First ionization potential of the heaviest actinide lawrencium, element 103

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Abstract. The first ionization potential (IP_1) of element 103, lawrencium (Lr), has been successfully determined for the first time by using a newly developed method based on a surface ionization process. The measured IP_1 value is $4.963^{0.08}_{0.07}$ eV. This value is the smallest among those of actinide elements and is in excellent agreement with the value of $4.963(15)$ eV predicted by state-of-the-art relativistic calculations also performed in this work. Our results strongly support that the Lr atom has an electronic configuration of $[Rn]7s^25f^{14}7p_{1/2}^1$, which is influenced by strong relativistic effects. The present work provides a reliable benchmark for theoretical calculations and also opens the way for studies on atomic properties of heavy elements with atomic number $Z > 100$. Moreover, the present achievement has triggered a controversy on the position of lutetium (Lu) and Lr in the Periodic Table of Elements.

1. Introduction

The chemical properties of an element are primarily governed by the configuration of electrons in its valence shell. The relativistic effects on the electronic structure of heavy elements in the seventh row of the Periodic Table become so strong that in some cases even their ground-state configurations may differ from those expected from lighter elements in the same group [1].

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According to the actinide concept established by G.T. Seaborg [2], element 103, lawrencium (Lr), is placed at the tail end of the actinide series of the Periodic Table as the heaviest actinide element. By analogy with Lu, which is the lanthanide homologue of Lr and has an electronic structure of $[Xe]4f^{14}6s^25d^1$, the electronic configuration of Lr would be expected to be $[Rn]5f^{14}7s^26d^1$. Theoretical relativistic calculations, however, have predicted that the ground-state configuration of Lr is $[Rn]5f^{14}7s^27p^1_{1/2}$ since the $7p_{1/2}$ orbital would be stabilized below the $6d$ orbital in Lr by strong relativistic effects [3]. Since this prediction came out about 40 years ago, Lr has attracted interest of theoretical and experimental chemists.

Different electronic configuration yields different chemical behaviour. If the ground state configuration of Lr has a $7p_{1/2}$ valence electron, this would have implications of high volatility of Lr, as Eichler pointed out as a result of a semi-empirical consideration [4]. This prompted Jost and his colleagues to investigate the volatility of atomic Lr using a gas chromatographic technique [5]. In their experiment, no evidence for Lr as a volatile element with a $7p_{1/2}$ configuration was found.

In practice, chemical investigation of heavy elements such as Lr poses some difficulties. Elements heavier than fermium (Fm, $Z = 100$) must be produced at accelerators using reactions of heavy ions with heavy target materials. Moreover, both half-lives and cross sections of the isotopes of the still heavier elements are rapidly decreasing. Thus, they are usually available in quantities of a few atoms only at a time. Consequently, beginning with about the end of the actinides, properties of the elements must be studied on an atom-at-a-time scale. So far, it has been experimentally shown that Lr exhibits a stable $+3$ oxidation state in solution [6], and its ionic radius was evaluated as 88.6 ± 0.3 pm [7]. Based on the empirically developed "actinide concept", and in agreement with theoretical calculations, in today's Periodic Table, the actinide element series terminates with Lr. However, it has not yet been experimentally confirmed that Lr has appropriate properties as the last member of the actinide series.

2. The first ionization potential of Lr

Experimental determination of the ground-state electronic structure of Lr could demonstrate the magnitude of the influence of relativistic effects and provide new insights into the chemical properties of the heaviest elements.

The first ionization potential (IP_1) is a fundamental physical and chemical property of an element, which is qualitatively defined as the amount of energy required to remove the valence electron of an atom to form a positive ion. Experimentally determined IP_1, therefore, would give information on the outermost electronic orbital of the atom. In addition, IP_1 is one of the few physical quantities which can be estimated directly by theoretical calculations. A precise and accurate experimental determination of IP_1 can therefore benchmark electronic structure calculations.

