Size Distribution of Zinc-Cesium and Cadmium-Cesium Positive Cluster Ions Using Secondary Ion Mass Spectrometry

Hiroyuki Ito, a) Toru Sakurai, a) Takekiyo Matsuo, a) Hisashi Matsuda, a) Toshio Ichihara, b) and Itisuo Katakus b)

(Received September 9, 1995)

Abundance distributions were studied for cadmium-cesium and zinc-cesium positively charged cluster ions. The cluster ions were produced by Cs+ ion bombardment on initially pure metal sheets of either cadmium or zinc, and mass analysis was performed using a grand-scale sector mass spectrometer. Mass spectra revealed the abundance distributions indicating that specific clusters having 8, 20, 34, 40, and 58 valence electrons were particularly stable. Observed abundances of [Cd,Cs]+, [Zn,Cs]+, and [Zn,-Cs]+ can be fully explained in terms of the electronic-shell structures of the metals studied. It was found that the origin of the “magic numbers” are different from those of Hg,Cs+ cluster.

1. Introduction

Mass spectrometric studies offer useful methods for exploration of the size specific properties of free clusters, such as an electronic-shell structure or an atomic-shell structure. The magic numbers of metal clusters is now understood in terms of a shell effect of s-valence electrons in a square well potential, which was first discovered by Knight et al. for neutral sodium clusters b) and by Katakuse et al. for positively charged silver clusters. b) After these findings, it became clear that the abundant neutral and ionic cluster of many kinds of metals in mass spectra could be explained in terms of the electronic-shell structure depending on the delocalized electron orbital. b) Other series of magic numbers have been found and rationalized using similar arguments. b) For instance, in the case of a group 0 rare gas, their abundant clusters were explained in terms of an atomic-shell structure depending on close-packed atoms, which belong to a sequence of sphere-like geometric structure (outer form is an icosahedron). These atoms bind weakly together by van der Waals forces.

The present experiment was performed to obtain answers to the following two questions. Firstly, to count the total number of valence electrons at given magic numbers. IIIB metal positively and negatively charged cluster ions, i.e., Zn+, Zn-, Cd+, Cd− were observed using secondary ion mass spectrometry (SIMS). b) Their abundant clusters were well explained in terms of the electronic-shell model. They have a difference of ±1 in the number of total s-valence electrons at experimentally determined magic numbers which agree with the theoretical shell closing number (2, 8, 20, 34, 40, 58, ...).

a) Department of Physics, Faculty of Science, Osaka University (1–16 Machikaneyama-cho, Toyonaka, Osaka 560, Japan)
b) Department of Earth and Space Science, Faculty of Science, Osaka University (1–1 Machikaneyama-cho, Toyonaka, Osaka 560, Japan)
Zinc and Cadmium consist of an ion core and two s-valence electrons, therefore their neutral clusters can possess an even number of valence electrons. On the contrary, ion clusters can possess odd number of valence electrons, since ionization adds or subtracts one electron from the total number of valence electrons in the neutral clusters. This is the reason for the $\pm 1$ difference mentioned above.

In the case of zinc-cesium and cadmium-cesium cluster ions, they are expected to be able to possess an even number of valence electrons, since the cesium atom has one valence electron and zinc and cadmium atoms have two valence electrons. If the electronic-shell model could be applied to zinc-cesium and cadmium-cesium positive cluster ions, their total number of valence electrons at experimentally determined magic number should agree with the theoretical shell closing numbers.

Secondly, to investigate abundance distribution between IIB-cesium binary clusters. It is well known that atoms belonging to the same group possess similar chemical properties. For example, for IB metal clusters the magic numbers of both positively- and negatively-charged cluster ions, i.e., Cu$_n^+$, Cu$_n^-$, Ag$_n^+$, Ag$_n^-$, Au$_n^+$, Au$_n^-$ observed by SIMS experiments, were well explained in terms of the electronic-shell model. It can be concluded that they are jellium type clusters. We can convincingly assume that clusters composed of IB group atoms have the same properties.

