, the charactoristic number of n = 18 was observed for $Hg_nAg_2^+$. The stable $Hg_{18}Ag_2^+$ was considered to be geometrical double icosahedron structure.

The fragmentation patterns of Hg_nAg^+ was also investigated. There were many fragmentation channels for small cluster ions. At the cluster size *n* is larger than 20, the one atom evaporation was the dominate channels.

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4. Competition of fission and evaporation processes of multiply charged mercury cluster ions

4.1 Introduction

The natures of multiply charged cluster ion are critically different from singly charged ones because the coulomb repulsive force effects on their stabilities. Roughly speaking, when the cluster size is small enough, the coulomb repulsive force is comparable to binding force of the cluster. In the case, the cluster ion which has enough internal energy cause the fragmentation into two charged fragments, i.e. fission process.

Experimental study about the multiple charged cluster ions was first reported for different kinds of bonding: metal clusters, Pb_n^{2+} , ionic clusters, $(NaI)_n^{2+}$, and van der Waals clusters, Xe_n^{2+} [4.1]. In this work, doubly charged cluster ions above certain cluster size, were recognized as at peaks half-size values of singly charged cluster ions in mass spectra. These sizes were called "critical size, n_c " and were 33 for Pb_n^{2+} , 23 for $(NaF)_n^{2+}$, and 53 for Xe_n^{2+} , respectively. Authors concluded that only if doubly charged cluster ions exceeded a critical size, they survive from "Coulomb explosion". This result about xenon cluster ions was coincident with the computer simulations [4.2] that the lifetime of Xe_{55}^{2+} (10^{-4} sec) was remarkably longer than Xe_{51}^{2+} (10^{-10} sec). The subsequent experimental work about critical sizes of n_c^{z+} up to z = 4 of van der Waals bonding clusters were reported. The ratio of critical sizes was n_c^{4+} : n_c^{3+} : $n_c^{2+} = 16$: 9: 4 while the values of the critical sizes vary widely between different substances [4.3].

The metal clusters were known to have an analogues with atomic nuclei that both systems consist of fermions moving nearly freely in a confined space. The shell model of nuclear physics was successfully applied to electronic properties of metal cluster [1.3, 4]. The giant dipole reso-

nances in the excitation spectra of nuclei have their similarity in the plasmon resonances of metal clusters [4.4]. Finally, the droplet model describing the fission of unstable nuclei was applied to fragmentation of highly charged metal cluster ions although the nuclei were uniformly charged droplets while metal clusters were surface charged objects.

In the cluster cases, the relative weight of repulsive and cohesive forces is expressed through the fissility parameter as well as nuclei, $X = E_{coulomb}/2E_{surface}$. The cluster ions that fission parameter of X < 1 are unstable to fission. The fission parameter can also expressed as $X = (Z^2/N)/(Z^2/N)_{crit}$, where $(Z^2/N)_{crit}$ corresponding to X = 1 is $(Z^2/N)_{crit} = 16Br_{ws}{}^3F/e^2$. Here, r_{ws} is the Wigner-Seitz radius, e is the elementary charge, and F is the surface tension. The $(Z^2/N)_{crit}$ value of mercury cluster ions is calculated to 0.6.

In case of X < 1, however, the fragmentations of multiply charged cluster ions are competition of evaporation (neutral atom loss) and fission (split into two charged fragments) processes although physical underlying are distinct each other. Generally speaking, evaporation is prior to fission at the cluster size lager than called "appearance size, N_a " which defined as the size evaporation and fission occurred with equal probability.

Direct observations of fission fragments from doubly charged alkali-metal [4.5-7] and noblemetal [4.8-10] cluster ions were reported in succession before and after the 1990.

Almost all possible fission channels of doubly charged silver cluster ions made by sputtering method, which produced relatively high temperature cluster, were observed [4.8]. They were preferred to emit the odd-size cluster which have even number of electrons especially Ag_3^+ and Ag_9^+ known as magic number.

The fragmentation of gold cluster ions Au_n^{2+} (n = 12 - 18) made by LMIS (liquid metal ion source) were studied by collisions with stationary krypton gas [4.9,10]. The probabilities of fission channels have the odd-even alternation that the product ions having even number of electron were

prior, especially the channel yielding singly charged trimer was dominant for all clusters. The appearance size were determined to $N_a^{2+} = 14$ experimentally.

The fragmentations around critical sizes of alkali metal cluster ions, (lithium, sodium and potassium) made by supersonic expansion method were also reported [4.5-7]. The major fission channels were emission of singly charged trimer and pentamer that have even-number of electrons.

Furthermore, *z*-fold charged sodium and cesium cluster ions were reported up to z = 7, and z = 4 for potassium and rubidium [4.11,12]. The critical sizes for appearance of each charged states in the mass spectra, which were called "effective appearance sizes, N_a^{eff} ", were determined. What these experiments showed were appearance sizes lied in narrow interval of *X*-values (0.25 < X < 0.35) irrespective of charge state *z* and substances. It is simply considered the appearance sizes lie so close to a line of constant Z^2/N because the fission barrier heights will scale with the surface energy, i.e. $N^{2/3}$, whereas the activation energy for the competing evaporation process is essentially independent of *N*.

There were several reports about multiply charged mercury cluster ions. The doubly charged mercury cluster ions made by both adiabatic expansion [4.13-15] and sputtering methods [4.16] were reported. The observed critical sizes of Hg_n^{2+} were $n_c^{2+} = 5$ for former and $n_c^{2+} = 2$ for latter. The triply charged mercury cluster ions, Hg_n^{3+} , made by adiabatic expansion method was only reported and its critical size was $n_c^{3+} = 46$ [4.15].

