Calcium ion generation from calcium iodide by surface ionization in mass spectrometry

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Abstract

The process of calcium ionization on a rhenium filament was studied at different heating conditions of the evaporation filament (EF) loaded with a CaI_2 sample. The analysis indicated that three different ionization processes are involved in the ionization; (1) $CaI_2 \rightarrow Ca^+$, (2) $CaI \rightarrow Ca^+$, and (3) $Ca \rightarrow Ca^+$. Reaction (1) appears at the low temperatures of EF, reaction (2) is dominant in the medium temperature region, and reaction (3) appears at the high temperature of EF. These facts suggest that the EF assists the dissociation of CaI_2. Experiments are extended to the isotopic ratio measurement using different materials of Ta, Re, and Pt for the evaporation filament. (Int J Mass Spectrom 193 (1999) 29–34) © 1999 Elsevier Science B.V.

1. Introduction

Anomalous isotope effects were found in odd number isotopes of uranium, U-233 and U-235, in the U(IV)–U(VI) chemical exchange system [1]. This phenomenon was elucidated as the interaction between outer *s* electrons and the nuclei charge distribution in the chemical isotope exchange equilibrium. Although such effects are expected to appear in the chemical exchange of heavy elements such as lanthanide and actinide elements, the interactions between electrons and nuclei may cause another type of isotope effect that have never considered before. The elements involving many odd and even isotopes are very interesting materials from the view of the isotope effect study, and calcium is a typical element consisting of many isotopes. For such studies, isotope analysis by mass spectrometry is the most important measure and the precise method should be developed on the calcium isotope ratio measurement.

Historically, a surface ionization utilizing double or triple filaments has been used for the isotope analysis of calcium [2,3]. In the conventionally recommended process, a calcium sample is fed in the form of CaI_2 and the chemical form of CaI_2 is changed to CaO at a very high heating condition of the sample evaporation filament. In a previous paper [4] it was proposed that the isotope analysis at lower temperatures of the evaporation filament where calcium is estimated to evaporate in the form of CaI_2 before the sample is changed to CaO. This method is

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very convenient but the mechanism of the ionization has not yet been studied.

Kawano and co-workers reported that the chemical form of the sample affects the ionization efficiency [5]. In a previous work [6] it was also found that copper, with a very high ionization potential of 7.7 eV, is ionized at a relatively low heating condition of evaporation and ionization filaments, and the low heating condition is appropriate to produce very stable ion beams. In general, isotope effects in ionization are small but isotope fractionation occurs in the evaporation process even at very high temperatures; the lighter isotope evaporates faster than the heavier [7]. To establish appropriate conditions for the isotope analysis, we have to know the mechanism of the ionization. Thus, the present work focuses on the mechanism of the calcium surface ionization producing Ca^+ ions from a CaI_2 sample and the calcium isotopic ratio measurement using different materials of evaporation filaments.

2. Theory of the ionization sequence

The surface ionization has been theoretically expressed by the Saha-Langumuir equation,

$$n_+/n_0 = (g_+/g_0) \exp\left[-(\phi_I - W_I)/kT_I\right] \qquad (1)$$

where n_+ and n_0 are the number of the ion and the neutral species, g_+ and g_0 are the statistical weights of the ion and the neutrals, W_I, ϕ_I, k, and T_I are the work functions of the ionization filament surface, the ionization potential, Boltzmann's constant, and the temperature of the filament surface, respectively.

In a previous paper [8], ionization of Li^+ from lithium halides was studied and it was pointed out that the ionization process involves not only ionization from metal but also dissociation of halides compounds. For the purpose of practical analysis, the following equation has been proposed to deal with the ionization process, which includes dissociation steps of the sample compounds:

$$n_+/n_0 = A \exp(-\varepsilon/kT_I) \qquad (2)$$

where ε represents the ionization parameter, A is constant, and n_0 is the neutral atom density. The neutral atom density n_0 is related with the evaporation filament temperature, T_E, as

$$n_0 = (B/kT_E) \exp(-\Delta H/kT_E) \qquad (3)$$

where B is constant and ΔH is the vaporization enthalpy.

The ionization parameter ε is expressed as

$$\varepsilon = \phi_I + \phi_D - W_I \qquad (4)$$

where ϕ_D is the dissociation energy of the chemical compound. In a very special case, such as alkali halides [8,9], ionization may occur simultaneously at dissociation. In such cases, ε is observed as

$$\varepsilon = \phi_{DI} - W_I \qquad (5)$$

where $\phi_{DI} = \phi_I + \phi_D - \phi_e$ is the dissociative ionization potential and ϕ_e is the electron affinity of the halide atom.

