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Fragmentation of Doubly and Triply Charged Mercury Cluster Ions

Takaya SATOH,^{*a)} Hiroyuki ITO,^{b)} Toshio ICHIHARA,^{b)}
Hiroki SAKAE^{c)} and Itsuo KATAKUSE^{b)}

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The fragmentation of doubly and triply charged mercury cluster ions were investigated. The cluster ions were produced by Xe ions bombardment on a mercury-silver amalgam. The size where evaporation and fission occur with equal probability is called appearance size. The appearance sizes of doubly and triply charged mercury cluster ions were determined to be $N_a^{2+}=20$, and $N_a^{3+}=46$, respectively. The fission channels were investigated and their probability was estimated by calculation of Q -values. The van der Waals bonding of small mercury clusters caused the symmetric fission of doubly charged cluster ions. The fission channels of triply charged cluster ions were asymmetric since the metallic character came into prominence for both precursor and large one of fission fragments.

1. Introduction

The fragmentation of multiply charged cluster ions can be classified into the fission and the evaporation:

$$M_n^{i+} \rightarrow M_m^{j+} + M_{n-m}^{(i-j)+} \quad (i=j: \text{evaporation}, i>j: \text{fission}).$$

The fission of multiply-charged noble or alkali metal cluster ions was well reported as an analogy with nuclei.¹⁾ The fission parameter, X , was adopted for clusters as well as nuclei. It is defined as $X=E_c/2E_s$, where E_c is the coulomb energy and E_s is the surface energy. It can also be expressed as $X=(Z^2/N)/(Z^2/N)_c$, where $(Z^2/N)_c$ corresponding to $X=1$ is $16\pi r_w^3 \sigma/e^2$. Here, Z is number of the charge, and N is the cluster size, r_w is the Wigner-Seitz radius, e is the elementary charge, and σ is the surface tension. The nuclei are unstable to cause the fission when $X<1$. However, the fission and evaporation compete even if $X<1$ in the cluster case. The evaporation is preferred to the fission at the cluster size larger than appearance size, N_a , where the evaporation and fission occur with equal probability.

The fragmentation, especially fission, of multiply-charged cluster ions have been reported mainly about metal cluster ions. The z -folded charged sodium and cesium cluster ions were reported up to $z=7$, and $z=4$ for potassium and rubidium.^{2), 3)} The critical sizes for appearance of each charged states in the mass spectra, which were called "the effective appearance size," were determined in these reports. The facts these experiments showed were appearance sizes lay in narrow interval of X values ($0.25<X<0.35$) irrespective of

charge state z and substances. The fission processes of doubly charged alkali-metal⁴⁾⁻⁶⁾ and noble-metal⁷⁾⁻⁹⁾ cluster ions were also reported. The fission channels were well interpreted by superposition of the metal droplet model and the electronic shell structure.

The electronic shell structure of mercury atom is $5d^{10}6s^2$ closed shell, which is isoelectronic with helium. Therefore the diatomic molecule and small clusters are bound by the van der Waals force. For the inter-mediated cluster size, the $6s$ and $6p$ orbits broaden. For bulk Hg, the overlapping of $6s$ and $6p$ bands gives the metallic behaviors. The metal to nonmetal transition occurred at $n\sim 15$ was well reported by several authors by various experimental methods.¹⁰⁾⁻¹³⁾ It is expected that the fragmentation of multiply-charged mercury cluster ions are different from that of metal cluster ions, because of the van der Waals bonding at small size. In this article, we investigated (i) the appearance sizes and (ii) the fission channels of doubly and triply charged mercury cluster ions. Furthermore, (iii) the probabilities of fission channels were estimated by calculation of Q -values, which are the total energy difference between initial and final states.

2. Experiment

Mercury and mercury-silver binary cluster ions were produced by the Xe ions bombardment on the mercury-silver amalgam. Primary Xe ions were obtained using a discharge type compact ion gun.¹⁴⁾ Cluster ions were mass analyzed using a double focusing mass spectrometer¹⁵⁾ (radius of magnet: 1.25 m, maximum flux density of magnet: 1.8 T, flight path length: 7.64 m), of which field arrangement is QQHQC (Q denotes electric quadrupole, H: a homogeneous magnetic sector, C: an cylindrical electric sector). In order to increase the conversion efficiency from ions to electrons at the conversion dinode of the electron multiplier, the ions were post accelerated by 13 kV after passing through a detector slit. The secondary electrons were amplified by a conventional sixteen-stage electron multiplier. Mass spectra were obtained by scanning the magnet current in a linear mode and were recorded

^{*a)} JEOL LTD. (1-2 Musashino 3-chome, Akishima, Tokyo 196-8558, Japan)

^{b)} Department of Physics, Graduate School of Science, Osaka University (1-16 Machikaneyama, Toyonaka, Osaka 560-0043, Japan)

^{c)} CREST (1-16 Machikaneyama, Toyonaka, Osaka 560-0043, Japan)

using a PC with an analog to digital converter.

