Open access • Journal Article • DOI:10.1038/NATURE14342

Measurement of the first ionization potential of lawrencium, element 103

Tetsuya Sato, Masato Asai, Anastasia Borschevsky, Thierry Stora ...+21 more authors

Institutions: Japan Atomic Energy Agency, Massey University, CERN, Ibaraki University ...+4 more institutions

Published on: 09 Apr 2015 - Nature (Nature Publishing Group)

Topics: Lawrencium, Transactinide element, Relativistic quantum chemistry, Periodic trends and Atomic number

Measurement of the first ionization potential of lawrencium (element 103)

T. K. Sato[1], M. Asai[1], A. Borschevsky[2,3], T. Stora[4], N. Sato[1], Y. Kaneya[1,5], K. Tsukada[1], Ch. E. Düllmann[3,6,7], K. Eberhardt[3,7], E. Eliav[8], S. Ichikawa[1,9], U. Kaldor[8], J. V. Kratz[7], S. Miyashita[10], Y. Nagame[1,5], K. Ooe[11], A. Osa[1], D. Renisch[7], J. Runke[6], M. Schädel[1], P. Thörle-Pospiech[3,7], A. Toyoshima[1], N. Trautmann[7]

[1]Japan Atomic Energy Agency (JAEA), Tokai, Ibaraki 319-1195, Japan

[2]Centre for Theoretical Chemistry and Physics, New Zealand Institute for Advanced Study, Massey University , 0745 North Shore MSC, Auckland, New Zealand

[3]Helmholtz-Institut Mainz, 55099 Mainz, Germany

[4]ISOLDE, CERN, CH-1211 Geneva 23, Switzerland

[5]Graduate School of Science and Engineering, Ibaraki University, Mito, Ibaraki 310-8512, Japan

[6]GSI Helmholtzzentrum für Schwerionenforschung, 64291 Darmstadt, Germany

[7]Institut für Kernchemie, Johannes Gutenberg-Universität Mainz, 55099 Mainz, Germany

[8]School of Chemistry, Tel Aviv University, 69978 Tel Aviv, Israel

[9]Nishina Center for Accelerator-Based Science, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

[10]Graduate School of Science, Hiroshima University, Kagamiyama, Higashi-Hiroshima 739-8526, Japan

[11]Institute of Science and Technology, Niigata University, Niigata 910-2181, Japan

The quest for new chemical elements, a subject of intense research efforts[1], is driven by the desire to explore the limits of existence of matter. Ordering these elements in the Periodic Table is a milestone in chemical and physical science and provides an ongoing challenge[2-4]. Chemical studies[2,3] unravel properties which are governed by the configuration of the outermost electrons. It is well known that relativistic effects have a strong influence on the electronic structure of the heavy elements and even on the ground state configuration[4,5]. The first ionization potential (IP_1) is an atomic property which most sensitively reflects the outermost electronic configuration. Precise and accurate determination of the IP_1 provides significant information on the binding energy of the valence electrons and, thus, on increasingly strong relativistic effects. Here we report that the IP_1 of the heaviest actinide element lawrencium (Lr, atomic number Z = 103) is $4.96^{+0.08}_{-0.07}$ eV. Heaviest elements, including Lr, are only available in quantities of one or a few atoms at a time[2,3]. The IP_1 of Lr was measured with ^{256}Lr (half-life, $T_{1/2}$ = 27 s) produced in fusion reactions between ^{249}Cf and ^{11}B, using an efficient surface ion-source and a radioisotope detection system coupled to a mass separator. The measured IP_1 is in excellent agreement with 4.963(15) eV predicted by state-of-the-art relativistic calculations. The present work provides a reliable benchmark for theoretical calculations and also paves the way for IP_1 measurements of superheavy elements on an atom-at-a-time scale for their characterization.

The chemical characterization of the heaviest elements to probe their positions in the Periodic Table[2,3,6-10] has been, so far, conducted by rapid chemical separation techniques, such as gas-phase and liquid-phase chromatography. The influence of relativistic effects on electronic orbitals has indirectly been inferred through a comparison of chemical properties of the heaviest elements with those of their lighter homologs and those predicted by theoretical calculations. The first ionization potential (IP_1), one of the most fundamental physical and chemical properties of an element, gives direct information about the binding energy of an electron in an outermost electronic orbital of an atom. Accurate IP_1 values of heavy elements provide crucial tests for our understanding of the electronic structure of the heaviest elements. IP_1 values of weighable amounts of nuclear-reactor produced heavy elements up to einsteinium (Z = 99) were successfully measured by Resonance Ionization Mass Spectroscopy (RIMS)[11,12]. Recently, Resonance Ionization Laser Ion Source (RILIS) studies optimized also for short-lived atoms made it possible to determine the 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[13]. IP_1 values of heavy elements with $Z \geq 100$, however, could not be determined experimentally, because production rates are drastically decreasing for elements with increasing atomic number. This requires studying these elements with new techniques on an atom-at-a-time scale.