As mentioned in chapter 1, metal to non-metal transition of mercury cluster ions was occurred at cluster size $n \sim 20$. The characteristics of multiply charged cluster ions are very interesting subjects while only the critical sizes are known. In this section, competition of fission and evaporation processes of doubly charged mercury, Hg_n^{2+} , mercury-silver cluster ions , Hg_nAg^{2+} , and triply charged mercury cluster ions, Hg_n^{3+} , were reported and determined the appearance size from experimental data. The fission channels were also investigated and compared with calculated Q value (the total energy difference before and after).

4. 2 Determination of fragmentation channels of doubly and triply charged cluster ions

The fragmentations of multiply charged cluster ions can classify into evaporation and fission processes. In this experiment, the fragmentations occurred at region2 were observed. The voltage applied to electric sector was fixed so that the ions of 5 keV/charge could path through it.

4. 2. 1 Evaporation of multiply charged cluster ions

The schematic diagram of evaporation process of multiply charged ions is shown in Fig.4.1. The acceleration voltage must fix to $5M_0/M_1$ (M_0 denotes the mass of precursor ion, M_1 ; mass of product ion), in order to detect the product ions when the kinetic energy of precursor ion is as-



Fig. 4. 1. The schematic diagram of evaporation process of *m*-charged ion, M_0^{m+} .

sumed to be divided into products proportional to their masses. The appearance acceleration voltage is larger than 5 kV because the mass ratio is $M_0/M_1 > 1$.

The evaporation processes were investigated by acquiring the mass spectra where the acceleration voltage was changed from 5080 to 5280 V by every 20 V step. The fragment peaks were appeared at m/z values of product ions.

4. 2. 2 Fission of doubly charged cluster ions

The schematic diagram of fission process of doubly charged cluster ion is shown in Fig.4.2. In case of fission processes, both of fragments are singly charged ion and basically they can be observed. However, I observed heavier fission fragment, M_1 , which has the kinetic energiy of $2V_aM_1/M_0$ (keV). The appearance acceleration voltage, $5M_0/2M_1$ (kV), will be less than 5 kV because the mass ratio M_0/M_1 is between 1 and 2. The most advantageous point for observing the fission processes under 5 kV acceleration voltage is the exclusion of the effect from evaporation processes mainly that of singly charged ions. Unfortunately, fragmentation peaks can not be observed, when the mass ratio is $M_1/M_0 = 1/2$ (i.e. the precursor ion is decomposed to two same fission fragments), because the fragments and same size of non-fragmented ions are not distinguishable.

4. 2. 3 Fission of triply charged cluster ions

The schematic diagram of fission process of triply charged cluster ions is shown in Fig. 4. 3. In this case, singly and doubly charged fission fragments are yielded when the precursor ions decompose into two fragments. The kinetic energies of singly and doubly charged product ions are $3V_aM_1/M_0$ and $3V_aM_2/M_0$ (keV) (M_1 denotes the mass of singly charged product ion, M_2 ; mass of doubly charged product ion), respectively. Furthermore, the appearance acceleration voltages are $5M_0/3M_1$ (kV) and $10M_0/3M_2$ (kV), respectively. If the mass ratio of M_1/M_0 is more than 1/3, the



Fig. 4. 2. The schematic diagram of fission process of doubly charged cluster ions.



Fig. 4. 3. The schematic diagram of fission process of triply charged cluster ions.

singly charged fragment will be observed at acceleration voltage under 5 kV. On the other hand, in case of the mass ratio $M_1/M_0 < 1/3$ (or $M_2/M_0 > 2/3$), the doubly charged fragment will be observed at acceleration voltage under 5 kV. As well as the doubly charged fission, when the mass ratio is $M_1/M_0 = 1/3$, fission fragments can not distinguish from same size of non-fragmented ions. Furthermore, doubly charged fragments are indistinguishable from the singly charged one which have the half mass of doubly charged ones. For example, fragmentation channels Hg_{46}^{3+} $Hg_{40}^{2+} + Hg_{6}^{+}$ is indistinguishable from Hg_{46}^{3+} $Hg_{26}^{2+} + Hg_{20}^{+}$.

The fission processes were investigated using the acceleration voltage scan method. The scanned acceleration voltage range was under 5 kV in order to exlude the evaporation of singly charged ions.

4.3 Results

4. 3. 1 Observation of Hg_nAg²⁺ survived 10⁻⁴ sec

The mass spectrum of m/z = 1700 - 4400 is shown in Fig. 4. 4. (a). As mentioned in section 3, the dominant peaks were the Hg_nAg⁺ (n = 8 - 21), and the peaks of Hg_{n+1}⁺ and Hg_nAg₂⁺ (n = 8 - 20) were observed between Hg_nAg⁺ and Hg_{n+1}Ag⁺.

The enlarged mass spectrum of Fig. 4. 4. (a) within the m/z = 1780 - 3080 is shown in Fig. 4. 4. (b) which I focused on the critical size of Hg_nAg²⁺. The abscissa is expressed the cluster size of Hg_nAg²⁺. The ions must survive at least 10⁻⁴ sec in order to reach detector without fragmentation considering the flight time in the mass spectrometer at acceleration voltage of 5 kV. The odd-even alternation was appeared in intensities of peaks observed at integer values, but it seems to be not reflecting the character of Hg_nAg²⁺. Unfortunately, the even size peaks of Hg_nAg²⁺ were overlapped



Fig. 4. (a) Typical mass spectrum of m/z = 1700 - 4400. (b) Enlarged mass spectrum of (a) within the m/z = 1780 - 3080. where the abscissa is expressed in the cluster size of Hg_nAg²⁺.

with $Hg_{n/2}Cr^+$ and $Hg_{n/2}Fe^+$. The chromium and iron were originated from electrode of the primary ion gun. There were no peaks at the position of odd size of Hg_nAg^{2+} smaller than cluster size n = 21. There was ambiguity about critical size whether $n_c^{2+} = 20$ or 21.