The cluster ions produced by the sputtering of ions have high internal energy enough to cause the spontaneous fragmentations. The kinetic energy of precursor ion is divided into products in proportional to each of their mass. The fragmentation occurring at region between the ion source and the magnetic sector was observed. In order to observe the fragmentation, we fixed the voltage of the electric sector so that the ion of 5 keV per charge number could path through it, and changed the acceleration voltage.

The evaporation can be observed when the acceleration voltage was $5M_i/M_p$, where M_i is mass of precursor and M_p is mass of product ions. The acceleration voltage must set higher than 5 kV for observation of the evaporation. The evaporation was 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 appeared at m/z values of product ions in mass spectra.

The fission products of doubly charged cluster ions can be observed when the acceleration voltage is $5M_i/2M_p$. Differing from the evaporation, the fission product larger than $M_i/2$ can be observed at acceleration voltage under 5 kV. The spectra, which are free from evaporation peaks of singly charged cluster ions can be obtained at under 5 kV acceleration voltage. Main process in sputtered cluster ions is the evaporation.

In the case of triply charged cluster ions, a doubly and a singly charged fragments are yielded. When $M_{p1} > M_i/3$, where M_i is mass of precursor and M_{p1} is mass of singly charged fragment, the singly charged fragment is observed at under 5 kV. On the other hand, the doubly charged fragment is observed at under 5 kV when $M_{p1} < M_i/3$. However, doubly charged fragment, Hg_{2m}^{2+} , is indistinguishable from the singly charged one, Hg_m^+ , which has the half mass of doubly charged one. For example, the fragmentation channel $Hg_{46}^{3+} \rightarrow Hg_{40}^{2+} + Hg_6^+$ is indistinguishable from $Hg_{46}^{3+} \rightarrow Hg_{26}^{2+} + Hg_{20}^+$.

The fission channels were investigated by selecting the given fission fragments by the magnetic and electric sectors, and scanning the acceleration voltage under 5 kV.

3. Results and Discussions

3.1 The evaporation of Hg_nAg^{2+}

The mass spectra at acceleration voltages 5220–5280 V are shown in Fig. 1. The abscissa expressed the cluster size of Hg_nAg^{2+} which corresponded to mass region of $m/z=1460$ –2660. The large and saturated peaks are the fragmentation of singly charged cluster ions. The peaks indicating product ions of the fragmentation channel, $Hg_{n+1}Ag^{2+} \rightarrow Hg_nAg^{2+} + Hg$, were marked with open circle (○). The observed smallest product ion was $Hg_{19}Ag^{2+}$, so that the $Hg_{20}Ag^{2+}$ was the smallest ion came out from acceleration region and caused the evaporation. It took about 10^{-6} s for passing through the acceleration region. The evaporation process of Hg_{2n}^{2+} could not be observed because these peaks were overlapped with fragmentation peaks of singly charged clusters, Hg_n^{2+} and Hg_nAg^{2+} .

Fig. 1. The mass spectra of acceleration voltage (a) 5220 V, (b) 5240 V, (c) 5260 V, and (d) 5280 V. The peaks marked with open circle (○) indicate the fragmentation channel, $Hg_{n+1}Ag^{2+} \rightarrow Hg_nAg^{2+} + Hg$. The observed smallest product ion is $Hg_{19}Ag^{2+}$.

3.2 The evaporation of Hg_n^{3+}

The mass spectra of acceleration voltages of (a) 5120 and (b) 5140 V are shown in Fig. 2. The abscissa expressed the cluster size of Hg_n^{3+} which corresponded to mass region of $m/z=2450$ –4000. The peaks indicating product ions of the fragmentation channel, $Hg_{n+1}^{3+} \rightarrow Hg_n^{3+} + Hg$, were marked with open circle (○). These channels were well resolved from fragmentation peaks of singly charged cluster ions for only $n=3m+1$ (m ; integer). The observed smallest product ion was Hg_{46}^{3+} .