IP_1 values of weighable amounts of nuclear-reactor-produced heavy elements up to einsteinium (Es, $Z = 99$) have been measured by resonance ionization mass spectrometry (RIMS) [8]. RIMS was also applied to an investigation of Fm with a sample of 2.7×10^{10} atoms of ^{255}Fm (half-life $T_{1/2} = 20.1$ h). In that experiment, the atomic level structure, but not the IP_1, was determined [9]. Recently, resonance ionization laser ion source (RILIS) studies optimized for short-lived nuclides made it possible to determine IP_1 of astatine (At, $Z = 85$) using ^{199}At ($T_{1/2} = 7.2$ s) produced in the proton-induced spallation reaction of uranium [10]. IP_1 values of heavy elements with $Z \geq 100$, however, could not be determined experimentally so far, as the produced amounts of the atoms were too low for the above techniques.

A sufficiently long-lived and detectable isotope for chemical experiments with Lr is ^{256}Lr ($T_{1/2} = 27$ s). It is produced at a rate of one atom per several seconds in the fusion-evaporation reaction of a ^{249}Cf target with a ^{11}B beam [11]. A new and highly efficient experimental method was thus required to determine an IP_1 value of Lr with such short-lived Lr atoms and in such low amounts.

In order to determine the IP_1 value of Lr, we have developed a novel method based on the surface ionization technique. The surface ionization is an ionization process which takes place on a solid surface kept at high temperature [12, 13]. Based on the Saha-Langmuir equation, an analytical model describes the surface ionization process in a hollow tube (cavity)-type ion-source. The ionization efficiency, I_{eff}, of an element in a small hot cavity can be expressed as:

$$I_{\text{eff}} = \frac{N \exp\left(\frac{\phi - IP_1^*}{kT}\right)}{1 + N \exp\left(\frac{\phi - IP_1^*}{kT}\right)}, \tag{1}$$

where ϕ is the work function which is material-dependent, k the Bolzmann constant, T the temperature of the ionizing surface, and N a parameter that depends on the effective number of atom-surface interactions in the cavity. IP_1^*, the effective IP_1, is directly related to IP_1 as:

$$IP^* = IP_1 - kT \ln\left(\frac{Q_1}{Q_0}\right), \tag{2}$$

where Q_i and Q_o are the partition functions of electrons in an atom and an ion at a given temperature, respectively, which can be calculated using excitation energies and statistical weights of their ground and excited states. In the present study, tantalum (Ta) was chosen as a cavity material. The IP_1 value of the element of interest is deduced from Eq. (1) where the parameter N is determined from a set of experimental ionization efficiencies (I_{eff}) of known IP_1 of some elements [14].

A schematic experimental set-up used in the measurement is shown in Fig. 1. To investigate surface ionization behaviour of short-lived Lr and other isotopes, we employed an ISOL (Isotope Separator On-Line) system which has a surface ion-source coupled to an aerosol gas-jet transport system at the tandem accelerator facility of Japan Atomic Energy Agency (JAEA). The ion-source has been newly developed for this purpose. The set-up consists of a target recoil chamber, a gas-jet transport system [15], a surface ion source installed in the ISOL system [16], and α/γ spectrometry systems. For an efficient α-particle measurement, we applied a rotating catcher wheel apparatus MANON (Measurement system of Alpha particle and spontaneous fission events ON-line) [17]. Nuclear reaction products produced in the target recoil chamber were attached on CdI_2 aerosol flowing into the chamber with 1.4 L/min He carrier gas. The radioactivity-laden aerosol particles were transported continuously into the ion-source via a Teflon capillary. Surface-ionized nuclear reaction products were extracted from the ion source and accelerated for mass separation. After the mass separation, ions of the isotope of interest are collected and detected to determine the ionization efficiency. For ^{256}Lr, I_{eff} values of $(33 \pm 4)\%$ and $(36 \pm 7)\%$ were measured at 2700 K and 2800 K, respectively [14].