Existence of the doubly charged mercury cluster ions, Hg_n^{2+} , survived at least 10⁻⁴ sec was not clear because the even and odd-size of ions were overlapped with $Hg_{n/2}^{+}$ and $Hg_{(n-1)/2}Ag^{+}$, respectively. The triply charged cluster ions, Hg_n^{3+} and Hg_nAg^{3+} were also not observed.

4. 3. 2 Evaporation processes of Hg_nAg²⁺

The mass spectrum at acceleration voltage 5160V is shown in Fig. 4. 5. (a). The peaks labeled with open circle (), indicated the product ions of fragmentation channels, $Hg_{n+1}Ag^+$ $Hg_nAg^+ + Hg$ (region 1). They appeared at m/z = 200.6n + 107.9 (n = 11 - 18). The peaks appeared between these peaks, labeled with solid circle (), were corresponding to the fragmentation channels, Hg_nAg^+ $Hg_{n-1}Ag^+ + Hg$ (region 5). The increasing of peak intensities at m/z = 2900 - 3500 were caused by overlapping with fragmentation channels, Hg_nAg^+ $Hg_n^+ + Ag$ and $Hg_nAg_2^+$ $Hg_n^-Ag^+ + Ag$ (region 2).

The enlarged spectrum of Fig. 4. 5. (a) at m/z = 2560 - 3565 is shown in Fig. 4. 5. (b). The abscissa is expressed in the cluster size of Hg_nAg²⁺. The peaks labeled with open star () were indicating the product ions of the evaporation processes, Hg_{n+1}Ag²⁺ Hg_nAg²⁺ + Hg (region2).

The mass spectra at acceleration voltages 5220 - 5280 V are shown in Fig. 4. 6. The abscissa expressed the cluster size of Hg_nAg^{2+} which correspond to mass region of m/z = 1460 - 2660. The peaks indicating product ions of fragmentation channels, $Hg_{n+1}Ag^{2+}$ $Hg_nAg^{2+} + Hg$ (region2), were also labeled with open star (). The observed minimum product ion was $Hg_{19}Ag^{2+}$ so that the $Hg_{20}Ag^{2+}$ was the smallest ions came out from acceleration region (region1) and cause the evaporation. In this case, it took about 10⁻⁶ sec for passing through the acceleration region.



Fig. 4. 5. (a) The mass spectrum of acceleration voltage 5160 V. (b) The enlarged mass spectrum of (a) within the m/z = 2560 - 3565. which the abscissa is expressed in the cluster size of Hg_nAg²⁺. The peaks labeled with open star () were indicating fragmentation channels, Hg_{n+1}Ag²⁺ Hg_nAg²⁺ + Hg.



Fig. 4. 6. (a) The mass spectrum of acceleration voltage (a) 5220 V, (b) 5240 V, (c) 5260 V and (d) 5280 V. The peaks labeled with open star () were indicating fragmentation channels, $Hg_{n+1}Ag^{2+}$ $Hg_nAg^{2+} + Hg$. The observed minimum product ion was $Hg_{19}Ag^{2+}$.

The evaporation processes of Hg_n^{2+} could not observe because these peaks were overlapped with fragmentation peaks of Hg_n^{+} , Hg_nAg^+ and $Hg_nAg_2^+$ occurred at region 1.

4. 3. 3 Evaporation processes of triply charged Hg_n^{3+}

The mass spectrum at acceleration voltage 5100 V is shown in Fig. 4. 7. (a). The peaks mainly appeared in this spectrum corresponded to fragmentation channels, $Hg_{n+1}Ag^+$ $Hg_nAg^+ +$ Hg (region1), $Hg_{n+1}Ag^+$ $Hg_nAg^+ +$ Hg (region5), superposition of Hg_{n+1}^+ $Hg_n^+ +$ Hg and $Hg_nAg_2^+$ $Hg_{n-1}Ag_2^+ +$ Hg (region1) which were labeled with symbols , and , respectively.

Enlarged spectrum of Fig. 4. 7. (a) at m/z = 2450 - 4000 which abscissa expressed cluster size of Hg_n³⁺ is shown in Fig. 4. 7 .(b). The peaks labeled with open stars () indicating the product ions of evaporation channels, Hg_{n+1}³⁺ Hg_n³⁺ + Hg (region2). These peaks could not distinguish from Hg_nAg₂³⁺ Hg_{n-1}Ag₂³⁺ + Hg (region2) because of insufficient mass resolving power. However, the latter channels were excluded from consideration. It was believed that the multiply charged mercury-silver binary cluster ions were difficult to produce in this experimental conditions in view of the triply charged evaporation processes of Hg_nAg³⁺ were not observed. The evaporation channels, Hg_{n+1}³⁺ Hg_n³⁺ + Hg (region2), were well resolved from fragmentation peaks of singly charged cluster ions for only n = 3m+1 (*m*; integer).

The mass spectra of acceleration voltage of 5120 and 5140 V which took notice on minimum product ion of evaporation channels, Hg_{n+1}^{3+} $Hg_n^{3+} + Hg$ (region2), are shown in Fig.4. 8. These peaks were also labeled with open stars (). The observed minimum product ion was n = 46.

As mentioned in section 3, the fragmentation channels of successive two atoms emission were prior to one atom emission in cluster size over n = 40. The mass spectra at acceleration voltage 5200 and 5220 V are shown in Fig. 4. 9 that payed attention to product ions yielded by two



Fig. 4. 7. (a) The mass sepctrum at acceleration voltage 5100 V. (b) Enlarged spectrum of (a) at m/z = 2450 - 4000 which absicca is expressed in cluster size of Hg_n³⁺.