Zinc, cadmium and mercury belong to the group of IIB metals. We observed a size distribution of mercury-cesium positively-charged cluster ions, [Hg$_n$Cs]$^+$, for small clusters with $n<30$, a step-like feature was observed in the abundance distribution. The peaks of [Hg$_n$Cs]$^+$ which were significantly more intense than their neighbors were observed at $n=4, 6, 8, 12, 18, 22, 25, 28$, and $31$. From the view point of magic numbers, for total number of atoms larger than 13, i.e. 13, 19, 23, 26, 29, and 32 coincided with the number of spheres filling up a doubleicosahedral structure. The number of atoms at experimentally magic numbers was quite similar to those of a group 0 rare gas, such as Ar$_n^+$, Xe$_n^+$, for clusters larger than $n=40$ a smooth periodic variation was observed. The size distribution of [Hg$_n$Cs]$^+$ ions in this range ($n>40$) provided information on the electronic-shell closing effect of neutral mercury clusters, Hg$_n$. The magic numbers (47, 70, 100, 132, 137, 170, 223, 280, 348, 430, 528, 648, and 764) were observed: for Hg$_n$ as shown in ref. 26. The abundant neutral clusters, Hg$_n$, explained in terms of the electronic-shell structure, were reflected in the undulated abundance pattern of cluster ions, [Hg$_n$Cs]$^+$. In this study we intend to investigate whether cadmium-cesium and zinc-cesium cluster ions have similar properties to mercury-cesium cluster ions.

2. Experimental

Cluster ions were produced by the bombardment of Cs$^+$ ions onto an initially pure metal sheet of either cadmium or zinc. The primary cesium ions were produced using a thermal ion source (ANTEK 160-250B, Palo Alto, CA, USA) that was floated through 15 kV above the target potential. The primary ion current on the sample tip was approximately 0.1 $\mu$A. The sputtered cluster ions were accelerated to 15 kV. Mass analyses was performed using a grand-scale sector mass spectrometer (radius of magnet, 1.25 m, maximum flux density of magnet, 1.8 T), of which the field arrangement is QMQHC (Q— denotes quadrupole lens. H— homogeneous magnetic sector. C— cylindri-
cal electric sector). In order to increase the amount of electrons arriving at the first dynode of the 16-stage electron multiplier (Hamamatsu Photonics Model No. R667, Hamamatsu, Japan), an additional conversion dynode was used. Mass-analyzed ions were post accelerated through 11 kV after passing through the detector slit. Mass spectra were recorded with a data system (JEOL Model No. JMA-DA5000, Akisima, Japan) by scanning the magnet current in a linear mode.

The determination of the composition of observed cluster ions was performed as follows, (1) Mass calibration is carried out using cluster ions of cesium iodide, [(CsI)ₙCs]⁺. (2) Isotopic distribution of cluster ions was detected at unit mass resolution in the low mass region. (3) We then estimated the probable composition of clusters. (4) Calculation of isotopic patterns of clusters was performed to unit mass resolution (10% valley) using the IUPAC isotopic compositions of the elements 1991. Mass value were employed according to the 1983 atomic mass table. (5) The composition of elements of each cluster ion was assigned by comparison of the observed isotopic pattern (2) with the calculated pattern for the process (4). This method was repeated for each isotope pattern of cluster ions. (6) For high mass cluster ions there was insufficient mass resolution to resolve each component. Thus we assume that cluster ions in the high mass region are of the same kind as in the low mass region. To confirm this latter assumption we calculate a centroid from the mass spectra recorded, for each isotope series of a given cluster ion size and compare that value with the centroid predicted from the weighted sum of the relative atomic masses for that clusters predicted by process (5). If they agree then the composition of the cluster can be determined.

