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Surface ionization of alkaline-earth iodides in double-filament system

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Abstract

The ionization sequences of alkaline iodides in a double-filament surface-ionization mass spectrometry system were studied. The test samples were strontium iodide and barium iodide. The ionization parameters, ϵ, at the surface of the ionization filament (IF) ϵ were determined by Arrhenius' plots. It was found that ionization parameters are dependent on evaporation filament (EF) temperature. This phenomenon is the same as that observed in the case of calcium iodide in our previous study. The findings can be explained in the following way. At low EF temperatures, the sample vapor arrives at the ionization filament in the chemical form in which the sample was initially loaded on the EF. Therefore, the sample vapor must gain the sum of dissociation and ionization energies at the IF. At high EF temperatures, the sample vapor can dissociate on or near the EF. As a result, the apparent ionization parameters changed with the EF temperature. (Int J Mass Spectrom 206 (2001) 1–5) © 2001 Elsevier Science B.V.

Keywords: Mass spectrometry; Double filament; Surface ionization; Alkaline-earth iodide; Dissociation

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1. Introduction

Molecular vibrations were considered to be the primary influence on isotope effects in chemical exchange reactions. Ever since anomalous isotope effects were found in odd-numbered isotopes of uranium [1], however, nucleus–electron interactions have become prominent. Anomalous isotope effects have been observed in various elements such as zinc [2], lead [3], and gadolinium [4]. Alkaline-earth metals such as calcium, strontium, and barium have many stable isotopes, including odd-number isotopes, and these elements are the good subjects for the study of isotope effects. To conduct such studies, highly accurate isotope analysis by mass spectrometry is required. Surface-ionization ion sources with a double or triple filament are appropriate for such analysis. In general, the lighter molecules vaporize more easily, leading to Rayleigh distillation if the sample is entirely liquid [5]. To avoid Rayleigh distillation, the sample should not be entirely liquid. Such conditions can be realized by keeping the evaporation filament temperature low and evaporating the sample molecules from the surface by radiant heat from the ionization filament.

In this study, SrI_2 and BaI_2 are used as samples to establish appropriate conditions for isotope analysis and to examine whether the samples exhibit the same ionization sequence as we have previously reported of CaI_2 [6].

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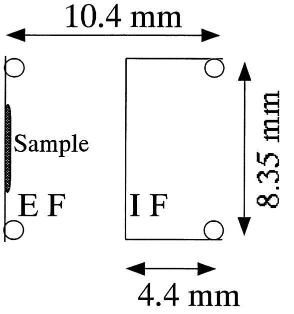

Fig. 1. Filament arrangement. EF is evaporation filament and IF is ionization filament.

2. Experimental

The experiments were conducted using a surface-ionization ion source with a double filament (evaporation and ionization filament) installed in a mass spectrometer, Model Finnigan MAT 261. The ion currents were detected by a secondary electron multiplier and a Faraday cup collector. The arrangement of the filaments is shown in Fig. 1. Rhenium (Re) ribbon (thickness 0.04 mm, width 0.7 mm) was used for both the ionization filament (IF) and evaporation filament (EF). The samples of MI_2 solution were loaded on the evaporation filament and heated to dryness in air, where M represents the alkaline-earth metals of Sr or Ba. The mass of M loaded on the EF was ~40 μg in all experiments. Filament temperature, T, was determined by the equation $T = AI^{2/3}$, as described in our previous report [5], where A is a constant determined from the pyrometer measurements. Before ionization-sequence study, the IFs were heated to ~2000 K to remove impurities of low ionization potential and the oxidized surface layer. This pretreatment process standardizes the filament surface.