Fig. 4. 8 The mass spectra of acceleration voltage of 5120 V (a) and 5140 V (b). Evaporation channels, Hg_{n+1}^{3+} $Hg_n^{3+} + Hg$ (region2), were labeled with open stars ()



Fig. 4. 9 The mass spectra of acceleration voltage of 5200 V (a) and 5220 V (b). Succesive emission of two Hg atoms from Hg_{n+2}^{3+} were labeled with open stars ()

successive Hg atoms loss, Hg_{n+2}^{3+} $Hg_n^{3+} + 2Hg$ (region2), which were corresponded to the peaks labeled with open stars (). These fragmentation peaks were well resolved from others in case n = 3m + 1 and 2. When n = 3m, these peaks were superposed on the peaks corresponding to the fragmentation, Hg_{m+1}^{+} $Hg_m^{+} + Hg$ (region1), however, the former would be larger content. The minimum size of product ions was n = 44. The smallest triply charged mercury cluster survived 10^{-6} sec was concluded in Hg_{46}^{3+} from the results of both one and two atoms emission cases.

4. 3. 4 Fission processes of Hg_n²⁺ and Hg_nAg²⁺

The fission processes of doubly charged mercury and mercury-silver binary cluster ions were investigated using an acceleration voltage scan method by selecting the fission fragments of Hg_n^+ (n = 2 - 19) and Hg_nAg^+ (n = 8 - 19) of 5 keV kinetic energy.

The acceleration voltage scan spectrum is shown in Fig. 4. 10. (a) where the selected fission fragment is Hg_3^+ . Two peaks appeared at acceleration voltage 3333 V and 4166 V, indicating the product ions from precursor ions Hg_4^{2+} and Hg_5^{2+} , respectively. In addition to fission peaks, the peak corresponding to the charge transfer process with residual gas, $Hg_3^{2+} + (gas)^0 = Hg_3^+ + (gas)^+$ (region2), was observed at 2500 V.

The charge transfer process was observed for only doubly charged dimer and trimer. The second ionization potential of neutral cluster is generally noted as $V_{IP}^{2+} = A + Bn^{-1/3}$. As the cluster size decreases, the ionization potential increases. Moreover, the electron affinity of doubly charged cluster ion also increases. The electron affinities of dimer and trimer are considered to be high enough to cause the charge transfer with residual gas.

The acceleration voltage scan spectrum is shown in Fig. 4. 10. (b) where the selected fission fragment is Hg_{9}^{+} . The fission peaks were assigned from the acceleration voltages. The acceleration voltage to detect the fission fragment Hg_{9}^{+} from Hg_{n}^{2+} (n = 13 - 17) and $Hg_{n}Ag^{2+}$ (n = 16, 17) is



Fig. 4. 10. The acceleration voltage scan spectra where selected product ions are (a) Hg_3^+ and (b) Hg_9^+ of 5keV kinetic energies.

given by $1.385M_{pre}$ (M_{pre} denotes the mass of precorsor ions where 200.6*n* for Hg_n²⁺, and 200.6*n* + 107.9 for Hg_nAg²⁺).

The intensities of fission channels of Hg_n^{2+} (n = 3 - 22) are shown in Table. 4.1. The fission fragments which had the mass larger than half of precursor's could observed at under 5 kV acceleration voltage. The open triangle () showed the channels which decomposing into two same fission fragments. Such a channel could not be observed. The cross (\times) symbols showed the channels which were not observed (under detection limit).

Any peak was observed corresponding fission fragments of Hg_n^+ (n = 14 - 17) and Hg_nAg^+ (n = 8 - 18) from Hg_n^{2+} or Hg_nAg^{2+} . It was found out that intensities of doubly charged mercury cluster ions were considerably higher than that of doubly charged mercury-silver binary cluster ions. It was conincident with assumption that multiply charged silver complex cluster ions were less produced in this experimental conditions.

The largest precursor ion caused the fission processes was Hg_{22}^{2+} . The appearance sizes of doubly charged mercury and mercury-silver binary cluster ions were both determined as $N_a^{2+} = 20$ by taking account the result of evaporation process.

4. 3. 5 Fission processes of Hg_n^{3+}

The fission processes of triply charged mercury cluster ions were also investigated using an acceleration voltage scan method by selecting the product ions Hg_n^+ (n = 15 - 45) of 5 keV kinetic energy and Hg_n^{2+} (n = 30 - 45) of 10 keV kinetic energy. The acceleration voltage scan spectra are shown in Fig. 4. 13, where the selected fission fragments are Hg_{38}^{2+} , Hg_{39}^{2+} and Hg_{40}^{2+} . As mentioned in section 4. 2. 3, even-size of doubly charged fission fragments such as Hg_{38}^{2+} and Hg_{40}^{2+} are indistinguishable from half size of singly charged fragments, Hg_{19}^+ and Hg_{20}^+ , respectively. For example, the fission channel corresponding to peak observed in Fig. 4. 11. (a) could not assign

	Observed product ions (Hg_n^+)											
		2	3	4	5	6	7	8	9	10	11	12
Precursor ions (Hg _n ²⁺)	3	108										
	4		28									
	5		139	32								
	6			78	8							
	7			81	31	1						
	8				59	4	×					
	9				47	15	2	×				
	10					22	7	×	×			
	11					15	10	2	×	×		
	12						10	5	×	×	×	
	13						18	8	3	×	×	×
	14							14	6	6	×	×
	15							7	9	8	4	×
	16								9	8	5	2
	17								8	7	4	2
	18									5	4	2
	19									5	4	1
	20										3	3
	21										2	3
	22											2

Table. 4. 1. Intensities of fission channels of Hg_n^{2+} (n = 3 - 22). The symbol of open triangle () showed the channels that could not observe because the precursor ions were decomposed into two same products. The symbol of cross (\times) showed the channels not observed.



