Research Article

Investigation of Optical Ionization of Strontium via $5s^2\ ^1S_0 \longrightarrow 5s5p\ ^3P_1^o \longrightarrow 5s5d\ ^3D_2 \longrightarrow 4dnp$ (or $4dnf$, $n = 39$) for Isotope Selectivity Enhancement

Donguk Cheon ¹, Yoshihiro Iwata ², Masabumi Miyabe,³ Ikuo Wakaida,³ and Shuichi Hasegawa ^{1,2}

¹Department of Nuclear Engineering and Management, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

²Nuclear Professional School, The University of Tokyo, Shirakata-shirane 2-22, Tokai-mura, Naka-gun, Ibaraki 319-1188, Japan

³Remote Analytical Technology Group, Collaborative Laboratories for Advanced Decommissioning Sciences, Japan Atomic Energy Agency, Shirakata-shirane 2-4, Tokai-mura, Naka-gun, Ibaraki 319-1195, Japan

Correspondence should be addressed to Yoshihiro Iwata; yiwata@tokai.t.u-tokyo.ac.jp

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We investigated a promising three-step resonance ionization scheme of strontium (Sr) $5s^2\ ^1S_0 \longrightarrow 5s5p\ ^3P_1^o \longrightarrow 5s5d\ ^3D_2 \longrightarrow 4dnp$ (or $4dnf$, $n = 39$) using the first-step intercombination transition for the enhancement of isotope selectivity. The power broadening observed in the 2^{nd} transition indicates that laser power of less than 0.2 mW is sufficient for saturating this transition. Isotope separation can be successfully expected with application of the 3^{rd} transition due to the narrow width of the $4dnp$ (or $4dnf$, $n = 39$) autoionization level, paving the way for analysis of trace ^{90}Sr in environmental applications.

1. Introduction

Radioactive isotope determination in nature remains a topic of high research interest due to their hazardous nature [1–6]. In particular, the radioactive isotope of strontium, ^{90}Sr ($T_{1/2} = 28.8$ years, $\beta_{\text{emit}} = 0.546$ MeV), is one of the several fission nuclides typically produced in large amounts from the operation of nuclear facilities. The chemical characteristics of Sr are very similar to those of calcium and may substitute for it in chemical reactions. Regarding radioactive isotope accumulation through the food chain (fish, oysters, milk, etc.), the Japanese government has set the limit of food contamination at the level of 100 Bq/kg [7]. Developing isotope determination methods for these kinds of samples is therefore required.

Many groups have performed research for ^{90}Sr monitoring, using such methods as radiometric techniques and mass spectrometric analysis methods. Some research groups have reported applied radiometric techniques to separate and determine the ^{90}Sr content from field samples with high

selectivity. However, these methods make use of relatively complicated chemical procedures and have detector limitations due to the relatively weak energy emission during decay of ^{90}Sr . Furthermore, they are time-consuming, generally requiring several weeks for separation and quantification [4, 5, 8].

Several research groups have also reported measurement of ^{90}Sr in an environmental sample by accelerator mass spectrometry (AMS). However, although the AMS method shows enhancement of measurement results with a relatively less time-consuming process, they had to perform complex chemical pretreatment. Moreover, the experimental system has a very large facility/apparatus footprint [4–6, 9–11].

Other groups have explored alternative approaches, such as inductively coupled plasma mass spectrometry (ICP-MS) with additional application of dynamic reaction cells (DRCs) to suppress the interference of isobars. However, these reports also comment that there still remains some existences of isobaric interference (due to ^{90}Y and ^{90}Zr), which is an

issue due to the relatively low natural abundance of ^{90}Sr ($^{90}\text{Sr}/\text{Sr} \sim 10^{-13}$) in nature [12, 13].

Alternatively, other groups have suggested resonance ionization mass spectrometry (RIMS) for the determination of isotope content by multiphoton excitation ionization applications [4, 5, 11–14]. Regarding these methods, this technique offers outstanding properties. For example, firstly, effective isobaric suppression due to the unique isotope-dependent optical transition properties; secondly, high ionization efficiency; thirdly, high sensitivity with effectively low detection limit; and lastly, high isotopic selectivity ($\sim 10^{13}$). In particular, the isotope selectivity enhancement can be achieved with the Doppler broadening reduction, through effective multistep resonance ionization transition [14–16].