The ground-state electronic configuration of Lr is predicted to be [Rn]$5f^{14}7s^2 7p_{1/2}$, in contrast to that of its lanthanide homolog Lu, [Xe]$4f^{14}6s^2 5d$, as the $7p_{1/2}$ orbital is expected to be stabilized below the $6d$ orbital in Lr by strong relativistic effects[14-18]. Thus, Lr is expected to be the first element where relativistic effects directly change the electronic ground state configuration with respect to straightforward extrapolations based on the structure of the Periodic Table. The determination of the IP_1 sheds light on the important role of relativistic effects in heavy elements by comparison with theoretical predictions. For Lr, theory predicts an exceptionally low IP_1 value. A sufficiently long-lived and detectable isotope for ionization experiments is ^{256}Lr ($T_{1/2}$ = 27 s). It is produced with a rate of one atom per several seconds in the fusion-evaporation reaction of a ^{249}Cf target with a ^{11}B beam[19, 20]. With this constraint, a new and highly efficient experimental set-up based on the ionization and detection of the $^{256}Lr^+$ ion has been devised and implemented to determine the IP_1 value of Lr.

The surface ionization process takes place on a solid surface kept at high temperature, which is coupled to an on-line mass separator; i.e. an atom is ionized to the 1+ charge state via the interaction with a solid (metal) surface at high temperature and is selectively mass-separated. Figure 1 depicts the experimental set-up schematically. It consists of a target-recoil chamber coupled to an aerosol gas-jet transport system, a surface ion-source, a mass separator, and a detection system for nuclear decays[20]. Nuclear reaction products of the reaction of ^{249}Cf with ^{11}B were transported from the

target-recoil chamber to the ion-source by the gas-jet system. Transported products were injected into the ionization cavity of the ion-source. Here they were surface-ionized. Produced ions were extracted and accelerated by a potential of 30 kV, and then mass-separated. The number of ^{256}Lr ions after mass-separation was determined by α spectroscopy. For details of the setup, see ref. 20.

Based on the Saha-Langmuir equation[21, 22], an analytical model[23] describes the surface ionization in a hollow-tube (cavity) type ion-source. The ionization efficiency I_{eff} can be expressed as,

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

where ϕ is the work function, which is material-dependent, T the temperature of the ionizing surface, N a parameter which depends on the effective number of atom-surface interactions in the cavity, and k the Boltzmann constant. IP_1^*, the effective IP_1, is directly related to the IP_1 as[22],

$$IP_1^* = IP_1 - kT \ln\left(\frac{Q_i}{Q_o}\right), \quad \ldots (2)$$

where Q_i and Q_o are the partition functions at a given temperature for the ion and the atom, respectively, which can be calculated using excitation energies and statistical weights of their ground and excited states. As the cavity material, tantalum (Ta) was chosen. The ionization experiments were conducted at T = 2700 K and 2800 K. For

^{256}Lr, the I_{eff} values of (33 ± 4)% and (36 ± 7)%, respectively, were determined by the procedure given in ref. 20.

The following procedure was applied to determine the value of the free parameter N in Eq.1: 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 were produced in bombardments of ^{136}Ce/^{141}Pr/^{159}Tb, ^{142}Nd/^{148}Sm/^{159}Tb, ^{162}Dy, and Ge targets with ^{11}B, and their I_{eff} values were experimentally determined at T = 2700 K and 2800 K. Fig. 2 shows the I_{eff} values at 2700 K as a function of IP_1^*. The IP_1^* value for each element was calculated with Eq. 2. Energies and statistical weights of low-lying states in the ion and the atom of each element were taken from the National Institute of Standards and Technology (NIST) atomic data base[24]. The I_{eff} values determined for all isotopes were best fitted with Eq. 1 using N values of 43 ± 3 and 50 ± 3 at T = 2700 K and 2800 K, respectively.

The Lr IP_1^* values of $5.29^{+0.08}_{-0.07}$ eV and $5.33^{+0.11}_{-0.10}$ eV were determined from Eq. 1 at T = 2700 K and 2800 K, respectively. The result at 2700 K is illustrated in Fig. 2. Errors of the IP* values mainly came from uncertainties of surface temperatures, I_{eff} based on counting statistics, and the fitting procedures. The Lr IP_1 can be calculated from the IP_1^* using Eq.2 with Q_i and Q_0. No experimental data on excited states of the Lr atom and ion are available. Thus, the energies and statistical weights for calculating Q_i and Q_0 were taken from relativistic Fock space coupled cluster (FSCC) calculations[17]. The