Fig. 4. 11. The acceleration voltage scan spectra of which the selected cluster ions of (a) Hg_{38}^{2+} and Hg_{19}^{+} , (b) Hg_{39}^{2+} , and (c) Hg_{40}^{2+} and Hg_{20}^{+} .

whether Hg_{45}^{3+} $Hg_{38}^{2+} + Hg_7^+$ or Hg_{45}^{3+} $Hg_{26}^{2+} + Hg_{19}^+$. However, former would be plausible since the nearly same intense peak was observed in acceleration voltage scan spectrum selecting the odd size of doubly charged fission fragment, Hg_{39}^{2+} (Fig. 4. 11. (b)), which was not selected with singly charged fission fragments.

The fission processes were increased for clusters smaller than Hg_{47}^{3+} . The appearance size of triply charged mercury cluster ions was determined as $N_a^{3+} = 46$. The prior fission channels of triply charged mercury cluster ions, Hg_n^{3+} , were emission of Hg_6^+ and Hg_7^+ . In contrast to doubly charged cluster ions, the fission channels of triply charged mercury cluster ions were asymmetric.

4.3.6 Calculation of Q value

A schematic diagram representing fission process is shown in Fig. 4. 12, where B_f is fission barrier and Q is the total energy difference between initial and final states. The total energy, $E_{tot}(n,z)$, of *z*-charged *n*-atom cluster, X_n^{z+} , is defined as the energy required for the process:



Fig. 4. 12. A schematic diagram representing fission process, where B_f is fission barrier and Q is the total energy difference between before and after.

$$X_n^{z+} (n-z) e^{-} + nX^{+}$$
$$E_{tot}(n, z) = -(n-z)V_{IP} - E_{at}(n)$$

where V_{IP} is the ionization potential of the atom X and $E_{at}(n, z)$ is the atomization energy, which is the energy for the process

$$X_n^{z+}$$
 $zX^+ + (n-z)X$.

Using the Born-Herber cycle:

$$X_n \quad nX$$
$$X_n^{z+} \quad zX^{+} + (n-z)X$$

one deduced

$$E_{at}(n, z) = E_{at}(n) + zV_{IP} - V_{IP}^{z+}(n),$$

where $E_{at}(n)$ is the atomization energy of neutral cluster X_n , and $V_{IP}^{z+}(n)$ is the z-ionization potential of *n*-atom neutral cluster. The total energy is expressed as sum of the atomization and the ionization term:

$$E_{tot}(n, z) = -E_{at}(n) - nV_{IP} + V_{IP}^{z+}(n).$$

The Q value for fission process shown in Fig. 4. 11 is

$$Q = E_{tot}(m, j) + E_{tot}(n-m, i-j) - E_{tot}(n, i).$$

The difference between the ionization potential for the state of charge z+ and (z+1)+ was considered to be an added term $e^2/4B_{r_0}r_{ws}n^{1/3}$ for z+1 with respect to z. The second, $V_{IP}^{2+}(n)$, and third, $V_{IP}^{3+}(n)$, ionization potentials are expressed as

$$V_{IP}^{2+}(n) = 2V_{IP}^{+}(n) + \frac{e^2}{4\boldsymbol{p}\boldsymbol{e}_0 r_{ws} n^{1/3}}$$
$$V_{IP}^{3+}(n) = 3V_{IP}^{+}(n) + \frac{3e^2}{4\boldsymbol{p}\boldsymbol{e}_0 r_{ws} n^{1/3}}$$

In the case of alkali metal clusters [4.17], first ionization potential is theorigically given by

$$V_{IP}^{+}(n) = W_{\infty} + a \frac{e^2}{4pe_0 r_{ws} n^{1/3}}$$

where W is the work function of the bulk and is 1/2 or 3/8 according to different authors. The cluster ion is considered as metal droplet in this model although it is not true for mercury cluster case. The first ionization potential and atomization energy of mercury cluster used in the calculation were experimental data reported by Haberland *et al.* [1.8] which represented in two straight lines by Blanc *et al.* [4.15]. They were

$$V_{IP}^{+}(n) = 16.53 n^{-1/3} + 1.818 (n > 19)$$

= 4.112 n^{-1/3} + 6.397 (n 19),

and

$$E_{al}(n) = 0.83 n - 1.77 n^{2/3} (n > 17)$$
$$= 0.228 n - 0.228 n^{2/3} (n = 17)$$

The Q values for fragmentation processes

$$Hg_n^{2+}$$
 $Hg_m^{+} + Hg_{n-m}^{+}$

are calculated from equation:

$$Q = E_{tot}(m,1) + E_{tot}(n-m,1) - E_{tot}(n,2)$$

= $-E_{at}(m) - E_{at}(n-m) + E_{at}(n) + V_{IP}^{+}(m) + V_{IP}^{+}(n-m)$
 $-2V_{IP}^{+}(n) - \frac{e^2}{4pe_0r_{ws}n^{1/3}}.$

The calculated Q values of precursor ion of Hg_{20}^{2+} using the experimental data and the metal droplet model are shown in Fig. 4. 13. In the case of metal droplet model, fragmentation channel favored asymmetric at low fission parameter as it was observed for alkali or noble metal cluster ions around appearance size. However, the van der Waals bonding of small mercury clusters cause the symmetric fission even at near the appearance size which matched to our experimental results. The Q values about precursor ions of Hg_{20}^{2+} , Hg_{15}^{2+} and Hg_{10}^{2+} are shown in Fig. 4. 14. These



Fig. 4. 13. The *Q*-values for precursor ions of Hg_{20}^{2+} calculated using experimental data and metal droplet model.