3. Results and discussion

For the purpose of practical analysis, the following equation has been used for the study of ionization sequences [6–8]:

$$n_+/n_0 = B\exp(-\epsilon/kT_{IF}), \tag{1}$$

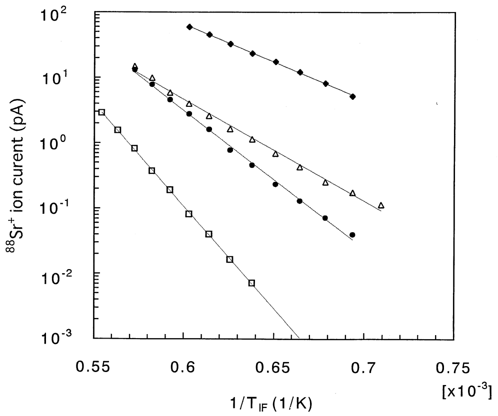

Fig. 2. $^{88}Sr^+$ ion current as a function of the inverse of ionization filament temperature, $1/T_{IF}$. Ion currents were observed at evaporation filament temperatures of 908 K (open square), 948 K (closed circle), 987 K (open triangle), and 1026 K (closed diamond).

where n_+ and n_0 are ion and neutral atom densities, B is a constant, ϵ is the ionization parameter, k is Boltzmann's constant, and T_{IF} is the temperature of the ionization filament.

Strontium, $^{88}Sr^+$ and barium, $^{138}Ba^+$, ion currents are plotted as a function of IF temperature, $1/T_{IF}$, in Figs. 2 and 3, respectively. The slopes of the plots in Figs. 2 and 3 give the ionization parameter, ϵ, at any given EF temperature. The values of ϵ determined from these plots are shown in Fig. 4, together with the

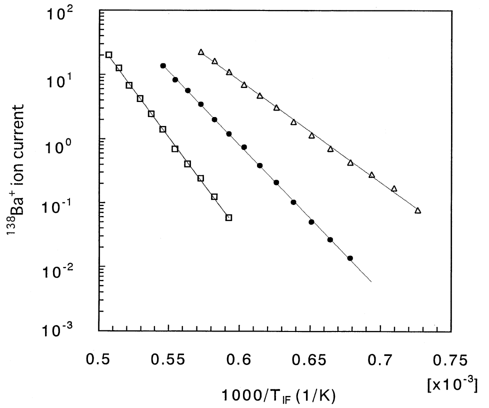

Fig. 3. $^{138}Ba^+$ ion current as a function of the inverse of ionization filament temperature, $1/T_{IF}$. Ion currents were observed at evaporation filament temperature of 908 K (open square), 948 K (closed circle), and 987 K (open triangle).

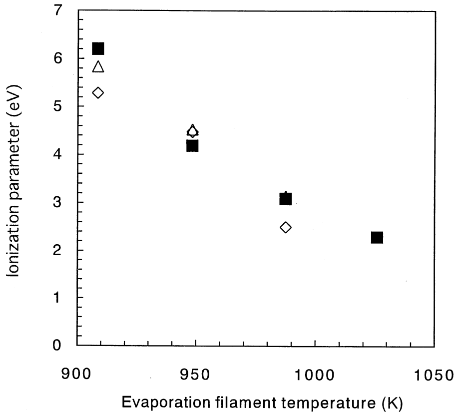

Fig. 4. Ionization parameters of alkaline-earth iodides as a function of evaporation filament temperature. Open diamonds represent the ionization parameter of calcium [6], closed squares represent that of strontium, and open triangles represent that of barium.

ionization parameters observed for CaI_2 [6]. It can be seen that the ionization parameter exhibits a dependency on EF temperature in all cases. The ionization parameter is a decreasing function of EF temperature T_{EF}.

