The stability of multiply charged vanadium, niobium and tantalum clusters

Naoaki Saito *, Kazuyoshi Koyama, Mitsumori Tanimoto

Electrotechnical Laboratory, 1-1-4, Umezono, Tsukuba 305-8568, Japan

Received 29 June 1998; in final form 10 November 1998

Abstract

We have studied the stability of multiply charged vanadium, niobium and tantalum clusters with charges up to \( z = 4 \). Although the multiply charged clusters are less stable compared with the predictions of the symmetric liquid droplet models, the experimental results can be explained well by an asymmetric fission model assuming an emission of an atomic ion.

1. Introduction

The stability of multiply charged small clusters is one of the fundamental subjects in the field of cluster research. Depending on cluster size, charge state, and material, multiply charged clusters may be stable, meta-stable or unstable. In some cases, fission is caused by the Coulomb repulsion of like charges concentrated in a cluster smaller than a critical size. Several experimental results on metal clusters have been summarized in Ref. [1]. The stability of the multiply charged alkali metal and alkaline earth metal clusters was studied up to \( z = 7 \) [2–4]. As for transition metal clusters, most of the studies were only on a doubly charged state. In the present Letter, we report on the stability of multiply charged vanadium, niobium and tantalum clusters up to \( z = 4 \).

2. Experimental and results

The low-pressure condensation cluster sources with ovens have been used to produce continuous cluster beams of the materials with sufficiently high vapor pressure [2–5]. Tast et al. have recently introduced laser ablation targets into these sources to produce clusters with low vapor pressure. The condensation source based on the oven and laser vaporization technique can produce clusters of most of materials under a wide range of growth conditions in a source of a relatively large volume [6]. We have recently developed a similar condensation source [7], which has been used for the present study.

* Corresponding author. Fax: +81 298 54 5754; e-mail: naoaki@etl.go.jp

0009-2614/99/$ - see front matter © 1999 Elsevier Science B.V. All rights reserved.

PII: S0009-2614(98)01300-1
The vanadium, niobium and tantalum clusters were produced in a low-pressure He gas using the 2nd harmonic wave of a Nd:YAG laser. The cluster source with a nozzle was kept in room temperature. The clusters were photoionized with a 6.4 mJ, 5 ns, ArF excimer (6.42 eV) laser pulse focused onto the neutral cluster beam. The mass spectra of the positively ionized clusters were measured by a time-of-flight mass spectrometer (TOFMS) as a function of the ArF excimer laser fluence. The present TOFMS is a table top size (< 1.8 m long) and a high mass resolution up to 4000 is achieved [7]. The ArF excimer laser can ionize M_n clusters (M = V, Nb, Ta; n > 2) by a single-photon process since their first ionization potentials are lower than 6.42 eV [8–10]. The multiply charged clusters are produced by a multi-photon process.

Niobium has a single natural atomic isotope. Both vanadium and tantalum have two isotopes but the dominant isotopes are much more abundant (99.75% of ^{51}V and 99.988% of ^{181}Ta) than the minorities. As the mass spectrometer resolves the mass-to-charge ratio m/z one cannot distinguish between multiply charged clusters with the same value of m/z for a given element.

Typical mass spectra of the niobium clusters (Nb_n^{+}) at various ionizing laser fluences are shown in Fig. 1. Depending on the laser fluence, different charged states of the clusters appeared. Only singly charged niobium clusters (Nb_n^{+}) were observed at a low laser fluence as seen in Fig. 1a. These clusters were ionized by a single photon of the ArF excimer laser. The satellite peaks were due to the presence of small contamination of Nb_{C}^{+}.