Fig. 4. 14. The *Q*-values for precursor ions of Hg_{20}^{2+} , Hg_{15}^{2+} and Hg_{10}^{2+} calculated using experimental data.



Fig. 4. 15. The *Q*-values for precursor ions of Hg_{45}^{3+} calculated using experimental data and metal droplet model.

calculations supported the symmetric fission occurred for Hg_n^{2+} (n = 20).

The Q values for fragmentation processes

$$Hg_n^{3+}$$
 $Hg_m^{2+} + Hg_{n-m}^{++}$

are calculated equation:

$$Q = E_{tot}(m,2) + E_{tot}(n-m,1) - E_{tot}(n,3)$$

= $E_{at}(n) - E_{at}(m) - E_{at}(n-m) + 2V_{IP}^{+}(m) + V_{IP}^{+}(n-m)$
 $- 3V_{IP}^{+}(n) - \frac{3e^2}{4pe_0r_{ws}n^{1/3}} + \frac{e^2}{4pe_0r_{ws}m^{1/3}}$

The Q values for precursor ion of Hg₄₅³⁺ which calculated using experimental data and metal droplet model are shown in Fig. 4. 15. The asymmetric fission channels were favored in both cases which roughly fitted to my experimental results. There was slight difference about emitted cluster ions between experimental results and Q values calculations. The singly charged 6-mer and 7-mer emissions were prior channels for our experimental results compared to the singly charged dimer or trimer emissions likely to occur according to Q values calculated. However, these calculations took into account neither the stabilities of product ions nor fission barrier.

4.4 Conclusions

The appearance sizes of doubly and triply charged mercury cluster ions were experimentally determined as $N_a^{2+} = 20$ and $N_a^{3+} = 46$, respectively. Moreover, appearance size of doubly charged mercury-silver cluster ion was determined to $N_a^{2+} = 20$. The fission parameters at appearance sizes were X = 0.33 in both doubly and triply charged cases. It was coincident with the results reported for multiply charged alkali-metal cluster of which fission parameter X at appearance size was not

depend on charge state z.

The fission channels of doubly and triply charged cluster ions were also investigated. It was interesting that the fission channels of doubly charged mercury cluster ions were symmetric which could not interpreted by metal droplet model. It may be caused by the van der Waals bonding of small cluster ions. On the other hand, triply charged cluster ions caused the asymmetric fragmentation channels.

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5. Lifetime distribution of cluster ions from a sputtering ion source

5.1 Introduction

The interaction of keV energy ions with a solid leads to the sputtering of the clusters. A lot of experiments were carried out using this phenomenon to investigate the electronic state, stability of the cluster and so on [1.2,4, 5.1-6]. The "magic number" appearing in size distributions provided useful informations about stabilities and structures of clusters.

In addition to the size distribution, the study of fragmentation pattern, occurred within 10^{-6} - 10^{-4} sec, presented useful data [5.1, 5, 6] to understand the more accurate characters of clusters. It is well known that clusters made by sputtering are relatively "hot" and cause the spontaneous fragmentations. It would be advantage for investigating the fragmentation pattern. On the other hand, spontaneous decompositions make difficult to know the mechanisms of cluster production by sputtering because the informations about nascent clusters are lost.

To say nothing of the internal energy distribution of the clusters at the production time, it is little known about the internal energy of clusters in the experimental time range, i.e. $10^{-7} - 10^{-4}$ sec. The main duty of mass spectrometer in cluster analyses is separate the cluster ions by their masses or sizes, although the internal energies of cluster ions are considered to widely distribute even they are same size.

According to a Rice-Ramsperger-Kassel (RRK) theory [5.7], the dissociation rate constant k, a reciprocal of lifetime, of the cluster ion is correlated with the relative internal energy, E_{int}/E_{dy}

$$k = k_0 (1 - E_d / E_{int})^{s-1}$$

where E_{int} is the internal energy, E_d is the dissociation energy and *s* is the number of modes. Using this theory, investigation of lifetime distribution of cluster ions gives the information about internal energy distribution.

A simulation was carried out using molecular-dynamics (MD) on nascent Ag_n clusters [5.8]. The nascent Ag_n clusters sputtered by keV Ar⁺ ions had an average internal energy about 1 eV per constituent atom and branching or chain decay occurred in the time range of 10^{-11} sec that is quite early stage compared with experimental one. Determination of the internal energy distribution of cluster ions from a sputtering ion source was only reported for sputtered Ta_n⁺ (n = 4 - 8) about the experimental time range of $10^{-9} - 10^{-4}$ sec [5.9]. The authors concluded that the average internal energy per constituent atom depended weakly upon their cluster sizes.

In this chapter, one of the method for obtaining the lifetime distributions using a typical double focusing mass spectrometer is introduced. The time dependences of fragmentation rates, within the experimental time range of $10^{-7} - 10^{-4}$ sec, were studied about fragmentation channels, $Hg_{n+1}Ag^+$ $Hg_nAg^+ + Hg$ (n = 8 - 14) and Ag_{n+1}^+ $Ag_n^+ + Ag$ (n = 12, 14). The dissociation energies of mercury and silver cluster ions were reported as about 0.2 eV [5.10] and 2 eV [5.11], respectively that was quite different each other. The lifetime distribution of each fragmentation channel was calculated using fragmentation rate experimentally obtained. Furthermore, its size dependence was argued about mercury-silver binary cluster ions.

5. 2 Experimental conditions

Fragmentation processes were observed by following procedures. (1) The deflection potential of the cylindrical electric sector and energy slits were kept constant so that the ions of 5000 \pm 20 eV/charge could pass through the sector. (2) The acceleration voltage was changed from 5000 V to 6000 V for every 40 V step and mass spectra were obtained by scanning the magnet current in a linear mode (B scanning) for each acceleration voltage.

