

# Ionization Energy Difference between Isotopes and its Effect on Isotope Abundance Measurement by Surface Ionization Method

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In mass spectrometric measurement of isotope abundance, it has been assumed that ionization energy is same for isotopes. In this paper the finite nucleus mass effect and finite nucleus volume effect on ionization energy are considered. Theoretical calculation and spectroscopic data show that the ionization energy difference between  ${}^7\text{Li}$  and  ${}^6\text{Li}$  is  $1 \cdot 10^{-4}$  eV, and only for Li the isotope effect by ionization energy difference can amount to the same order of magnitude as those mass discriminations by evaporation of the sample from the filament, by ion optics in the ion source chamber and so on.

## 1. Introduction

In mass spectrometric measurement of isotope abundance, it has been assumed that the abundance ratio of the ionized isotopes is equal to that of the neutral ones, in other words, ionization efficiency is same for isotopes. However, it seems necessary to estimate the isotope effect on ionization efficiency, in order to get higher accuracy. We consider the isotope effect on surface ionization method, since the ionization energy difference between isotopes, if any, is expected to have the biggest effect on this method because of smallness of thermal energy.

For surface ionization method the ionization efficiency is given by Saha-Langmuir equation,

$$i/n = C \cdot \exp\left(\frac{W - I}{kT}\right),$$

where  $i$  and  $n$  are the numbers of ions and neutral atoms respectively,  $C$  is a coefficient which depends on the property and temperature of the ionization filament and other factors,  $W$  is the work function of the filament,  $I$  is the ionization

energy of the element,  $k$  is Boltzmann's constant and  $T$  is the absolute temperature of the filament.

From this equation is easily derived the relation between the abundance ratio of the ionized isotopes  $i_2/i_1$  and that of the neutral  $n_2/n_1$ ,

$$i_2/i_1 = (n_2/n_1) \cdot \exp\left(\frac{I_1 - I_2}{kT}\right)$$

where  $I_1$ ,  $I_2$  are the ionization energy of isotopes of mass number  $M_1$ ,  $M_2$  respectively.

Alkali elements are usually ionized about  $1000^\circ\text{K}$  ( $= 8.6 \cdot 10^{-2}$  eV) by single filament, then the ionization energy difference of  $1 \cdot 10^{-4}$  eV can bring an error of 0.1 %. It may be sufficient to consider the next two, which can cause the difference of this magnitude.

- 1) Finite nucleus mass effect-significant in light elements
- 2) Finite nucleus volume effect-significant in heavy elements

The energy level difference between isotopes has been investigated both experimentally and theoretically as "isotope

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shift "in spectroscopy. (For example see Condon and Shortley (1951),<sup>1)</sup> Kopfermann (1958),<sup>2)</sup> Landau and Lifshits (1963)<sup>3)</sup> and so on). In this paper the author reduces the spectroscopic data of isotope shift written in wave number into ionization energy difference, and estimates the isotope effect for those elements of which spectroscopic data are not available.

## 2. Finite nucleus mass effect

The theory for a nucleus of finite mass in  $N$  electron problem has been considered by Hughes and Eckart (1930)<sup>4)</sup> and also by Bartlett and Gibbons (1933).<sup>5)</sup> The kinetic energy of a system of  $N$  electrons, each of mass  $m$ , and a nucleus of mass  $M$  is given by

$$T = \frac{1}{2M} P_{\text{nuc}}^2 + \frac{1}{2m} \sum_i^N p_i^2$$

where  $P_{\text{nuc}}$  and  $p_i$  are the momenta of the nucleus and  $i$ -th electron. Since the translational energy of the center of mass cannot change in a radiation or ionization process, we can put

$$P_{\text{nuc}} + \sum_i^N p_i = 0$$

Therefore we obtain

$$T = \frac{1}{2\mu} \sum_i^N p_i^2 + \frac{1}{M} \sum_{i \neq j} p_i \cdot p_j$$

where  $\mu$  is the reduced mass  $mM/(m+M)$ .