The optical isotopic selectivity is strongly dependent on the particular photoexcitation scheme and its resonance ionization transitions. The isotope shift, particularly, is one of the dominant factors in achieving isotopic selectivity and is required to be optimized for each excitation transition by identification. The isotope selectivity can be defined as below [17–19]:

$$\text{isotope selectivity } S = \left[\frac{2\Delta\nu}{\Gamma_{\text{nat}}} \right]^2, \quad (1)$$

where Γ_{nat} is the homogeneous natural linewidth and $\Delta\nu$ is the isotope shift of the specific transition. Enhancement of isotope selectivity can be obtained by implementing multistep resonance ionization using narrow natural linewidth transitions as described in Reference [15].

Bushaw and Cannon conducted three-step resonance ionization of ^{90}Sr using the 689.4 nm–688 nm–487.6 nm excitation transition scheme ($5s^2 \ ^1S_0$ – $5s5p \ ^3P_1^\circ$ – $5s6s \ ^3S_1$ – $4d6p \ ^3P_1^\circ$) with two diode lasers and one high power Ar⁺ laser [16]. In this scheme, the first-step transition at 689.4 nm ($5s^2 \ ^1S_0$ – $5s5p \ ^3P_1^\circ$) is the so-called intercombination transition with narrow natural linewidth (~ 7.4 kHz). They showed that the optical selectivity of Sr-90 of the scheme is around 10^6 ; however, the linewidth of the third-step transition of 487 nm is so large that the isotope shift cannot be evaluated [16]. Thus if one can find an autoionizing transition of which linewidth is narrower than the isotope shift, higher optical isotope selectivity can be realized.

In this context, it is therefore required to investigate alternatives for effective resonance ionization transition schemes of Sr based on the first-step narrow linewidth excitation transition (689.4 nm, $5s^2 \ ^1S_0$ – $5s5p \ ^3P_1^\circ$). Spectroscopic studies of autoionization transitions of Sr have been reported by several research groups [20–22]. Kompitsas et al. studied a detailed autoionizing Rydberg spectrum converging to the 4d threshold [20]. According to their report, the linewidths of the series members decrease with increasing principal quantum number and approach typical pulse dye laser bandwidths in the vicinity of $n = 30$. Thus, to access the autoionizing Rydberg levels in this region with a three-step ionization scheme using commercially available diode lasers, in this study, we focus on a novel ionization scheme of 689.4 nm–487.4 nm–393.8 nm ($5s^2 \ ^1S_0$ – $5s5p \ ^3P_1^\circ$ – $5s5d \ ^3D_2$ – 4dnp (or 4dnf , $n = 39$)). A partial energy-level diagram including the $5s^2 \ ^1S_0$ – $5s5p \ ^3P_1^\circ$ transition is shown in Figure 1.

FIGURE 1: Excitation transition schemes described in the present study. The left-side transition (689.4 nm–688 nm–487.6 nm) is quoted from Reference [16].

In the following sections, we will describe the experimental setup used in this study, and discuss measurement results of spectra for the 2nd and 3rd transitions.