5.3 Results

5. 3. 1 Dissociation rate on time

As a preparation to examine the lifetime distributions, the fragmentation rate as a function of time, $F_{exp}(t) = dI_f/dt$ (I_f denotes the fragmentation intensity), is investigated from experimental data. As an example, the fragmentation channel, $Hg_{13}Ag^+$ $Hg_{12}Ag^+ + Hg$, is explained in the followings.

The appearance of fragmentation channel occurred in each region was already descrived in section 2. 3. 1. In the case of channel, $Hg_{13}Ag^+$ $Hg_{12}Ag^+ + Hg$, the fragmentation peaks of plateaus were appeared with in acceleration volgate of $5 < V_a < 5M_{13}/M_{12}$ (kV), where M_{13} and M_{12} denoted the mass of $Hg_{13}Ag^+$ and $Hg_{12}Ag^+$, respectively. The value of $5M_{13}/M_{12}$ is 5.4 (kV). The mass spectra of acceleration voltage 5100 V and 5400 V are shown in Fig. 5. 1. (a) and (b). Four peaks and one plateau labeled with region r (r = 1 - 5) in Fig. 5. 1. (a) and (b) corresponded to the fragmentation channel, $Hg_{13}Ag^+$ $Hg_{12}Ag^+ + Hg$, occurred at each region.

Basically, fragmentation rate was derived from peak or plateau areas $(dI_f)_r$, (r = 1 - 5;denoted the each fragmentation region) divided by travel time of cluster ions in each region, $(dt)_r$. The representing time of given region was travel time from the start point of the electrostatic lens system in the ion source to the center of the region. The $(dI_f/dt)_r$ values at region1-5 were obtained by following procedures.

The peaks that indicated the fragmentation occurred in region1 appeared in mass spectra of



Fig. 5. 1. The mass spectra at acceleration voltage of (a) 5100 V and 5400 V. The labeled letters "region r (r = 1-5)" indicate the fragmentation position of the peaks and plateau about fragmentation channel; $Hg_{13}Ag^+$ $Hg_{12}Ag^+ + Hg$.

acceleration voltages $5 < V_a < 5M_{13}/M_{12}$. The area of the peak in each mass spectrum at acceleration voltage V_a (V) was defined as $(dI_f)_{1, Va}$. Assuming that the electrostatic lens system was a pair of parallel plates and fixing the acceleration voltage, V_a , the kinetic energy of product ion, U_{pro} (eV), the function of x as

$$U_{pro} = V_a \left\{ I - \frac{M_{13} - M_{12}}{M_{13}} \frac{x}{L} \right\} \quad (0 < x < L)$$

where M_{13} and M_{12} are masses of Hg₁₃Ag⁺ and Hg₁₂Ag⁺, *L* is length of lens system. This relation can be also expressed as

$$x = L \left(\frac{V_a - U_{pro}}{M_{13} - M_{12}} \frac{M_{13}}{V_a} \right).$$

The kinetic energy of product ions, U_{pro} , was limited by width of energy slit to 000 ± 20 eV/ charge. According to kinetic energy limitation, the fragmentation place at given acceleration voltage was also limited. The very place limitation at each acceleration voltage was related directly with the travel times, $(dt)_{l, kr}$.

The fragmentation peaks (region2, 4) and plateaus (region3) were observed in three mass spectra acquired at acceleration voltages neighboring the value of $5M_{13}/M_{12}$ (keV) caused by the dispersive energy of secondary ions. The fragmentation intensities of region2 - 4, (dI_f)₂₋₄, were defined by summing up peak or plateau areas obtained from three mass spectra. The travel times of region r (r = 2 - 4) could obtain by calculating the time of flight to each end of region r. These were calculated from potential shape of acceleration region (electric field of lens system, mentioned above), acceleration voltage $5M_{13}/M_{12}$ (keV) and the length of region r (r = 1 - 4).

As well as the case of region1, the peaks corresponded to fragmentation at region5 were appeared in mass spectra at acceleration voltage of $5 < V_a < 5M_{13} / M_{12}$. But it was difficult to determine the correlation between the fragmentation time and the acceleration voltage. In order to derive (dI_f)₅, peak areas which were not overlapped with other fragmentation were averaged and multiplied by the number of spectrum within $5 < V_a < 5M_{13} / M_{12}$ since the peak area of each mass spectrum was almost same. Travel time, $(dt)_5$, was obtained as well as region2 - 4.

One must take attention to the effect from other fragmentation channels because the one neutral atom loss was not only fragmentation channels for both silver and mercury silver cluster ions. The intensities of fragmentation occurred in region1 were the most which need to pay attentions.

In case of the silver cluster ions, there was odd-even alternation in the fragmentation pattern. The neutral dimmer loss, Ag_{n+2}^+ $Ag_n^+ + Ag_2$, was comparable to one atom loss for odd-*n* while little was observed for even-*n*. It leaded to the fragmentation intensities of one neutral atom loss for only odd-*n* occurred in region1 was expected to be increased by that of dimmer loss. For this reason, the argument of lifetime distribution about odd-*n* was excluded from discussion.

In the case of the mercury-silver cluster ions, there was little size dependence about fragmentation pattern, however, the successive atom emission was observed in this experimental time range. The successive two emissions of an atom occurred first in region1 and second in any region, $Hg_{n+1}Ag^+$

 $Hg_nAg^+ + Hg$ (region1) $Hg_{n-1}Ag^+ + Hg$ (region1-5), was not counted in the fragmentation intensity of $Hg_{n+1}Ag^+$ $Hg_nAg^+ + Hg$ (region1), and that would be reduction factor. The increment factors also existed such as the fragmentation channels, $Hg_{n+2}Ag^+$ $Hg_nAg^+ + 2Hg$ or Hg_2 (region1) which a part of them was counted in. The ratio of the increment and reduction factor was unknown, however, the effect to the fragmentation intensity of one atom loss at region1 was thought to be negligible as long as the dissociation rate on time was argued in logarithmic scale since the two atoms losses at region2 were about a few dozens of percents of one atom loss at same region.