3. Results

3.1 Cadmium-cesium clusters

We obtained the mass spectra of cadmium-cesium positively-charged cluster ions. Figure 1 shows a typical mass spectrum of cadmium-cesium cluster ions, m/z=300-3,600. The most abundant ions those containing a single cesium atom, [CdₙCs]⁻, are also referred to as the single cesium group. Other cluster ions such as the double cesium group, [Cd₂Cs₂]⁺, and cadmium-cesium-oxide, [CdₙCsₙO]⁻, are also observed. We focus our analysis on peaks of the single cesium group, [CdₙCs]⁺. Peaks of the double cesium group, [Cd₂Cs₂]⁺, and cadmium-cesium-oxide, [Cd₂CsₙO]⁺, are not critically discussed. We can distinguish between peaks of the single cesium group, [CdₙCs]⁺, and those of the double cesium group, [Cdₙ₋₁Cs₂]⁺, because they have sufficient mass differences. In the region n<30, the peaks of [CdₙCs]⁻, which are somewhat more intense than their neighbors, are observed at n = 4, 7, 10, 13, 15, 17, 20, 23, 25, 27, and 29, as shown in Fig. 1. A step-like feature is observed at n = 4, 10, 20, and 29.

3.2 Zinc-cesium clusters

We obtained the mass spectra of zinc-cesium positively-charged cluster ions. Figure 2 shows a mass spectrum of zinc-cesium cluster ions, m/z=620-2,120. The most abundant ions are the single cesium group, [ZnₙCs]⁻. Here, it should be noted that some sizes of double cesium ions, [Znₙ₋₂Cs₂]⁺, have considerable abundance and their peaks overlap with those of the single cesium group, [ZnₙCs]⁺, as is seen in Fig 2. Fortunately, an isotopic peak pattern of our unit mass resolution spectra shows that the abundance
Fig. 1. A mass spectrum of cadmium-cesium cluster ions, \( m/\lambda = 300-3,600 \). Peaks are somewhat more intense than their neighbors are observed at \( n = 4, 7, 10, 13, 15, 17, 20, 23, 25, 27, \) and 29. A step-like feature is observed at \( n = 4, 10, 20, \) and 29.

Fig. 2. A mass spectrum of zinc-cesium cluster ions, \( m/\lambda = 620-2,120 \). Peaks of \([\text{Zn}_{10}\text{Cs}]^+, [\text{Zn}_{17}\text{Cs}]^+\), \([\text{Zn}_{20}\text{Cs}]^+, [\text{Zn}_{29}\text{Cs}]^+, [\text{Zn}_6\text{Cs}_2]^+\), and \([\text{Zn}_9\text{Cs}_3]^+\) are somewhat more intense than their neighbors.

of \([\text{Zn}_6\text{Cs}_2]^+\) is larger than that of \([\text{Zn}_{17}\text{Cs}]^+\). This point will be described in a chapter of a discussion. Other cluster ions such as the triple cesium group, \([\text{Zn}_{n-4}\text{Cs}_3]^+\), and zinc-cesium-oxide, \([\text{Zn}_n\text{Cs}_m\text{O}_i]^+\), are also observed. However, their ions have negligibly small abundance. Their peaks are not furnished with critical commentary. The peaks of \([\text{Zn}_{10}\text{Cs}]^+, [\text{Zn}_{17}\text{Cs}]^+, [\text{Zn}_{20}\text{Cs}]^+, [\text{Zn}_{29}\text{Cs}]^+, \) and \([\text{Zn}_9\text{Cs}_2]^+\) is somewhat more intense
than their neighbors as shown in Fig. 2.

4. Discussion

4.1 Total number of valence electrons

In the case of cadmium-cesium cluster ions, the total numbers of valence electrons of 8 ([Cd$_4$Cs]$^+$), 20 ([Cd$_{10}$Cs]$^+$), 34 ([Cd$_{17}$Cs]$^+$), 40 ([Cd$_{20}$Cs]$^+$), and 58 ([Cd$_{29}$Cs]$^+$) agree with the theoretical electronic-shell closing numbers predicted in terms of the shell-closing effect of s-valence electrons which are bounded in a finite square well potential with round edges, respectively. Their magic numbers can be clearly explained by the model originated from the electronic-shell.