average absolute error for the 20 lowest excitation energies of Lu (where comparison with experiment is possible) was 0.05 eV using the same approach[17]. We expected a similar accuracy for the predicted transition energies of Lr. The evaluated values of $kT \ln(Q_i/Q_0)$ for Lr at T = 2700 K and 2800 K are $-0.34^{+0.06}_{-0.04}$ and $-0.36^{+0.06}_{-0.04}$, respectively. The errors include uncertainties in the calculated excitation energies indicated in Ref 17, 0.087 eV (700 cm^{-1}) for each state, and in the temperatures. From this, IP_1 values of $4.95^{+0.10}_{-0.08}$ eV and $4.97^{+0.13}_{-0.11}$ eV were obtained at T = 2700 K and 2800 K, respectively. Based on these results, our experimentally determined value for the first ionization potential of Lr is $4.96^{+0.08}_{-0.07}$ eV.

A theoretical calculation of the IP_1 of Lr was also performed within the framework of the Dirac Coulomb (DC) Hamiltonian in combination with the coupled cluster approach with single, double, and perturbative triple excitations (CCSD(T)). The IP_1 was obtained by taking the difference between the calculated energies of the neutral state and the 1+ state. To assess the accuracy of our predicted IP_1 of Lr, we have also calculated the IP_1 of Lu. The calculations were performed with the Dirac13 program package[25] and Faegri basis sets[26] were used for both elements, consisting of 25*s* 23*p* 15*d* 14*f* 6*g* 3*h* orbitals for Lu and 27*s* 25*p* 17*d* 14*f* 6*g* 3*h* 2*i* orbitals for Lr. The contribution of the Breit term was assessed and was found to be small: 6 meV for Lu and -12 meV for Lr. A Lamb shift of 16 meV was found for the IP_1 of Lr, and of 0.3 meV for the IP_1 of Lu[27]. Calculations showed that the Lr $7s^2 7p_{1/2}$ level is lower in

energy than $7s^2 6d$, confirming earlier identification of the former as the atomic ground state. For Lu the same procedure yields the experimentally confirmed $6s^2 5d$ ground state. The calculated IP_1 values, corrected for the Breit contribution and the Lamb shift, are 5.418 eV for Lu and 4.963 eV for Lr. The calculated IP_1 for Lu is in good agreement with the experimental IP_1 of 5.425871(12) eV[28]. Similar accuracy is expected for the calculated IP_1 of Lr.

The experimental and calculated IP_1 results obtained in our work are shown in Table 1 together with earlier theoretical predictions. It should be noted that the calculated excitation energies of Lr, which we used to get Q_i and Q_0 values to derive the experimental IP_1 from IP_1*, were obtained with a different method compared to the one employed here for the calculation of the IP_1 itself. As the two calculations are independent, we can compare the present experimental and theoretical IP_1 values. Our experimental result on the first ionization potential of Lr of $4.96^{+0.08}_{-0.07}$ eV is in excellent agreement with the theoretical value of 4.963(15) eV also obtained in this work.

Thus, we experimentally showed that the first ionization potential of Lr is significantly lower than that of Lu. Lr has the lowest IP_1 value of all lanthanides and actinides. For the last actinide element, this quantitatively reflects and confirms the theoretically predicted situation of a closed $5f^{14}$ and $7s^2$ shell with an additional weakly-bound electron in the valence orbital. The surface ionization method, successfully applied to determine the IP_1 of Lr, can provide experimental data which can benchmark quantum

chemical calculations of the heaviest elements. In addition, it opens up new perspectives to determine such a basic atomic property for superheavy elements.

The authors would like to thank the JAEA tandem accelerator crew for supplying intense and stable beams for the experiments. The ^{249}Cf was made available by Prof. H. Nitsche of University of California, Berkeley, USA. It was produced in the form of ^{249}Bk through the former Transplutonium Element Production Program at Oak Ridge National Laboratory (ORNL) under the auspices of the Director, Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division of the U. S. Department of Energy. Financial support by the Helmholtz-Institut Mainz is gratefully acknowledged. This work has been partly supported by the Grant-in-Aid for Scientific Research (C) No.26390119 of the Ministry of Education, Science, Sports and Culture (MEXT).

The authors declare that they have no competing financial interests.

Corresponding author: Yuichiro Nagame (email: nagame.yuichiro@jaea.go.jp).

1. Oganessian, Yu. Heaviest nuclei from ^{48}Ca-induced reactions. *J. Phys. G: Nucl. Part. Phys.* **34**, R165-R242 (2007).

2. Schädel, M. & Shaughnessy, D. (eds) *The Chemisty of Superheavy Elements*, Second Edition (Springer, Heidelberg 2014)

3. Türler, A. & Pershina, V. Advances in the production and chemistry of the heaviest elements. *Chem. Rev*. **113**, 1237-1312 (2013).