We also observed the two atoms emission channel, $Hg_{n+2}^{3+} \rightarrow Hg_n^{3+} + 2Hg$. The peaks corresponding to these fragmentation channels were also marked with open circle (○) in Figs. 3(a) and (b) that are the mass spectra at acceleration voltages of (a) 5200 and (b) 5220 V. The observed smallest product ion was Hg_{44}^{3+} .

3.3 The fission process of Hg_n^{2+} and Hg_nAg^{2+}

The acceleration voltage scan spectra are shown in Fig. 4(a) where the selected fission fragment is Hg_3^+ . Two peaks appeared at acceleration voltages 3333 V and 4166 V, indicating the product ions from precursor ions Hg_{42}^+ and Hg_{52}^+ , respectively. In addition to fission peaks, the peak corresponding to the charge transfer with residual gas, $Hg_{32}^+ + (gas)^0 \rightarrow Hg_3^+ +$

Fig. 2. The mass spectra of acceleration voltage (a) 5120 V and (b) 5140 V. The peaks marked with open circle (○) indicate the fragmentation channel, $\text{Hg}_{n+1}^{3+} \rightarrow \text{Hg}_n^{3+} + \text{Hg}$.

Fig. 3. The mass spectra of acceleration voltage (a) 5200 V and (b) 5220 V. The peaks marked with open circle (○) indicate the fragmentation channel, $\text{Hg}_{n+1}^{3+} \rightarrow \text{Hg}_n^{3+} + 2\text{Hg}$. The observed smallest product ion is Hg_{44}^{3+} .

(gas)⁺, 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 $V_{\text{IP}}^{2+} = A + Bn^{-1/3}$. 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(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 $\text{Hg}_n\text{Ag}^{2+}$ ($n=16, 17$) is given by $1.385M_0$ (M_0 denotes the mass of precursor ions, $200.6n$ for Hg_n^{2+} , and $200.6n + 107.9$ for $\text{Hg}_n\text{Ag}^{2+}$).

The intensity of fission channels of Hg_n^{2+} ($n=3-22$) is shown in Table 1. The fission fragments, which had the mass larger than half of precursor, could be observed at under 5 kV acceleration voltage. The open triangles (△) show the channels which decomposing into two same fission fragments. Such a channel could not be

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

observed. The cross ($\times$) symbols show the channels which were not observed (under detection limit). Any peak was observed corresponding fission fragments of Hg_n^{2+} ($n=14-17$) and $\text{Hg}_n\text{Ag}^{2+}$ ($n=8-18$) from Hg_n^{2+} or $\text{Hg}_n\text{Ag}^{2+}$.

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; however, the evaporation of Hg_n^{2+} could not be observed. It was because the fission fragments from both Hg_n^{2+} and $\text{Hg}_n\text{Ag}^{2+}$ were quite similar, and the fission and evaporation processes were replaced clearly around N_a^{2+} . The fission parameters at appearance size was $X=0.33$. The fission channels of doubly charged cluster ions were symmetric which preferred to produce two fragments of almost the same size. The symmetric fission channels considered to be occurred at high X value using metal droplet model.¹⁾ The observed symmetric fission channels around N_a^{2+} could not be interpreted by metal droplet model.

3.4 The fission process of Hg_n^{3+}

The fission process of triply charged mercury cluster ions was also investigated using the 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. 5, where the selected fission fragments are Hg_{38}^{2+} , Hg_{39}^{2+} , and Hg_{40}^{2+} . As is mentioned above, doubly charged fission fragments of even size such as Hg_{38}^{2+} and Hg_{40}^{2+} are indistinguish-

able from half size of singly charged fragments, Hg_{19}^+ and Hg_{20}^+ , respectively. For example, the fission channel corresponded to the peak observed in Fig. 5(a) could be assigned as either $\text{Hg}_{45}^{3+} \rightarrow \text{Hg}_{38}^{2+} + \text{Hg}_7^+$ or $\text{Hg}_{45}^{3+} \rightarrow \text{Hg}_{26}^{2+} + \text{Hg}_{19}^+$. 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. 5(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 fission parameter at appearance size was $X=0.33$, which was equal to the doubly charged one. In contrast to doubly charged cluster ions, the fission channels of triply charged mercury cluster ions were asymmetric. The emissions of Hg_6^+ and Hg_7^+ were preferable for fission of Hg_n^{3+} .