As for a magic number like behavior, Nb_{7}^{+} and Nd_{14}^{+} are abundant. Doubly charged clusters (Nb_{2}^{2+}) and triply charged clusters (Nb_{3}^{3+}) appeared at the higher laser fluence as seen in Fig. 1b,c. The peaks observed exactly

Fig. 1. Mass spectra of niobium clusters at various ionizing ArF laser fluences. (a) 19 mJ/cm² (b) 30 mJ/cm² (c) 63 mJ/cm².
halfway between the Nb\(^+\) peaks are due to Nb\(^{2+}\). The peaks located exactly 1/3 and 2/3 of the interval of the Nb\(^+\) peaks correspond to Nb\(^{3+}\). Doubly charged niobium monomers (Nb\(^{2+}\)) were also observed. With increasing ionizing laser fluence (Fig. 1a→b→c), detected counts of the small clusters increase rapidly. Notice that the vertical scales in Fig. 1a–c are different. Monomer and dimer ions (Nb\(^+\), Nb\(^2+\)) were much more abundant and most of them were produced by evaporation from the large clusters within an ionizing laser pulse duration.

A typical mass spectrum of the tantalum clusters (Ta\(_n^{+}\)) is shown in Fig. 2. Notice that the vertical scale of the counts is plotted in a logarithmic form. In Fig. 2a, the first set of the mass peaks corresponds to Ta\(_n^{+}\). The second, third and fourth sets are those of Ta\(_n^{2+}\), Ta\(_n^{3+}\) and Ta\(_n^{4+}\), respectively. Again the monomer and dimer ions (Ta\(^+\), Ta\(^{2+}\)) were much more abundant and the doubly charged monomers (Ta\(_n^{2+}\)) were also observed. In Fig. 2b, we see the threshold region for the appearance of Ta\(_n^{2+}\) and Ta\(_n^{3+}\) in an expanded scale. Stepwise appearances of the peaks of Ta\(_n^{2+}\) and Ta\(_n^{3+}\) were observed. The satellite peaks just beside Ta\(_n^{+}\) are due to the presence of small contamination of Ta\(_nC^{+}\). Multiply charged clusters, Ta\(_n^{2+}\), with \(z = 1, 2, 3, 4\) are clearly distinguishable in Fig. 2c.

The ArF laser heats highly charged large clusters and then the clusters shrink down in size by evaporation, resulting in an unstable state which undergoes fission. For a given charge state \(z\), multiply charged clusters above the appearance size were observed. The minimum appearance sizes \(n^\text{app}\) were determined by careful measurement at the different laser fluences up to 70 mJ/cm\(^2\). As for vanadium clusters, the minimum

![Figure 2](image-url)
appearance size only of \( z = 2 \) could be specified since vanadium is susceptible to oxygen contamination and the peaks of the triply charged clusters, \( V_{3n+1}^{3+} \) and \( V_{3n+2}^{3+} \), could not be distinguished from the oxide peaks of \( V_o^{n+} \) and \( V_{2n}O^{2+} \), respectively.

### 3. Discussion

The minimum appearance sizes \( n_{app}^{pp} \) of the multiply charged clusters are summarized in Table 1. First, we compare \( n_{app}^{pp} \) with the prediction of the Rayleigh’s liquid droplet model, which is expressed as

\[
n_{app}^{Rayleigh} = \frac{e^2}{16 \pi \sigma r_S^2} z^2,
\]

where \( \sigma \) is the bulk surface tension and \( r_S \) the Wigner–Seitz radius of the constituent element. The critical size is determined by the balance between the Coulomb energy with a parameter of \( e^2/2r_S \) and the surface energy with a parameter of \( 4\pi \sigma r_S^2 \). Therefore, the dependence of \( n_{app}^{Rayleigh} \) on \( z \) is specified only by the parameter \( s \) of each constituent element. The \( n_{app} \) versus \( z \) plot is given in Fig. 3, which shows the \( z \)-dependence of \( n_{app}^{Rayleigh} \). The Rayleigh’s model, assuming the symmetric fission, predicts the lowest limit of the critical size. Asymmetric fission channels may be dominant for vanadium, niobium and tantalum clusters.