Then we see that the nuclear mass alters the kinetic part of the Hamiltonian in two ways, by the reduced mass in the first term and by the second term  $\frac{1}{M} \sum_{i \neq j} p_i \cdot p_j$ . As the second term has a smaller effect on isotope shift than the first, we neglect the second in our rough discussion.

Suppose we know the energy level  $E_\infty$  for the infinite nuclear mass, then we

get the difference of the corresponding energy levels  $E_1$  and  $E_2$  of two isotopes  $M_1$  and  $M_2$  as follows,

$$E_2 - E_1 = E_\infty \cdot \left( \frac{1}{1 + \frac{m}{M_2}} - \frac{1}{1 + \frac{m}{M_1}} \right)$$

In order to know the order of magnitude of the isotope effect, we might replace  $E_\infty$  by the mean energy. (See Condon and Shortley (1951)<sup>1)</sup>). Then for the ionization energy difference, we obtain

$$\begin{aligned} I_2 - I_1 &= I \cdot \left( \frac{1}{1 + \frac{m}{M_2}} - \frac{1}{1 + \frac{m}{M_1}} \right) \\ &\equiv I \cdot \left( \frac{m}{M_1} - \frac{m}{M_2} \right), \end{aligned}$$

where  $I$  is the mean ionization energy of the element.

## 3. Finite nucleus volume effect

The nucleus has a finite volume, then the departure from Coulomb field near the nucleus causes a difference in the energy levels between isotopes, which have different nucleus volumes. This effect, in fact, is significant only for  $s$ -state electrons, whose probability density at  $r=0$  are not zero. Therefore the isotope effect becomes the biggest for alkali and alkaline earth elements by duplicate reasons that their valence electrons are in  $s$ -state and their isotope abundance are usually measured by surface ionization method.

Put  $\varphi(r)$  equal to the true electrostatic potential field of the nucleus, then the difference of the electron energy from that for Coulomb field  $\frac{Ze}{r}$  is given by

$$\Delta E = -e \int \left( \varphi - \frac{Ze}{r} \right) \psi^2 dV,$$

where  $\psi$  is the wave function of the electron and  $e$  is elementary charge.

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Though this integral must be carried out over the all space, in fact,  $(\varphi - \frac{Ze}{r})$  is not zero only within the nucleus. On the other hand, the wave function of the s-state electron approaches to a finite value as  $r \rightarrow 0$ , and amounts to it already outside the nucleus. Consequently we can take  $\psi^2$  out of the integrand and replace it by  $\psi^2(0)$  calculated for Coulomb field of a point charge  $Ze$ .

$$\begin{aligned}\Delta E &= -e \psi^2(0) \int (\varphi(r) - \frac{Ze}{r}) dV \\ &= -\frac{1}{6} e \psi^2(0) \int (\varphi - \frac{Ze}{r}) \Delta^2 r dV \\ &= -\frac{1}{6} e \psi^2(0) \int r^2 \Delta (\varphi - \frac{Ze}{r}) dV,\end{aligned}$$

where we use the facts in the transformations of the integral that  $\Delta^2 r = 6$ , and the integrand is zero at infinitely remote surface. Now, for all  $r$   $\Delta(\frac{1}{r}) = -4\pi \delta(r)$  and  $r^2 \delta(r) = 0$ . According to Poisson's equation for electrostatic field,  $\Delta \varphi = -4\pi \rho$ , where  $\rho$  is the density of the charge distribution in the nucleus.

At last we obtain,

$$\begin{aligned}\Delta E &= \frac{2\pi}{3} \psi^2(0) Ze^2 \overline{r^2} \\ \overline{r^2} &= \frac{1}{Ze} \int \rho \overline{r^2} dV.\end{aligned}$$

Assuming that in the nucleus the electric charge distributes homogeneously,

$$\overline{r^2} = \frac{3}{5} \cdot R^2$$

where  $R$  is the geometric radius of the nucleus. The energy level difference between isotopes is the difference between the departures from Coulomb field obtained here for each isotope. That is,

$$E_2 - E_1 = \frac{2\pi}{3} \psi^2(0) Ze^2 (\overline{r_2^2} - \overline{r_1^2}).$$