The process of generating alkaline-earth ions from iodides is considered to occur as follows:

$$MI_2 \rightarrow MI + I \rightarrow M + 2I \rightarrow M^+ + 2I + e^-, \qquad (2)$$

These processes are presented in Fig. 5. The energy required in each step is shown in Table 1, where the work function of Re, W_{IF}, is assumed to be 5.1 eV. If the sample vapors arrive at the IF surface in the form of MI_2, then the energy required for M^+ production is the sum of the dissociation and ionization energies, ϕ_{sum}. In this ionization case, which includes the dissociation of MI_2 and ionization processes, the ionization parameter ϵ can be expressed as

$$\varepsilon_1 = \phi_{sum} - W_{IF} = \phi_{ND1} + \phi_{ND2} + \phi_1 - W_{IF}, \qquad (3)$$

where ϕ_{ND1} is the neutral dissociation energy from MI_2 to MI, ϕ_{ND2} is the neutral dissociation energy from MI to M and I, and ϕ_I is the ionization potential of M.

In the case where M^+ is produced from MI molecules adsorbed on to, or arrived at, the ionization filament, the ionization parameter ϵ can be expressed as

$$\varepsilon_2 = \phi_I + \phi_{ND2} - W_{IF} \qquad (4)$$

If neutral dissociation is included in the evaporation processes that occur on or near the EF, the ionization energy of M, ϕ_I, is the energy that should be gained at the IF for M^+ production. The ionization parameter is then expressed as

$$\varepsilon_3 = \phi_I - W_{IF}. \qquad (5)$$

As the observed values of ϵ are between 2 and 6 eV, it is considered that the process involves three distinct processes; $MI_2 \rightarrow M^+$, $MI \rightarrow M^+$, and $M \rightarrow M^+$. From these results, it is also suggested that the first reaction is dominant at very low EF temperatures, the second reaction is dominant at intermediate temperature, and the third reaction is dominant at very high temperatures.

Taking into account the fact that the degree of dissociation depends on EF temperature, the parameter ϵ can be expressed as

$$\varepsilon = x\phi_{ND1} + y\phi_{ND2} + \phi_I - W_{IF},\ 0 \le x \le y \le 1, \qquad (6)$$

where the parameters x and y indicate the contributions of the $MI_2 \rightarrow MI + I$ and $MI \rightarrow M + I$ dissociations, respectively. When the temperature of the evaporation filament becomes high, dissociation is promoted, in which case the parameters x and y would approach zero.

The total currents of the Ca, Sr, and Ba isotopes at an EF temperature of 908 K are plotted in Fig. 6 as a function of inverse IF temperature, $1/T_{IF}$. From the sublimation energies, ϕ_{sb}, shown in Table 1 and Fig. 6, it can be said that ϕ_{sb} is the main factor to determine ion beam intensity when ϵ and all other experimental conditions are the same. This is reasonable, as the ion density is expressed as

$$n_+ = \frac{C}{kT_{IF}} \exp\left(-\frac{\phi_{sub}}{kT_{EF}}\right) \exp\left(-\frac{\varepsilon}{kT_{IF}}\right), \qquad (7)$$

where C is a constant.