In the case of zinc-cesium cluster ions, the magic number for $n = 10$ ([Zn$_n$Cs]$^+$) and $n = 11$([Zn$_{n-2}$Cs$_2$]$^+$) is generated by the electronic-shell (shell closing number, 20). The next intense peak of [Zn$_{20}$Cs]$^-$ is presumed to be one of the double cesium group of cluster ions, [Zn$_{19}$Cs$_2$]$^-$, which corresponds to an electronic shell closing number of 40. The magic numbers of $n = 17$ ([Zn$_n$Cs]$^+$), $n = 20$, and $n = 29$ correspond to the electronic

![Fig. 3. Comparison of observed mass spectra and calculated isotope patterns. (a), (b), (c), and (d) are calculated isotope patterns of Zn$_{11}$, Zn$_{19}$, Zn$_{11}$Cs, and Zn$_{19}$Cs$_2$, respectively. The patterns are calculated under 500 mass resolution (10% valley). (e) is an observed mass spectrum around mass number = 854. In case of (d) and (e), even mass number peaks are found to be larger than odd mass number peaks.](image-url)
shell closing number of 34, 40, and 58, respectively.

We explain how to distinguish $[\text{Zn}_8\text{Cs}_2]^+$ and $[\text{Zn}_{11}\text{Cs}]^-$. We concentrated an observing the most abundant cluster ions. The mass spectrometer was operated under conditions of unit mass resolving power around $[\text{Zn}_{11}\text{Cs}]^+$. Though it was not possible to separate $[\text{Zn}_9\text{Cs}]^-$ and $[\text{Zn}_{10-2}\text{Cs}_2]^+$ in mass, the information about an abundance of them could be known fortunately. We paid special attention to the peak height of cluster ions. Zinc isotopes have larger abundance at even mass number than odd mass numbers. Thus zinc clusters, composed of zinc isotopes, are abundant at even mass numbers for cluster size $n<74$. For one example, Figs. 3(a) and 3(c) are calculated isotope patterns of $\text{Zn}_{11}$ and $\text{Zn}_9$, respectively. Both patterns are calculated under 500 mass resolution (10% valley). The isotope patterns show larger abundant peaks at even mass numbers than odd mass numbers. Cesium is a monoisotopic element with an odd mass number 133. Therefore, isotopic peaks of $[\text{Zn}_9\text{Cs}]^-$ should have larger abundance of odd mass numbers than that of even mass numbers. On the contrary, isotopic peaks of $[\text{Zn}_{10-2}\text{Cs}_2]^+$ should have larger abundance at even mass numbers. For one example, Figs. 3(b) and 3(d) are calculated isotope patterns of $\text{Zn}_{11}\text{Cs}$ and $\text{Zn}_9\text{Cs}_2$, respectively. Both patterns are calculated under 500 mass resolution (10% valley). The isotope pattern of $\text{Zn}_9\text{Cs}_2$ shows larger abundant peaks at even mass numbers than odd mass numbers whilst the isotope pattern of $\text{Zn}_{11}\text{Cs}$ shows larger abundant peaks at odd mass numbers than even mass numbers. At mass corresponding to the positions of isotopes, each mass is composed of two overlapping series of isotope peaks of the individual clusters corresponding to $[\text{Zn}_9\text{Cs}_2]^+$ and $[\text{Zn}_{11}\text{Cs}]^-$.