(After Landau and Lifshits (1963)<sup>3)</sup>)

Here we use the wave functions

for hydrogen-like atom, a system of a nucleus of point charge  $Ze$  and an electron, owing to the unavoidable fact that we are not given the complete wave function for the elements except hydrogen. Of course, this approximation is far from the truth, however it must give the upper limit of the isotope effect because the real probability density of the outer electrons at  $r=0$ , which are repelled by the inner electrons, are unquestionably smaller than those calculated by this approximation. For hydrogen-like atom the wave functions of s-state electrons are given as follows,

$$\begin{aligned}1s; \psi_{10} &= \frac{1}{\sqrt{4\pi}} (Z/a_0)^{3/2} \cdot 2 \cdot \exp(-r'/2), \\ r' &= 2Zr/a_0\end{aligned}$$

$$\begin{aligned}2s; \psi_{20} &= \frac{1}{\sqrt{4\pi}} (Z/a_0)^{3/2} \cdot \frac{1}{2\sqrt{2}} (2-r') \cdot \\ &\exp(-r'/2), \quad r' = Zr/a_0\end{aligned}$$

$$\begin{aligned}3s; \psi_{30} &= \frac{1}{\sqrt{4\pi}} (Z/a_0)^{3/2} \cdot \frac{1}{9\sqrt{3}} (6-6r' \\ &+ r'^2) \cdot \exp(-r'/2), \\ r' &= 2Zr/3a_0\end{aligned}$$

in general, for ns electron

$$ns; \psi_{n0}(0) = \frac{1}{\sqrt{4\pi}} (Z/a_0)^{3/2} \cdot \frac{2}{n\sqrt{n}},$$

where  $a_0$  is Bohr radius  $5.29 \cdot 10^{-9}$  cm.

It is known that nuclear volume is proportional to the number of its nucleons. We take an empirical formula  $1.5 \cdot 10^{-13} \cdot M^{1/3}$  cm for the geometric radius of the nucleus of mass number  $M$ , and we obtain

$$\begin{aligned}I_2 - I_1 &= -\frac{4}{5} \cdot \frac{Z^4}{n^3} \cdot \frac{e^2}{2a_0} \cdot (R_2^2/a_0^2 \\ &- R_1^2/a_0^2) = -0.874 \cdot (Z^4/n^3) \cdot \\ &(M_2^{2/3} - M_1^{2/3}) \cdot 10^{-8} \text{ eV}.\end{aligned}$$

## 4. Summary

Neglecting higher order effects, observed isotope shift should be explained by the sum of these two effects which have opposite sense each other. And spectroscopic data of isotope shift could be reduced to ionization energy difference between isotopes considering the weights of these two effects. However, the ambiguity in the magnitude of the nucleus volume effect due to hydrogen-like approximation makes the reduction difficult.

On reduction of the spectroscopic data for Li and Mg, it is considered that in these elements the mass effect is bigger than the volume effect and the nuclear mass shifts the energy levels uniformly. As for K and Rb for both two extreme cases the spectroscopic data are reduced that the isotope shift is only due to the mass effect and only due to the volume effect, then it relates to only s-state electrons. In Table 1. are given the

ionization energy differences reduced from the spectroscopic data, and theoretically calculated for alkali and alkaline earth elements.

The results show that the differences calculated by the mass effect are consistent with those reduced from the spectroscopic data owing the isotope shift to the mass effect in the sense and magnitude roughly. On the other hand, for K the difference calculated by the volume effect disagrees with that reduced from the spectroscopic data owing the isotope shift to the volume effect in the sense and magnitude. These facts show that the ionization energy difference between isotopes for Li, Mg and K is mainly due to the finite nucleus mass, and the hydrogen-like approximation overestimates the effect by a few orders of magnitude. Bearing in mind these conditions, the calculated values can be some indexes of the ionization energy difference

Table 1. Ionization energy difference between isotopes for alkali and alkaline earth elements