3.5 Calculation of Q -values

In this section, the fission channels observed in this experiments were estimated by Q -values. A schematic diagram representing the fission process is shown in Fig. 6, where B_f is the fission barrier and Q is the total energy difference between initial and final states. The total energy, $E_{\text{tot}}(n, z)$, of z -charged n -atom cluster, M_n^{z+} , is defined as the energy required for the process:

$$M_n^{z+} \rightarrow (n-z)e^- + nM^+, \quad (1)$$

Table 1. The Fission Channels of Hg_n^{2+} ($n=3-22$)

	Observed product ions: Hg_n^+											
		2	3	4	5	6	7	8	9	10	11	12
Precursor ions: Hg_n^{2+}	3	108										
	4	$\triangle$	28									
	5		139	32								
	6		$\triangle$	78	8							
	7			81	31	1						
	8			$\triangle$	59	4	$\times$					
	9				47	15	2	$\times$				
	10				$\triangle$	22	7	$\times$	$\times$			
	11					15	10	2	$\times$	$\times$		
	12					$\triangle$	10	5	$\times$	$\times$	$\times$	
	13						18	8	3	$\times$	$\times$	$\times$
	14						$\triangle$	14	6	6	$\times$	$\times$
	15							7	9	8	4	$\times$
	16							$\triangle$	9	8	5	2
	17								8	7	4	2
	18								$\triangle$	5	4	2
	19									5	4	1
	20									$\triangle$	3	3
	21										2	3
	22										$\triangle$	2

The symbol of open triangles ($\triangle$) show the channels that could not be observed because the precursor ions were decomposed into the two same products. The symbols of cross ($\times$) show the channels not observed.

Fig. 5. The acceleration voltage scan spectra where selected product ions are (a) Hg_{38}^{2+} and Hg_{19}^+ , (b) Hg_{39}^{2+} , and (c) Hg_{40}^{2+} and Hg_{20}^+ .

Fig. 6. A schematic diagram representing the fission process, where B_f is the fission barrier and Q is the total energy difference between the initial and final states.

$$E_{\text{tot}}(n, z) = -(n-z)V_{\text{IP}}^+(1) - E_{\text{at}}(n, z), \quad (2)$$

where $V_{\text{IP}}^+(n)$ is the ionization potential of the neutral M_n . $E_{\text{at}}(n, z)$ is the atomization energy of M_n^{z+} , which is the energy for the process

$$M_n^{z+} \rightarrow zM^+ + (n-z)M. \quad (3)$$

Using the Born-Herber cycle:

$$\begin{array}{ccc} M_n & \longrightarrow & nM \\ \downarrow & & \downarrow \\ M_n^{z+} & \longrightarrow & zM^+ + (n-z)M, \end{array} \quad (4)$$

one deduced

$$E_{\text{at}}(n, z) = E_{\text{at}}(n) + zV_{\text{IP}}^+(1) - V_{\text{IP}}^{z+}(n), \quad (5)$$

where $E_{\text{at}}(n)$ and $V_{\text{IP}}^{z+}(n)$ are the atomization energy and the z -th ionization energy of neutral M_n . The total energy is expressed as sum of the atomization energy and ionization terms:

$$E_{\text{tot}}(n, z) = -E_{\text{at}}(n) - nV_{\text{IP}}^+(1) + V_{\text{IP}}^{z+}(n). \quad (6)$$

The Q -value for fission process shown in Fig. 6 is

$$Q = E_{\text{tot}}(m, j) + E_{\text{tot}}(n-m, i-j) - E_{\text{tot}}(n, i). \quad (7)$$

The difference between the ionization potential for the state of charge z^+ and $(z+1)^+$ was considered to be an added term $V_{\text{IP}}^+(n) + ze^2/4\pi r_{\text{ws}} n^{1/3}$ for $z+1$ with respect to z . The second, $V_{\text{IP}}^{2+}(n)$, and third, $V_{\text{IP}}^{3+}(n)$, ionization

potentials are expressed as

$$\begin{aligned} V_{\text{IP}}^{2+}(n) &= V_{\text{IP}}^+(n) + V_{\text{IP}}^+(n) + e^2/4\pi\epsilon_0 r_{\text{ws}} n^{1/3} \\ &= 2V_{\text{IP}}^+(n) + e^2/4\pi\epsilon_0 r_{\text{ws}} n^{1/3} \end{aligned} \quad (8)$$

$$\begin{aligned} V_{\text{IP}}^{3+}(n) &= V_{\text{IP}}^{2+}(n) + V_{\text{IP}}^+(n) + 2e^2/4\pi\epsilon_0 r_{\text{ws}} n^{1/3} \\ &= 3V_{\text{IP}}^+(n) + 3e^2/4\pi\epsilon_0 r_{\text{ws}} n^{1/3}. \end{aligned}$$