Asymmetric fission was observed for doubly charged clusters of alkali metals and some noble metals [11]. Bréchignac et al. introduced a unimolecular model based on the liquid droplet model and explained the observed critical sizes for alkali metal clusters [12,13]. The total energy of the cluster of size \( n \) and charge \( z \) is given by

\[
E(n,z) = -a_n n + 4\pi \sigma r_S^2 n^{2/3} + zW_w + \left[ z^2 + (2\alpha - 1)z \right] \frac{e^2}{2r_S n^{1/3}}
\]

where \( a_n \) is the volume parameter, \( W_w \) the bulk work function and, classically, the coefficient should equal 1/2. Somewhat different expressions for the last term of Eq. (2) may be given depending on the models but the difference becomes less important for large values of \( z \) and \( n \). A decrease in the energy accompanying a fission process from a mother cluster \( M_{n-p}^{z} \) to daughters, \( M_{p}^{z} \) and \( M_{p}^{z} \), can be written as follows:

\[
\Delta E(n,z,p,q) = E(n,z) - E(p,q) - E(n-p,z-q) = 4\pi \sigma r_S^2 \left[ n^{2/3} - (n-p)^{2/3} - p^{2/3} \right]
\]

\[
\quad + \frac{e^2}{2r_S} \left[ \frac{z^2 + (2\alpha - 1)z}{n^{1/3}} - \frac{(z-q)^2 + (2\alpha - 1)(z-q)}{(n-p)^{1/3}} - \frac{q^2 + (2\alpha - 1)q}{p^{1/3}} \right].
\]

\( \Delta E(n,z,p,q) \) is a function containing the Coulomb term and the surface term with parameters of \( e^2/2r_S \) and \( 4\pi \sigma r_S^2 \), respectively. The expression of the critical size determined by \( \Delta E(n,z,p,q) = 0 \), again contains a

<table>
<thead>
<tr>
<th>( n_{app}^{pp} )</th>
<th>V</th>
<th>Nb</th>
<th>Ta</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n_{app}^{pp} )</td>
<td>19 (−1)</td>
<td>13 (−1)</td>
<td>7 (−1)</td>
</tr>
<tr>
<td>( n_{app}^{pp} )</td>
<td>−</td>
<td>70 (± 6)</td>
<td>36 (± 3)</td>
</tr>
<tr>
<td>( r_S (\text{Å}) )</td>
<td>1.49</td>
<td>1.63</td>
<td>1.63</td>
</tr>
<tr>
<td>( \sigma (\text{eV}/\text{Å}^2) )</td>
<td>0.106</td>
<td>0.127</td>
<td>0.178</td>
</tr>
<tr>
<td>( \sigma r_S^2 (\text{eV} \text{Å}) )</td>
<td>0.351</td>
<td>0.550</td>
<td>0.771</td>
</tr>
</tbody>
</table>
Fig. 3. The minimum appearance size $n_{\text{app}}$ as a function of the charge state $z$. Although the observed minimum appearance sizes are far above the Rayleigh limit (dashed lines), they can be reproduced well by the asymmetric fission model assuming an emission of an atomic ion dotted lines.

The single parameter for each constituent element $\sigma r_s^3$ as in the Rayleigh’s model described above. The values of the critical size for alkali metal clusters were given numerically in Ref. [12]. Here we give the analytical formula of the critical sizes for some cases. In the case of the symmetric fission ($p = n/2, q = z/2$), the critical size is given as follows:

$$n_{\text{cr}}^c = \frac{e^2}{16\pi\sigma r_s^3} \left\{ \left(2^{1/3} (2^{1/3} + 1) z^2 + 2(2\alpha - 1) z \right) \right\}$$

which gives a slightly larger value than that of the Rayleigh’s model. In the case of $n_{\text{cr}}^c \gg p$, the critical size is

$$n_{\text{cr}}^c = \left\{ \frac{2z - q - (2\alpha - 1) + \frac{2}{3} \frac{8\pi\sigma r_s^3 p}{e^2} q}{\frac{8\pi\sigma r_s^3 p}{e^2} q + q - (2\alpha - 1)} \right\}^3 \quad (n_{\text{cr}}^c \gg p)$$

which is approximately proportional to $z^4$ ($x \approx 3$) and predicts that a fission process yielding a daughter of a lowest $p(=1)$ is a dominant channel.