	I	$M_2 - M_1$	Theoretically calculated values		Reduced values from spectroscopic data $I_2 - I_1$
			of mass effect, $I_2 - I_1$	of volume effect $I_2 - I_1$	
Li	5.390eV	7-6	$+7.0 \cdot 10^{-5}$ eV	$-3.2 \cdot 10^{-8}$ eV	$+1.27 \cdot 10^{-4}$ eV (6)
Be	9.320	10-9	$+5.6 \cdot 10^{-5}$	$-8.8 \cdot 10^{-8}$	
Na	5.138	23-22	$+5.5 \cdot 10^{-6}$	$-1.1 \cdot 10^{-6}$	
Mg	7.644	25-24	$+6.9 \cdot 10^{-6}$	$-1.5 \cdot 10^{-6}$	$+2.85 \cdot 10^{-5}$ (7)
K	4.339	41-39	$+2.9 \cdot 10^{-6}$	$-6.9 \cdot 10^{-6}$	$+2.53 \cdot 10^{-6}$ (8a) $+0.94 \cdot 10^{-6}$ (8b)
Ca	6.111	41-40	$+2.0 \cdot 10^{-6}$	$-4.2 \cdot 10^{-6}$	
Rb	4.176	87-85	$+6.1 \cdot 10^{-7}$	$-4.0 \cdot 10^{-5}$	$(0 \pm 6.5) \cdot 10^{-7}$ (9a) $(0 \pm 2.5) \cdot 10^{-7}$ (9b)
Sr	5.692	87-86	$+4.1 \cdot 10^{-7}$	$-2.2 \cdot 10^{-5}$	
Cs	3.893	134-133	$+1.2 \cdot 10^{-7}$	$-4.8 \cdot 10^{-5}$	
Ba	5.210	138-137	$+1.5 \cdot 10^{-7}$	$-5.1 \cdot 10^{-5}$	

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between isotopes for those elements of which spectroscopic data are not available.

In conclusion, only for Li the isotope effect due to ionization energy difference between isotopes can amount to the same order of magnitude as those mass discrimination by evaporation of the sample from the filament, by ion optics in the ion source chamber, on secondary electron multiplier and so on. For the other elements we can neglect this effect within the accuracy of 0.1 %. However, someday when the larger isotope effects can be corrected sufficiently, we shall return to this problem with higher knowledge of wave function and nucleus.

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## References

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- 3) Landau and Lifshits (1963), "Kvantovaya mekhanika (Quantum mechanics)" in Russian, Fizmatgiz, Moscow, pp. 534 - 536.
- 4) Hughes and Eckart, *Phys. Rev.*, **36**, 694, (1930).
- 5) Bartlett and Gibbons, *Phys. Rev.*, **44**, 538 (1933).
- 6) Meissner, Mundie and Stelson, *Phys. Rev.*, **74**, 932 (1948).  
Li;  $2s^2S - 2p^2P$  (6707 Å, 1.85 eV),  $\tilde{\nu}_7 - \tilde{\nu}_6 = +0.350 \text{ cm}^{-1}$
- 7) Mundie and Meissner, *Phys. Rev.*, **65**, 265 (1944).  
Mg;  $3^1P - 3^1D$  (8806 Å, 1.41 eV),  $\tilde{\nu}_{25} - \tilde{\nu}_{24} = +0.0423 \text{ cm}^{-1}$
- 8) Jackson and Kuhn, *Proc. Roy. Soc.*, A 165, 303 (1938).  
K;  $4s^2S - 4p^2P$  (7664 Å, 1.62 eV),  $\tilde{\nu}_{41} - \tilde{\nu}_{39} = +0.0076 \text{ cm}^{-1}$   
8a); reduced only by mass effect, 8b); by volume effect.
- 9) Kopfermann and Krüger, *Z. Phys.*, **103**, 485 (1936).  
Rb;  $5s^2S - 5p^2P$  (7800 Å, 1.59 eV),  $\tilde{\nu}_{87} - \tilde{\nu}_{85} = 0 \pm 0.002 \text{ cm}^{-1}$   
9a); reduced only by mass effect, 9b); by volume effect
- 10) Needless to say,  $1 \text{ eV} = 8067 \text{ cm}^{-1}$ .