The Q -values are calculated using metal droplet model and experimental data reported by Haberland *et al.*¹³⁾ In the case of metal droplet, *e.g.* alkali metal clusters,¹⁶⁾ first ionization potential is theoretically given by

$$V_{\text{IP}}^+(n) = W + \alpha e^2/4\pi\epsilon_0 r_{\text{ws}} n^{1/3}, \quad (9)$$

where W is the work function of the bulk and α is 1/2 or 3/8 according to different authors. We used Eq. (9) for metal droplet model calculations. The first ionization potential and atomization energy of mercury cluster were reported by Haberland *et al.*¹³⁾ Blanc *et al.* represented these experimental data in two straight lines in their report.¹⁷⁾ They were

$$\begin{aligned} V_{\text{IP}}^+(n) &= 16.53n^{-1/3} + 1.818 \quad (n > 19) \\ &= 4.112n^{-1/3} + 6.397 \quad (n \leq 19), \end{aligned} \quad (10)$$

and

$$\begin{aligned} E_{\text{at}}(n) &= 0.83n - 1.77n^{2/3} \quad (n > 17) \\ &= 0.228n - 0.228n^{2/3} \quad (n \leq 17). \end{aligned} \quad (11)$$

We also used Eq. (10) for calculations using experimental data. The atomization energy, Eq. (11), was used for both cases.

The Q -values for fragmentation processes, $\text{Hg}_n^{2+} \rightarrow \text{Hg}_m^+ + \text{Hg}_{n-m}^+$, are calculated from equation:

$$\begin{aligned} Q^{2+} &= E_{\text{tot}}(m, 1) + E_{\text{tot}}(n-m, 1) - E_{\text{tot}}(n, 2) \\ &= -E_{\text{at}}(m) - E_{\text{at}}(n-m) + E_{\text{at}}(n) + V_{\text{IP}}^+(m) \\ &\quad + V_{\text{IP}}^+(n-m) - 2V_{\text{IP}}^+(n) - e^2/4\pi\epsilon_0 r_{\text{ws}} n^{1/3}. \end{aligned} \quad (12)$$

The calculated Q^{2+} values of precursor ion of Hg_{20}^{2+} using the experimental data, Eqs. (10) and (11), and the metal droplet model, Eqs. (9) and (11), are shown in Fig. 7. The calculated results were quite different from

Fig. 7. The Q -values for precursor ions of Hg_{20}^{2+} calculated using experimental data (●) and metal droplet model (○).

Fig. 8. The Q -values for precursor ions of Hg_{45}^{3+} calculated using experimental data (●) and metal droplet model (○).

each other. In the case of metal droplet model, the asymmetric fission channels were expected around the appearance size as it was reported for alkali or noble metal cluster ions. On the other hand, the result using experimental data showed that the symmetric fission channels were preferred around the appearance size. The later matched to our experimental results. It was caused by the van der Waals bonding of small mercury clusters.

The Q -values for fragmentation processes $\text{Hg}_n^{3+} \rightarrow \text{Hg}_m^{2+} + \text{Hg}_{n-m}^{+}$ were calculated from equation:

$$\begin{aligned} Q^{3+} &= E_{\text{tot}}(m, 2) + E_{\text{tot}}(n-m, 1) - E_{\text{tot}}(n, 3) \\ &= -E_{\text{at}}(m) - E_{\text{at}}(n-m) + E_{\text{at}}(n) + 2V_{\text{IP}}^{+}(m) \\ &\quad + V_{\text{IP}}^{+}(n-m) - 3V_{\text{IP}}^{+}(n) - 3e^2/4\pi\epsilon_0 r_{\text{ws}} n^{1/3} \\ &\quad - e^2/4\pi\epsilon_0 r_{\text{ws}} m^{1/3}. \end{aligned} \quad (13)$$

The Q -values for precursor ion of Hg_{45}^{3+} , which were calculated using experimental data and metal droplet model, are shown in Fig. 8. The asymmetric fission channels were favored in both cases, which roughly fitted to our experimental results. There was a 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 account of neither the stabilities of product ions nor fission barrier.

4. Conclusion

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. The fission parameters at appearance sizes were $X=0.33$ in both doubly and triply charged cases. It is consistent with the results reported for multiply charged alkali-metal cluster of which fission parameter X at appearance size do not depend on charge state z .

The fission channels of doubly and triply charged cluster ions were also investigated. It is interesting

that the fission channels of doubly charged mercury cluster ions are symmetric which cannot be interpreted by metal droplet model. The van der Waals bonding of small cluster ions may cause it. On the other hand, triply charged cluster ions caused the asymmetric fragmentation channels.

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