To determine the value of the parameter N in Eq. (1) at each temperature, short-lived lanthanide and alkali isotopes ^{142,143}Eu, ^{143}Sm, ^{148}Tb, ^{153,154}Ho, ^{157}Er, ^{162}Tm, ^{165}Yb, ^{168}Lu and ^{80}Rb produced in nuclear reactions of ^{11}B beams with mixed lanthanide targets and a Ge target were provided to the experimental set-up and their ionization efficiencies were measured. Figure 2 shows the I_{eff} values at 2800 K as a function of IP_1^*. The IP_1^* value for each element was calculated with Eq. (2) using energies and statistical weights of low-lying excited states in the ion and the atom of each element provided by the National Institute of Standards and Technology (NIST) atomic database [18]. The determined N
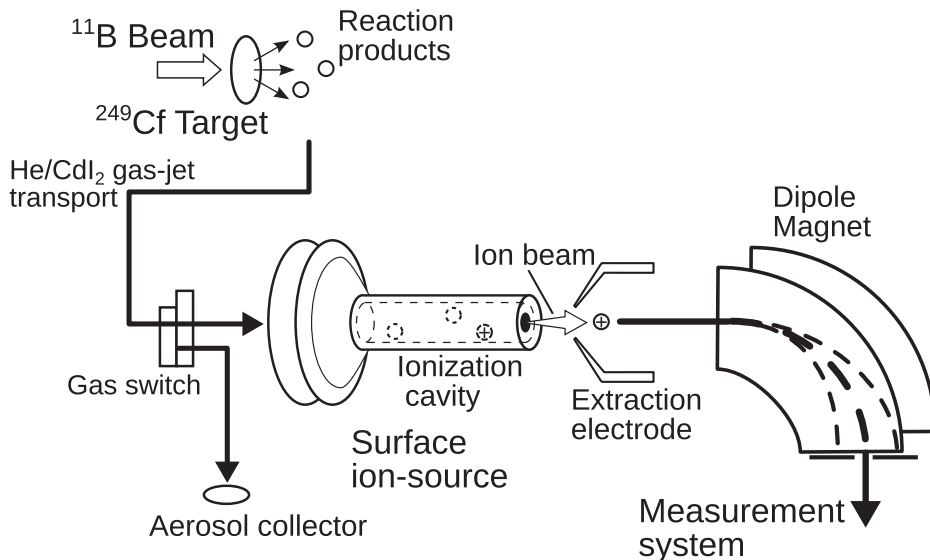
Figure 1. Schematic diagram of the experimental set-up for a measurement of the first ionization potential of Lr. The set-up was constructed based on the JAEA-ISOL system.
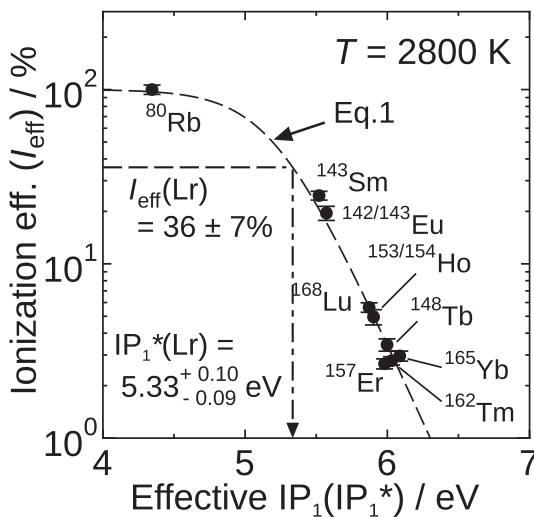

Figure 2. The ionization efficiency (I_{eff}) of various short-lived isotopes as a function of the effective IP_1 (IP_1^*) at 2800 K. The dashed curve is obtained by fitting the experimental data using Eq. (1). The position of the measured Ieff value of Lr, $(36 \pm 4)\%$, is also shown. From the fitted Eq. (1) with $N = 50 \pm 3$, IP_1^* of Lr is calculated to be $5.33^{+0.10}_{-0.09}$ eV. This corresponds to an IP_1 value of $4.97^{+0.13}_{-0.11}$ eV [14].