The ionization processes of CaI_2 studied in the present work are more complicated than the case of alkali halide since CaI_2 consists of three atoms. The ionization of calcium from evaporated CaI_2 is considered to proceed as

$$CaI_2 \rightarrow CaI + I \rightarrow Ca + 2I \rightarrow Ca^+ + 2I + e^-, \qquad (6)$$
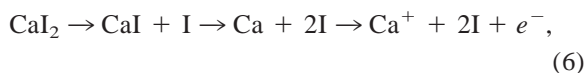
These processes are presented in Fig. 1 with the energy required in each step. The total energy that is needed for ionization via neutral dissociation from the gaseous state is 13.15 eV. Thus, in the case of ionization, including the dissociation of CaI_2 and ionization process, the ionization parameter ε can be expressed as

$$\varepsilon = \phi_I + \phi_{ND1} + \phi_{ND2} - W_I = 8.1 \text{ eV} \qquad (7)$$

where ϕ_{ND1} is the neutral dissociation energy from CaI_2 to CaI, ϕ_{ND2} is the neutral dissociation energy from CaI to Ca and I, and ϕ_I is calcium ionization potential. The value of W_I is assumed to be 5.1 eV for the Re filament.

In the case where Ca^+ is produced from CaI

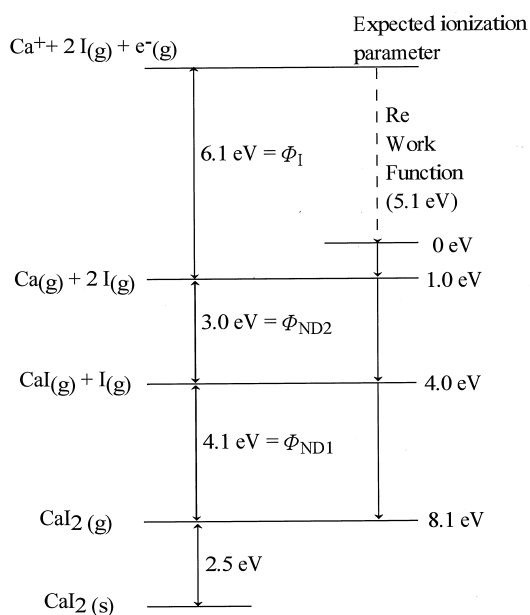Fig. 1. Dissociation and ionization energy for calcium iodide.

Fig. 2. Arrangement of the ionization filament (IF) and evaporation filament (EF) for (a) the study of CaI$_2$ ionization mechanism and (b) the isotope analysis.

molecules adsorbed on or arrived at the ionization filament, ionization takes place as

$$CaI \rightarrow Ca + I \rightarrow Ca^+ + I + e^- \qquad (8)$$

where the ionization parameter ε can be expressed as

$$\varepsilon = \phi_I + \phi_{ND2} - W_I = 4.0 \text{ eV} \qquad (9)$$

If the neutral dissociation is completed on the evaporation filament or in the surrounding area of the ionization filament, ionization of Ca becomes the controlling step of the ionization process, and calcium ionization energy, 6.11 eV, is the energy that should be given on the ionization filament for calcium ion production. The ionization parameter is expressed as

$$\varepsilon = \phi_I - W_I = 1.0 \text{ eV} \qquad (10)$$

It is considered therefore, that ε is observed as the value between 1.0 and 8.1 eV.

3. Experimental

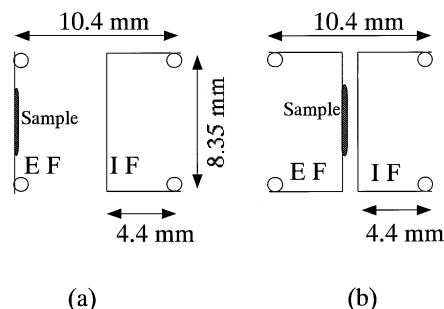The experiments were conducted by using a surface-ionization ion source that consists of double filaments (evaporation and ionization filaments) set in a Finnigan MAT 261 mass spectrometer. The ion currents were detected by a secondary electron multiplier and a Faraday cup collector. The type of filaments shown in the ionization (IF) and evaporation filaments (EF) for surface ionization are illustrated in Fig. 2. The arrangement of Fig. 2(a) was used for the study of surface ionization mechanism, where EF and IF were far enough separated to ensure that the radiation heating does not mutually affect each other. The filament shape of Fig. 2(b) is the regular arrangement for isotope analysis. Tantalum (Ta) filaments (thickness of 0.025 mm and width of 0.75 mm) and rhenium (Re) filaments (thickness of 0.05 mm and width of 0.75 mm) were used for EFs. For ionization, Re filaments were always used. The samples of CaI$_2$ solution were loaded on the evaporation filament and heated to dryness in air. The amount of Ca loaded was about 40 μg in all experiments. Filament temperature, T, was measured at different filament heating currents by a pyrometer through the glass window for the ion source.