The magic number like behavior for $M_n^+$ ($M = V, Nb, Ta$) was observed in the present experiment as already reported in Ref. [14]. The time-resolved emission measurements attribute this effect (‘the seven effect’) to a statistical rate process caused by a laser ionization [15]. The metal clusters tend to lose a single atom at a time (evaporation). The collision-induced dissociation measurement for small singly charged niobium clusters suggests that the primary dissociation pathway at low collision energies is an emission of a single atom, whereas sequential emission of atoms occurs at higher energy [16]. As a dominant fission process, we therefore consider an asymmetric fission process of a mother cluster, $M_n^{(x-)}$, to a daughter atomic ion $M^+$ and a cluster ion, $M^{(x-1)}_{n-1}^+$ for vanadium, niobium and tantalum clusters. We estimate the critical size, $n_{\text{cr}}^c$, corresponding to $p = q = 1$. The calculated results are plotted in Fig. 3 and can reproduce the experimental results. Although vanadium, niobium and tantalum clusters have large cohesive energies and large surface tensions $\sigma$, it is clear that the stability is determined only by $\sigma r_s^3$. The asymmetric model described above may explain the experimental results for the large clusters quantitatively. On the other hand, the observed ionization potentials of vanadium, niobium and tantalum clusters with small sizes are in disagreement with those predicted by the liquid droplet models [8–10] since the transition metals have both s- and d-electrons as valence electrons. The
d-valence electrons are localized within the atoms of the clusters and cause an anisotropic bonding. In order to study the fission process in more detail, a further improved model must be developed, taking into account the distinct geometrical and electronic structure of each cluster.

From a theoretical point of view, unstable, meta-stable and stable states are expected for the multiply charged clusters. We determined the critical size by comparing the initial energy of the charged non-deformed clusters with the final energy of non-interacting fission products. The critical size corresponds to that of between the stable state and others. The lowest energy barrier between the initial and final states (fission barrier) corresponds to the critical size between the unstable and meta-stable states. It is difficult to distinguish unstable, meta-stable and stable states exactly from one another by measurements, since a meta-stable state depends on temperature, an excitation and a life-time.

Doubly charged niobium clusters, Nb\textsuperscript{2+}\textsubscript{n} (2 \leq n \leq 15), were observed by an electron impact ionization method [17]. Although the mass peaks of Nb\textsuperscript{2+}\textsubscript{n+1} could not be distinguished from those of Nb\textsubscript{2}O\textsuperscript{+} in the spectrum, collision induced dissociation measurements indicate the presence of long-lived Nb\textsuperscript{2+} and Nb\textsuperscript{3+}. In the present measurement, Nb\textsuperscript{2+} (3 \leq n \leq 11) was not observed. This discrepancy may be attributed to the existence of the meta-stable clusters. We have used the laser fluence up to 70 mJ/cm\textsuperscript{2}. At such high intensities, fission, fragmentation and evaporation of the clusters are expected to occur and only the multiply charged clusters in a stable state may be observed. If the small, cold clusters are ionized without introducing a significant amount of excess energy, long-lived meta-stable clusters may survive. The observed minimum appearance size may also depend on the time scale. In the present measurements, most of the observed multiply charged clusters are stable for longer than a few tens of microseconds which corresponds to the time-of-flight before entering the reflector. Another possibility for explaining the discrepancy is the strong anisotropic bonding of the dimer and trimer. In the present work, doubly charged small clusters were produced by a shrinkage in size due to atomic evaporation from larger clusters. If the shrinking clusters have a passage through an unstable region of a mass size, the larger clusters cannot reach the states of the doubly charged dimer and trimer.

4. Conclusions

We have investigated the stability of the multiply charged vanadium, niobium and tantalum clusters and determined the minimum appearance sizes. An asymmetric fission model assuming an emission of an atomic ion from a mother cluster reproduces the experimental results well.

Acknowledgements

Some basic parts of our experimental setup have been developed based on that of the Max-Planck-Institut für Festkörperforschung, Stuttgart. The authors would like to thank Dr. T.P. Martin and Mr. H. Schaber for their helpful advice. NS also wishes to express his thanks to Dr. N. Malinowski, Dr. I.M.L. Billas, Dr. S. Frank, Dr. F. Tast, Dr. M. Heinebrodt and Dr. K. Wirth for their valuable discussions.

References

[7] N. Saito et al., to be published.