2. Experimental Setup

The complete experimental setup scheme is shown in Figure 2. For the experiment, we prepared three external cavity diode laser systems at three wavelengths (689.4 nm, 487.4 nm, and 393.8 nm). Each laser system was constructed using the Littrow configuration of diffraction grating external cavity. Each output beam, after optical isolation, was divided into three beams: main experimental beam, beam for wavelength monitoring, and beam for wavelength locking. The wavelengths of all lasers were continuously monitored with a Fizeau-type wavemeter (HighFinesse WS-U). Wavelength locking was achieved by a computer-controlled fringe offset lock system [23] incorporating a Fabry–Pérot interferometer and frequency-stabilized He-Ne laser (SIOS, SL-03, 5 mW). The two laser beams for the first (689.4 nm) and second (487.4 nm) transitions were overlapped with each other using a dichroic mirror and then introduced into the vacuum chamber from the same direction. The beam for the third transition (393.8 nm) was introduced from the opposite direction to suppress Doppler broadening, which would negatively affect the isotope selectivity. The Sr atomic vapor was produced by electrical heating of the titanium foil which is containing the dried liquid droplet of the strontium sample [24]. Due to the relatively low natural abundance ($\sim 0.56\%$) of ^{84}Sr , we prepared an ^{84}Sr enriched (68.7%) liquid sample mixed in equal amounts with a natural sample. A quadrupole mass spectrometer (HIDEN, EPIC-300) was installed at the top of the vacuum chamber to observe the spectra of the Sr stable isotopes: ^{84}Sr , ^{86}Sr , and ^{88}Sr . For the ionization efficiency evaluation, the giant resonance ionization transition (460 nm–405 nm; $5s^2 \ ^1S_0$ – $5s5p \ ^1P_1^\circ$ –($4d^2 + 5p^2$) 1D_2) of strontium was compared with the transition scheme of this study [25]. The resonance ionization

FIGURE 2: Experimental setup for the three-step resonance ionization 689.4 nm-487.4 nm-393.8 nm.

at the transition of 460 nm-405 nm revealed $\sim 10^{6-7}$ counts per second by the few milliwatt output two external cavity diode lasers (ECDLs), respectively.

3. Results and Discussion

In this work, we investigated the transition scheme 689.4 nm-487.4 nm-393.8 nm ($5s^2 \ ^1S_0-5s5p \ ^3P_1^o-5s5d \ ^3D_2-4dnp$ (or $4dnf$)) which is close to limitation of 4d transition ($n=39$) with narrow linewidth [20]. The first transition is the same as that reported in [16]; however, we were not able to find any other studies regarding resonance ionization spectroscopy of the 2nd and 3rd transitions. Therefore, regarding the above transition scheme, we observed the spectra of Sr stable isotopes (^{84}Sr , ^{86}Sr , and ^{88}Sr) to verify the narrow width of the 3rd autoionization transition are suitable for isotope separation.

Figure 3 shows an example of the obtained spectrum of ^{88}Sr for the 2nd (487.4 nm) transition, where the wavelength of the 1st laser at 689.4 nm was locked at the resonant wavelength. The beam powers of the 1st and 2nd lasers measured at near to the vacuum chamber were 12 mW and 0.2 mW, respectively. For this measurement, the 3rd laser at

FIGURE 3: The Voigt profile of the ^{88}Sr ion signal with respect to the 487.4 transition laser frequency.

393.8 nm was not introduced, so the photoionization was mainly achieved by additional absorption of the 1st laser light, as indicated by the “*” mark in Figure 1. In Figure 3,

the black dots with error bars were used for the Voigt function fitting to evaluate the Gaussian and Lorentzian components of the spectrum. The gray dots in the measurement data were not used for the fitting because they contained zero-value data, making the results of fitting as infinite, which were not suitable for weighted fitting. According to the fitting results, the full width at half maximum (FWHM) of the Gaussian component (Γ_G) was about 39 MHz. The magnitude of this value is mainly due to the Doppler broadening caused by the Sr atomic velocity distribution. This value is consistent with the value of 34.3 MHz, reported in [16], where the geometry of the Sr atomic vapor source was similar to that used in this study. The FWHM of the Lorentzian component (Γ_L) was about 42 MHz, which is attributed to the natural linewidth and power broadening. According to the database [26] published by NIST, the natural linewidth of this transition is $A_{ki}/2\pi \sim 7.6$ kHz. This is much lower than the measured Lorentzian component. Therefore, we consider the observed Lorentzian component to be mainly attributed to the power broadening. This means the saturation of the $5s5p\ ^3P_1^o - 5s5d\ ^3D_2$ transition may be achieved with a second-step laser power of less than 0.2 mW. The power broadening decreases isotope selectivity, so there is a trade-off relation between transition efficiency and isotope selectivity. We consider that the laser power of this transition should be tuned so that the Sr ion signal intensity is about $1-1/e$ (~ 0.6) of the maximum value observed at saturation.