4. Results and discussion

4.1. Ionization processes

Since the filament light source is small, the measurement of the temperature by a pyrometer is difficult to be completed in a short time when the heating condition is changed in the ionization experiments.
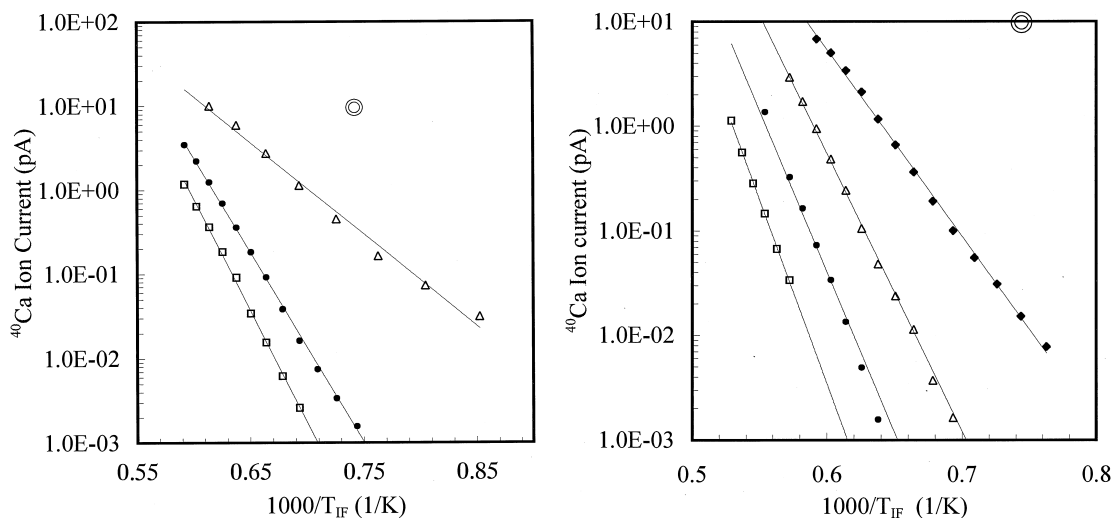
Fig. 3. Observed ion currents of $^{40}Ca^+$ as a function of the ionization filament temperature. Ion currents by using (a) Re EF at 908 (open square), 948 (closed circle), and 987 K (open triangle). (b) Ta EF at 856 (open square), 903 (closed circle), 949 K (open triangle), and 993 K (closed diamond). Concentric circles represent the condition for isotope analysis in both (a) and (b).

Besides, it is impossible to measure the temperature directly by a pyrometer when the temperature is lower than about 1300 K. Then the experiment was conducted to obtain the relation between filament current and the filament temperature as mentioned in Sec. 3.

Based on Stefan-Boltzmann's law, the temperature of the filament is determined by the following equation:

$$T^4 = (1/\sigma S) P = (1/\sigma S)I^2 R$$

where $\sigma = 5.67 \times 10^{-8}$ W m^{-2} K^{-4} is Stefan-Boltzmann constant, S is the filament section, P is the power consumed by the filament, and I is the filament current. The filament resistance R is approximated as

$$R = R_0 + \alpha T,$$

and in practice, we obtain the relation between the measured temperature and the heating current of the filament as

$$T = AI^{2/3} \qquad (11)$$

where A is constant. The relation of observed temperature ($\sim$2200 K) and filament current agree well with Eq. (11). The constant A is decided experimentally by the relation between measured temperature and heating current. All temperatures in the present work were evaluated by using Eq. (11) with monitored current I.