The fragmentation rates on time of the channels, $Hg_{13}Ag^+$ $Hg_{12}Ag^+ + Hg$ and Ag_{13}^+ $Ag_{12}^+ + Ag$, are shown in Fig. 5. 2. Both fragmentation rate and time are represented in logarithmic scales.



Fig. 5. 2. The fragmentation rate on time of the channels, $Hg_{13}Ag^+$ $Hg_{12}Ag^+ + Hg$ and Ag_{13}^+ $Ag_{12}^+ + Ag$. Both fragmentation rate and time are represented in logarithmic scales.

5. 3. 2 Lifetime distributions

The fragmentation rate $F_{exp}(t)$ was approximated by power function rather than by an exponential one in both silver and mercury-silver binary cluster ions cases. I assumed that the experimental data were simulated by the following function:

$$F_{exp}(t) = b t^{-a}$$

and acquired constants a and b using the least squares fitting.

The fragmentation rate on time of the channel, $Hg_{13}Ag^+$ $Hg_{12}Ag^+ + Hg$, with fitted line are shown in Fig. 5. 3. In case of fitting calculation, the point of region2 was excluded in both cases because of the wide range of flight time ($10^{-6} - 10^{-4}$ order). In Hg_nAg^+ case, the points superposed with the other fragmentation channel were also excluded. These points are shown with open circle in Fig. 5. 3.

In case of lifetime J, fragmentation rate $F_{J}(t)$ must be following function:

$$F_{J}(t) = exp(-t/J)/J$$

The non-exponential nature of $F_{exp}(t)$ shown in experimental data indicated that cluster ions of same size have different lifetime of the fragmentation reaction. By introducing the distributions of lifetime, (J), fragmentation rate was written as a superposition of the exponential functions:

$$F(t) = \{ (J) exp(-t/J)/J \} dJ$$

Comparing with the experimental function $F_{exp}(t)$, the lifetime distribution, (J), could determine analytically as

$$() = b J^{-a} / (a).$$

Limitation of lifetime should be $10^{-7} - 10^{-3}$ sec by taking the time window of this experimental conditions into account. It is well known that the cluster ions decomposed through chain or branch pathways from their production time and so that the derived lifetime distribution was not reflecting the character of the nascent cluster ions but of the cluster ions 10^{-7} sec after their production.



Fig. 5. 3. The fragmentation rate on time of fragmentation channel, $Hg_{13}Ag^+$ $Hg_{12}Ag^+ + Hg$, with fitted line obtained using least mean squares fitting.

There were two parameters, *a* and *b*, for each fragmentation channel. In the case of mercurysilver binary cluster ions, we could argue the size dependence of the parameter. The parameter *b* indicated the intercepts of $F_{exp}(t)$ so that the dissociation rate at 1 sec after the production time. Considering that the experimental time range, $10^{-7} - 10^{-3}$ sec, it was impertinence to argue the size dependence of the parameter *b*.

The size dependence of the *a* value of fragmentation channels, $Hg_{n+1}Ag^+$ $Hg_nAg^+ + Hg$ (*n* = 8 - 14) is shown in Fig. 5. 4. The *a* value reflected the relative abundance of long and short lived cluster ions. The large *a* value indicated the less of long-lived precursor ions. There were the singularity in size dependence of *a* value at *n* = 12. This fact indicated that $Hg_{12}Ag^+$ was relatively stable. It may be understood as due to icosahedron structure.

The relationship between lifetime and relative internal energy, E_{int} / E_d , could be expressed following equation according to a simple RRK theory:

$$k = 1/J = gv (1 - E_d/E_{int})^{3n-7}$$

where g is a degeneracy factor equal to number of surface atom which is adopted the cluster size n in this case, and v is a typical vibrational frequency (ca. 10^{12} Hz). The relative internal energy, E_{int} / E_d , as a function of lifetime is shown in Fig. 5. 5. It would be 1.8 to 2.6 in this experimental time rage, $10^{-7} - 10^{-3}$ sec. The corresponding internal energies of silver and mercury-silver binary cluster ions were quite different although the experimental time range were same.

In order to know the internal energy distributions for wider range, the lifetime shorter or longer than this experimental time range has to be investigated. The experiment to know about the lifetime of cluster ions at experimental time rage of $10^{-9} - 10^{-4}$ sec was performed successfully by devising the shape of the acceleration potential [5.9]. The ion trap method which could hold cluster ions for long time spatially may be useful for experimental time range longer than 10^{-3} sec.



Fig. 5. 4. The size dependence of the *a* value of fragmentation channels, $Hg_{n+1}Ag^+$ $Hg_nAg^+ + Hg$ (*n* = 8 - 14)



Fig. 5. 5. Relationship between lifetime and relative internal energy, E_{int} / E_d .

5.4 Conclusions

The lifetime distributions of silver and mercury-silver binary cluster ions were investigated experimentally. The widely distributed lifetime originated by spread of internal energy of cluster ions produced by a sputtering method was indicated. The size dependence of lifetime distribution allowed one to discuss about cluster stability. According to it, $Hg_{12}Ag^+$, which was understood by icosahedron structure, was rather stable than adjacent cluster ions. The stability of $Hg_{12}Ag^+$ was not appeared as "magic number" in size distribution (see section 3. 2. 1). The investigation of lifetime distribution might be the other useful method to know the stabilities of cluster ions.

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