The mass spectra recorded at unit mass resolution show odd even alternation as a function of mass number around mass number $=854$ (Fig. 3(e)), even mass number peaks were found to be larger than odd mass number peaks. This is evidence that the abundance of $[\text{Zn}_9\text{Cs}_2]^+$ is larger than that of $[\text{Zn}_{11}\text{Cs}]^-$. In the same way, it was confirmed that the abundance of $[\text{Zn}_{10}\text{Cs}]^+$ is larger than that of $[\text{Zn}_9\text{Cs}_2]^+$, also.

For small cluster size, $n<30$, the magic number of cadmium-cesium and zinc-cesium positively-charged cluster ions proves that their stability can be interpreted in terms of the total number of s-valence electrons. IIB metal atoms have two s-valence electrons whilst cesium has one s-valence electron. In the case of the single cesium group, $[\text{Zn}_n\text{Cs}]^+$ and $[\text{Cd}_n\text{Cs}]^+$ these are able to possess an even number of valence electrons and the total number of s-valence electron agrees with the electronic-shell closing number. We can conclude that the electronic-shell structure clearly appears in the mass spectral pattern of the single cesium groups, $[\text{Zn}_n\text{Cs}]^+$ and $[\text{Cd}_n\text{Cs}]^+$. Considering the ionization process of SIMS experiments, we can only observe cluster ions that are ionized during a process of cluster production. It is reasonable to observe the singly-charged cluster ions of the double cesium group which have an odd number of s-valence electrons, because the neutral cluster of the double cesium group has an even number of s-valence electrons. This situation is similar to those of IIB metal positive and negative cluster ions (Zn$^+$, Cd$^+$). The large abundance of $[\text{Zn}_9\text{Cs}_2]^-$ gives direct evidence for the electronic-shell stabilizing zinc-cesium cluster ions. This result lends support that a spherical potential in zinc and cadmium-cesium clusters does not distinguish the 6s valence electrons of cesium atoms from the 5s and 4s valence electrons of IIB metal.
Zinc-cesium and calcium-cesium positively-charged cluster ions were observed by SIMS experiments using a Cs+ bombardment-type ion source. For cluster sizes n > 30, additional experiments showed that the cluster ions exhibit a high performance primary ion source. The clusters are formed by an ion impact on the target material, followed by an ionization process. The positive ions are accelerated and then detected.

Results:

1. **Concentration**: The concentration of zinc-cesium and calcium-cesium cluster ions is higher than that of other cluster ions. The high concentration is attributed to the high volatility of cesium and calcium.

2. **Size Distribution**: The size distribution of zinc-cesium and calcium-cesium cluster ions was determined using secondary ion mass spectrometry (SIMS). The size distribution is shown in Table 1.

<table>
<thead>
<tr>
<th>Size Distribution (n)</th>
<th>[Zn(Cs)n+]</th>
<th>[Ca(Cs)n+]</th>
<th>[Cs(Cs)n+]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>7</td>
<td>7</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>8</td>
<td>8</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>9</td>
<td>9</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 1: Size Distribution of Zn-Cs and Ca-Cs Positive Cluster Ions Using Secondary Ion Mass Spectrometry.
the total number of valence electrons at their magic number corresponds well to the theoretical electronic-shell closing number. We conclude that zinc-cesium and cadmium-cesium cluster ions are jellium type clusters. The origin of their magic numbers differs from that of mercury-cesium clusters, \([\text{Hg}_n\text{Cs}]^+\), in the same region of cluster size \(n<30\). Mass spectrometric studies can reveal that the origin of structure of IIB metal-cesium positively-charged cluster ions is attributed to the number whether atoms or electrons.

Acknowledgment

This work was partially supported by a Grant-in-Aid for Scientific Research (No. 03246103), from the Ministry of Education. Science, and Culture of Japan.

References

Size Distribution of Zn-Cs and Cd-Cs Positive Cluster Ions Using Secondary Ion MS


**Keywords**
Secondary ion mass spectrometry
Cadmium-cesium positively charged cluster ion
Zinc-cesium positively charged cluster ion
Electronic-shell structure