values at $T = 2700$ K and 2800 K were 43 ± 3 and 50 ± 3, respectively. Using the N values, the Lr IP_1^* values at $T = 2700$ K and 2800 K were calculated to be $5.29^{+0.08}_{-0.07}$ eV and $5.33^{+0.10}_{-0.09}$ eV respectively. Since the excitation energies of Lr and Lr^+, which are required to calculate IP_1 using Eq. (2) are unavailable, we employed theoretical values proposed in [19]. Then, IP_1 values of $4.95^{+0.10}_{-0.08}$ and $4.97^{+0.13}_{-0.11}$ were determined at $T = 2700$ K and 2800 K, respectively, for Lr. Based on these results, our experimentally determined value for IP_1 of Lr is $4.96^{+0.08}_{-0.07}$ eV.
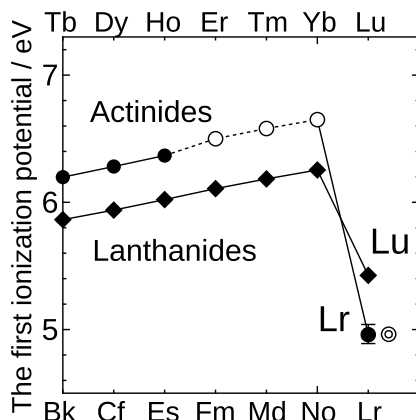
Figure 3. Variation of the experimental first ionization potentials of actinides(●) and lanthanides(♦). Open circles indicate estimated values for the heavy actinides [20], while the double circle shows the theoretically calculated value [14].

A state-of-the-art relativistic calculation of the IP_1 of Lr was also performed. The calculation was conducted using the relativistic coupled cluster approach with single, double, and perturbative triple excitations (DC CCSD(T)), and corrected for the Breit contribution and Lamb shift. The calculated IP_1 value is 4.963(15) eV. Our experimental result on the first ionization potential of $4.96^{+0.08}_{-0.07}$ is in excellent agreement with the theoretical value calculated in this work [14].

3. Where is the appropriate place of Lr in the Periodic Table?

The measured IP_1 value of Lr, 4.96 eV, is shown together with the theoretical values and experimental and/or estimated values [20–22] of lanthanide and actinide elements in Fig. 3. It is known that the IP_1 value increases monotonically from terbium to ytterbium and decreased dramatically at lutetium in the lanthanide series. As shown in Fig. 3, IP_1 of Lr is distinctly lower than that of Lu, 5.425871(12) eV [21] and the lowest among the actinides. This validates the position of Lr as the last actinide element (f-block element) in the Periodic Table, and quantitatively reflects and confirms the theoretically predicted situation of closed $5f^{14}$ and $7s^2$ shells with an additional weakly-bound electron in the valence orbital. The IP_1 of Lr is surprisingly low, with the valence electron even weaker bound than in sodium (5.1291 eV) [22]. The metallicity of Lr can be thus compared with an alkali metal.

On the other hand, our experimental result strongly supports that the outermost electronic orbital of Lr is the $7p_{1/2}$, due to the influence of the strong relativistic effects. This proposed electronic configuration of Lr, $[Rn]5f^{14}7s^27p^1_{1/2}$, suggests it would also not be out of the place in the p-block. A transition element is defined as "an element whose atom has an incomplete d sub-shell, or which can give rise to cations with an incomplete d sub-shell" by the International Union of Pure and Applied Chemistry (IUPAC) [23]. According to this definition, Lr would not belong to the transition elements.

It was also suggested that Lu and Lr should be placed below scandium and yttrium in the d-block, based on its ground-state valence-electron configuration and self-consistent group trends for various chemical and physical properties [24].

Since the introduction of the "actinide concept" as the most dramatic modern revision of the Periodic Table in the 1940s, the element with atomic number 103, lawrencium, played a crucial role as the last element in the actinide series. This special position has placed this

element into the focus of discussion on the influence of relativistic effects on electronic structure and motivated the determination of its atomic properties. Now, our study not only provides new information, both experimental and theoretical, but also poses a new question: "what are the appropriate positions of Lu and Lr in the Periodic Table?" This issue was already on the agenda of 48th IUPAC Council Meeting held in Korea in 2015 [25]. An IUPAC task group has been formed in order to make a recommendation regarding the membership of group 3 of the Periodic Table: Project No. 2015-039-2-200 [26].

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