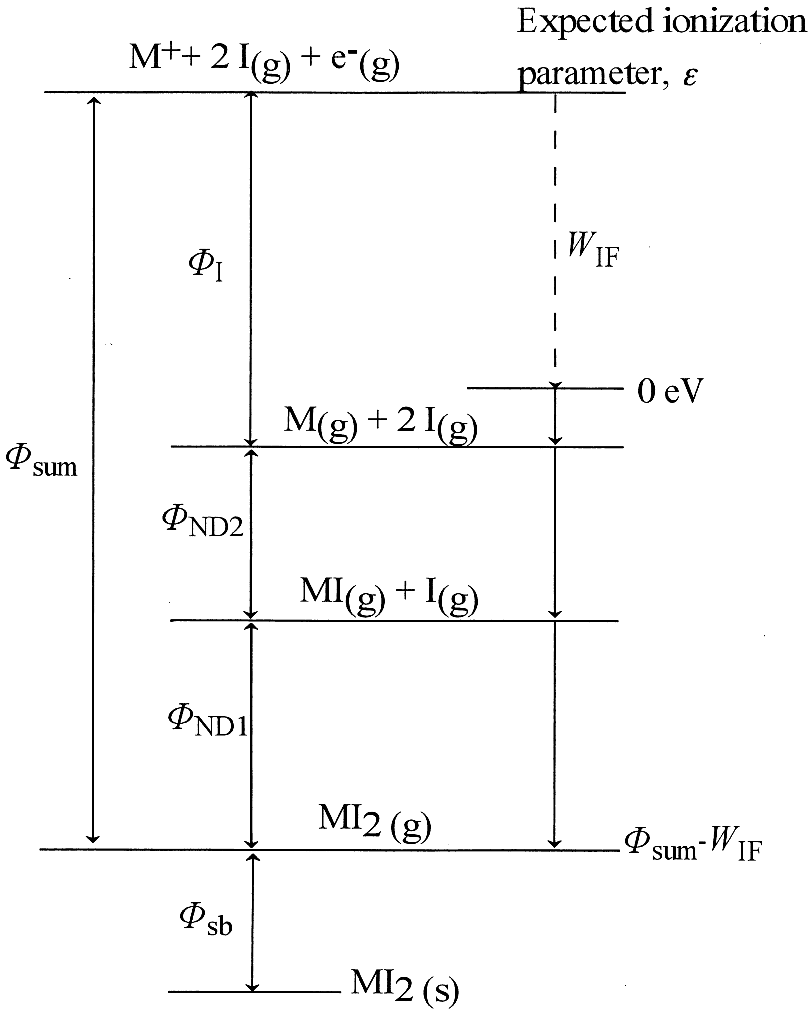

Fig. 5. Energy states of alkaline-earth iodides. M represents an alkaline-earth metal element and W_{IF} is the work function of the ionization filament surface.

5. Conclusion

The ionization of alkaline-earth metal, M, from MI_2 was studied in a double-filament surface-ionization system. It was found that the ionization parameter, ϵ, depends on the temperature of the evaporation filament. The ionization parameter was observed to be between 2 ~ 6 eV and to decrease as a function of the

Table 1
Dissociation and ionization energies for alkaline-earth iodides

Sample	ϕ_{sb} (eV)	ϕ_{ND1} (eV)	ϕ_{ND2} (eV)	ϕ_{I} (eV)	ϕ_{sum} (eV)	Expected ϵ (eV)	Observed ϵ (eV)
CaI_2	2.5	4.1	3.0	6.1	13.2	1.0–8.1	2.5–5.3
SrI_2	3.0	4.0	2.7	5.7	12.4	0.6–7.3	2.3–6.2
BaI_2	3.1	3.8	3.3	5.2	12.4	0.1–7.3	3.1–5.8

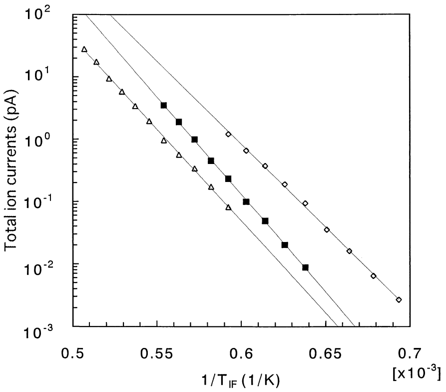

Fig. 6. Total ion currents of calcium, strontium, and barium isotopes at an evaporation filament temperature of 908 K. Open diamonds represent the ion current of calcium [6], closed squares represent that of strontium, and open triangles represent that of barium.

evaporation filament temperature. These results suggest that three different ionization processes are involved in the ionization: $MI_2 \rightarrow M^+$, $MI \rightarrow M^+$, and $M \rightarrow M^+$. As EF temperatures increase, the dominant reaction changes from the first process to the third process. It was confirmed that the sublimation energy, ϕ_{sb}, is an important factor in the determination of beam intensity, in addition to ϵ.

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