Figure 4 shows an example of the obtained spectra of ^{84}Sr , ^{86}Sr , and ^{88}Sr with the inclusion of the 3^{rd} (393.8 nm) transition. The wavelengths of the 1st and 2nd lasers were locked to the resonant wavelengths of each of the three isotopes. The 1st and 2nd step laser powers were the same as in the previous experiment, and the 3rd laser power at the vacuum chamber beam input was about 4 mW. The results of the Voigt function fitting for all isotopes are also shown in the same figure. The spectra show that the spectrum widths are substantially narrower than the isotope shifts. Unlike the 3rd transition (487.6 nm) reported in [16], a certain degree of isotope selectivity can be promised with this transition. Under the present system setup, the observed consistent background signal (about 1/7 of the maximum ion signal) limits the isotope selectivity. This background corresponds to the transition path indicated by the “*” mark in Figure 1. This transition was also used for ionization for observing the spectrum of ^{88}Sr with respect to the 2nd transition laser frequency as described above. Alternatively, a method of reducing the effect of this background signal would be to move the 1st (689.4 nm) laser beam crossover point with the atomic vapor closer to the atomic vapor source, about 5 mm from its initial position. Due to the long lifetime ($\sim 21\ \mu\text{s}$) of the 1st excited state ($5s5p\ ^3P_1^o$), ^{88}Sr atomic vapor at a temperature of 1000 K travels up to 10 mm during the 1st excited state lifetime. Also of note is the fact that the 1st intercombination transition efficiency is too low to be saturated by the laser output of about 12 mW. One future plan is to have a tapered amplifier [27] coupled with our ECDL, which would be effective for increasing the laser power up to watt class while maintaining the basic characteristics of our

FIGURE 4: Isotope shift of strontium for the 393.8 nm transition.

ECDL, such as its narrow linewidth. However, without optical amplification of the laser output, the resonance ion counts at the newly investigated 689 nm–487 nm–393 nm transition revealed near to the resonance ion counts at the referenced giant resonance transition (460 nm–405 nm). The relative resonance ionization efficiency presents $\sim 10^{-1}$ with few mW output ECDLs (Figure 4). This is higher than the relative resonance ionization efficiency ($\sim 10^{-2}$) between 689 nm–688 nm–487 nm and 460 nm–405 nm. The ionization rate would be enhanced further with applying the optical amplification system. Hence, the ionization efficiency is also relatively higher than the result of Reference [16].

4. Conclusion

The unreported three-step resonance ionization scheme of $\text{Sr } 5s^2\ ^1S_0 \rightarrow 5s5p\ ^3P_1^o \rightarrow 5s5d\ ^3D_2 \rightarrow 4\text{dnp (or } 4\text{dnf)}$, $n=39$ with an intercombination transition as the first step, has been investigated for isotope selectivity enhancement. We successfully observed the ion signal spectra of Sr-stable isotopes with respect to the 2nd and 3rd transition laser frequencies. The observed Lorentzian component was about 42 MHz in the 2nd step transition, which indicates that the laser power of 0.2 mW is sufficient for the saturation of the 2nd transition. This laser power has to be decreased for improvement of isotope selectivity to be obtained, due to power broadening, with the trade-off of reduced transition efficiency. The observed spectra of ^{84}Sr , ^{86}Sr , and ^{88}Sr with respect to the 3rd transition laser frequency indicate that the spectra widths are sufficiently narrow for isotope separation to be feasible. A consistent background signal was observed with the present system setup. And it could be decreased by spatially separating the 1st laser beam from the other two beams. The relative resonance ionization efficiency at the transition of our study revealed $\sim 10^{-1}$ with few milliwatt output power diode laser systems corresponding the reference, giant resonance, transition. This is 10 times higher than that of the ionization transition scheme of Bushaw (689.4 nm–688 nm–487.6 nm). A tapered amplifier system would be effective for dramatically increasing the 1st laser power to

improve the efficiency of the first-step intercombination transition. Higher isotope selectivity of Sr can be expected with our proposed transition, which would be useful for trace analysis of ^{90}Sr in environmental applications.

Data Availability

No data were used to support this study.

Conflicts of Interest

All the authors declare that there are no conflicts of interest regarding the publication of this article.

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