Ion currents of single charged calcium, $^{40}Ca^+$, were observed and plotted as a function of ionization filament temperature, $1/T_I$, in Fig. 3. Fig. 3(a) and (b) show the results of the ionization experiments with the evaporation filaments made of Re and Ta, respectively. The slopes of the plots in Fig. 3 give the ionization parameter, ε, at different evaporation filament temperatures. The observed values of ε, plotted in Fig. 4, show apparent dependence on the evaporation filament temperature. In the case of alkali halides, the role of the evaporation filament is considered to heat the sample for molecule vapor generation as shown in Eqs. (2) and (3), and ε is observed to be independent of EF temperature, T_E. In the present case, however, the parameter ε is decreased as the EF temperature T_E is increased. Apparently EF temperature affects the ionization process. In both cases of the Ta and Re filaments, ε decreases as the temperature of EF increases. Since the measured value of the ionization parameter is 2–7 eV, it is very likely that the process involves three distinct processes of (1) CaI$_2$ $\rightarrow$ Ca$^+$, (2) CaI $\rightarrow$ Ca$^+$, and (3) Ca $\rightarrow$ Ca$^+$, although CaI $\rightarrow$ Ca$^+$ is probably dominant among these pro-
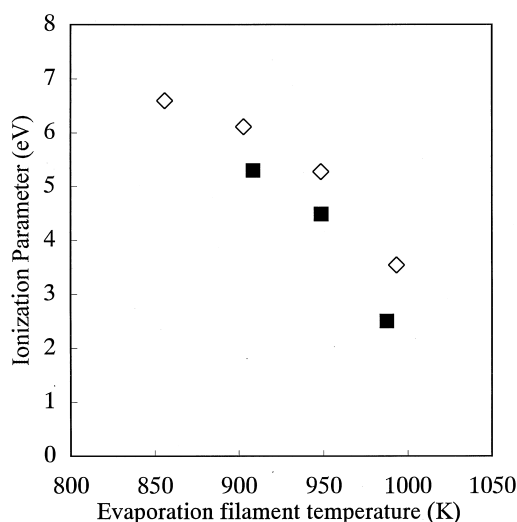
Fig. 4. Ionization parameter ε vs. the temperature of the evaporation filament. The closed square and the open diamond show the ionization parameter by using the Re and Ta evaporation filaments, respectively.

cesses in the regions of the experimental temperatures. From these results, it is also suggested that reaction (3) becomes predominant at very low temperatures of EF and reaction (1) becomes predominant at very high temperatures.

When ions are produced from molecules through dissociation, such as $CaI \rightarrow Ca^+$, the ionization process $Ca \rightarrow Ca^+$ is considered to be sufficiently rapid compared with the dissociation $CaI \rightarrow Ca + I$. Therefore, the dissociation becomes the controlling steps, but the total energy of dissociation and ionization would appear as the ionization energy.

Taking into account the fact that the dissociation degree depends on the filament temperature and material, the parameter ε is possibly expressed as

$$\varepsilon = \phi_I + x\phi_{ND1} + y\phi_{ND2} - W_I, \qquad 0 \leq x, y \leq 1$$
(12)

where the parameters x and y indicate the contribution of dissociations $CaI \rightarrow Ca + I$ and $CaI_2 \rightarrow CaI + I$, respectively. When the temperature of the evaporation filament becomes high, the dissociation is promoted, thus, the parameters x and y would approach zero. It is also seen that ε of Ta is always larger than that of Re. The difference becomes small when the EF

temperature is low. These results apparently indicate that the material property of EF is related to the dissociation degree. The acquired data are not sufficient but the dissociation may be assisted by the work function of the metal surface.

4.2. Isotope ratio analysis

Isotope abundance ratios of Ca were measured by using the filament presented in Fig. 2(b). In the isotope ratio measurements, ion beam intensities of $^{40}Ca^+$ were in the order of 10 pA at the heating conditions of the ionization filament of 2.6–2.7 A (1310–1340 K), and Re evaporation filaments of 0.53–0.58 A (450–480 K) or Ta evaporation filaments of 0.48–0.5 A (460–480 K). The current intensities were almost constant unless the filament conditions were changed. The beam stability, by using different materials of the evaporation filament, was almost the same in each case. The beam intensity at the ionization filament temperature is marked in Fig. 3(a). Since the distance between EF and IF in the isotope ratio measurements as shown in Fig. 2(b) is 1/4 of the distance in Fig. 2(a), the density of the molecules at the ionization filament in Fig. 2(b) is enhanced by 4^3 of the case in Fig. 2(a) on the assumption of the point source. Even if this enhancement factor of 64 is considered, the measured ion beam in the isotope analysis is much larger than that observed in the experiments for ionization mechanism study. By taking the factor of 64, the ionization condition of isotope analysis in Fig. 3 seems to correspond to the EF heating current of $\sim$1.7 A, which is much higher than the actual value of 0.5 A. These facts suggest that the sample is mainly heated by the radiation from the ionization filament. When the sample is mainly heated by the ionization filament, it is expected that the sample is evaporated from the surface.

The chemical exchange isotope effects become very small at high temperature but kinetic isotope effects in evaporation rates are independent of temperature and play an important role in the evaporation of the sample at high temperatures. In general, the light component evaporates easily and the Rayleigh
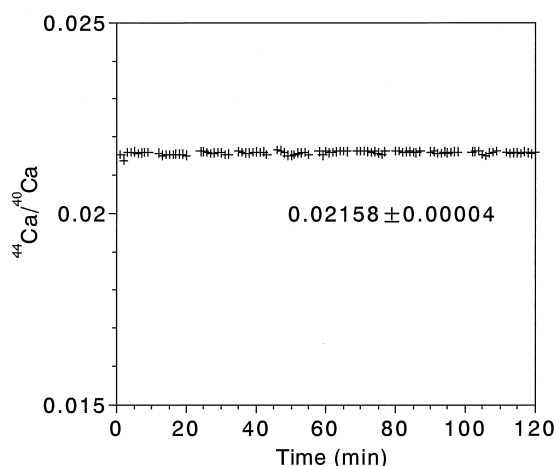
Fig. 5. Time variation of measured isotopic ratio, $^{44}Ca/^{40}Ca$, by using Re evaporation filament.

distillation process takes place when the sample is liquid. To avoid the Rayleigh distillation process in evaporation, the sample should not be totally lique-fied. From the above mentioned viewpoints, the present system, where molecules are expected to be evaporated from the surface of the solid sample, is appropriate for isotope analysis.

Time variation of the isotope ratio, $^{44}Ca/^{40}Ca$, is shown in Fig. 5, which was made by using the Re evaporation filament. The isotope ratio was constant, as shown in Fig. 5 for 2 h. The isotope ratios, $^{44}Ca/^{40}Ca$, determined by using different materials, Re, Ta, and Pt, for EFs are shown in Table 1. Although platinum is the material that has the highest work function, ~5.3 eV, it is not commonly used as a filament because of its low melting point of 2045 K

compared to the melting points of Re and Ta, 3453 and 3269 K, respectively. The observed isotope ratio was independent of the EF materials. This also sup-ports the fact that the evaporation proceeds from the surface of the sample.

5. Conclusion

Process of calcium ionization from CaI_2 was stud-ied with the double filament system. It was found that the apparent ionization parameter, ε, depends on the temperature of the evaporation filament. Theoretically suggested and experimentally confirmed, three differ-ent ionization processes are involved in the ionization; (1) $CaI_2 \rightarrow Ca^+$, (2) $CaI \rightarrow Ca^+$, and (3) $Ca \rightarrow Ca^+$. Reaction (1) appears at the low temperatures of EF, reaction (2) is dominant in the medium temperature region, and reaction (3) appears at the high tempera-tures of EF. The ionization parameter can be ex-pressed as $\varepsilon = \phi_I + x\phi_{ND1} + y\phi_{ND2} - W_I$. The parameters x and y indicate the contribution of disso-ciations $CaI \rightarrow Ca + I$ and $CaI_2 \rightarrow CaI + I$, respec-tively, and they depend on both the temperature and material of the evaporation filament.

Experiments are extended to the isotopic ratio measurement using different materials of Ta, Re, and Pt for the evaporation filament. The material of the evap-oration filament found to have no effect on the observed isotope ratio and the isotope ratio was stable for 2 h in a low heating condition. These facts suggest that the evaporation proceeds from the surface of the sample.

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Table 1
Observed calcium isotope ratio by using different materials as the evaporation filament

Filament material	IF (K)	EF (K)	$^{44}Ca/^{40}Ca$ ($\times 10^{-2}$)
Re	1310–1340	450–480	2.1586 ± 0.0040
Ta	1310–1340	460–480	2.1581 ± 0.0040
Pt	1310–1340	~570	2.1577 ± 0.0044
Average			2.1582 ± 0.0024