4. Pyykkö, P. Relativistic effects in structural chemistry. Chem. Rev. **88**, 563–594 (1988).

5. Pershina, V. Electronic structure and chemistry of the heaviest elements. In: Barysz, M., Ishikawa, Y. (eds) *Relativistic Methods for Chemists*, Challenges and Advances in Computational Chemistry and Physics 10, pp. 451-520. (Springer, Dordrecht 2010)

6. Schädel, M. *et al*. Chemical properties of element 106 (seaborgium). *Nature* **388**, 55-57 (1997).

7. Eichler, R. *et al*. Chemical characterization of bohrium (element 107). *Nature* **407**, 63-65 (2000).

8. Düllmann, Ch. E. *et al*. Chemical investigation of hassium (element 108). *Nature* **418**, 859-862 (2002).

9. Eichler, R. *et al*. Chemical characterization of element 112. *Nature* **447**, 72-75 (2007).

10. Even, J. *et al*. Synthesis and detection of a seaborgium carbonyl complex, *Science* **345**, 1491-1493 (2014).

11. Köhler, S. *et al*. First experimental determination of the ionization potentials of berkelium and californium. *Angew. Chem. Int. Ed*. **35**, 2856–2858 (1996).

12. Peterson, J. *et al*. Determination of the first ionization potential of einsteinium by resonance ionization mass spectroscopy (RIMS). *J. Alloy. Comp.* **271-273**, 876 – 878 (1998).

13. Rothe, S. *et al*. Measurement of the first ionization potential of astatine by laser ionization spectroscopy. *Nat. Commun.* **4**, 1835 (2013).

14. Desclaux, J.-P. & Fricke, B. Relativistic prediction of the ground state of atomic lawrencium. *J. Physique* **41**, 943–946 (1980).

15. Eliav, E., Kaldor, U. & Ishikawa, Y. Transition energies of ytterbium, lutetium, and lawrencium by the relativistic coupled-cluster method. *Phys. Rev.* A **52**, 291–296 (1995).

16. Zou, Y. & Fischer, C. F. Resonance transition energies and oscillator strengths in lutetium and lawrencium. *Phys. Rev. Lett.* **88**, 183001 (2002).

17. Borschevsky, A. *et al*. Transition energies of atomic lawrencium. *Eur. Phys. J. D* **45**, 115–119 (2007).

18. Dzuba, V. A., Safronova, M. S. & Safronova, U. I. Atomic properties of superheavy elements No, Lr, and Rf, *Phys. Rev. A* **90**, 012504 (2014).

19. Sato, N. *et al*. Production of ^{256}Lr in the ^{249,250,251}Cf + ^{11}B, ^{243}Am + ^{18}O, and ^{248}Cm + ^{14}N reactions. *Radiochim. Acta* **102**, 211-219 (2014).

20. Sato, T. K. *et al*. First successful ionization of Lr (Z = 103) by a surface-ionization technique. *Rev. Sci. Instrum*. **84**, 023304(5) (2013).

21. Stora, T. Radioactive ion sources, *CERN Yellow Report* CERN-2013-007, pp.331-349, http://cds.cern.ch/record/1693046, accessed Nov. 2014.

22. Zandberg, É. Y. & Ionov, N. I. Surface ionization. *Soviet Phys. Usp.* **67**, 255-281 (1959).

23. Kirchner, R. On the thermoionization in hot cavities. *Nucl. Instrum. Methods A* **292**, 203 – 208 (1990).

24. Kramida, A., Ralchenko, Y., Reader, J. & Team, N. A. NIST atomic spectra database (version 5.1) (2013). http://physics.nist.gov/asd, accessed Jul. 2014

25. DIRAC, a relativistic ab initio electronic structure program, Release DIRAC13 (2013), written by Visscher, L. *et al*. (see http://www.diracprogram.org).

26. Faegri, K. Relativistic Gaussian basis sets for the elements K-Uuo. *Theor. Chem. Acc*. **105**, 252-258 (2001).

27. Shabaev, V. M., Tupitsyn, I. I., & Yerokhin, V. A. submitted to *Comput. Phys. Commun*. (2014).

28. Maeda, H., Mizugai, Y., Matsumoto, Y., Suzuki, A., & Takami, M. Highly excited even Rydberg series of Lu I studied by two-step laser photoionization spectroscopy, *J. Phys*. *B* **22**, L511-L516 (1989).

29. Liu, W., Küchle, W. & Dolg, M. Ab initio pseudopotential and density-functional all-electron study of ionization and excitation energies of actinide atoms. *Phys. Rev. A* **58**, 1103–1110 (1998).

30. Cao, X., Dolg, M. & Stoll, H. Valence basis sets for relativistic energy-consistent small-core actinide pseudopotentials. *J. Chem. Phys.* **118**, 487–496 (2003).

Table. 1 Theoretical and experimental first ionization potentials (IP_1) of Lr.

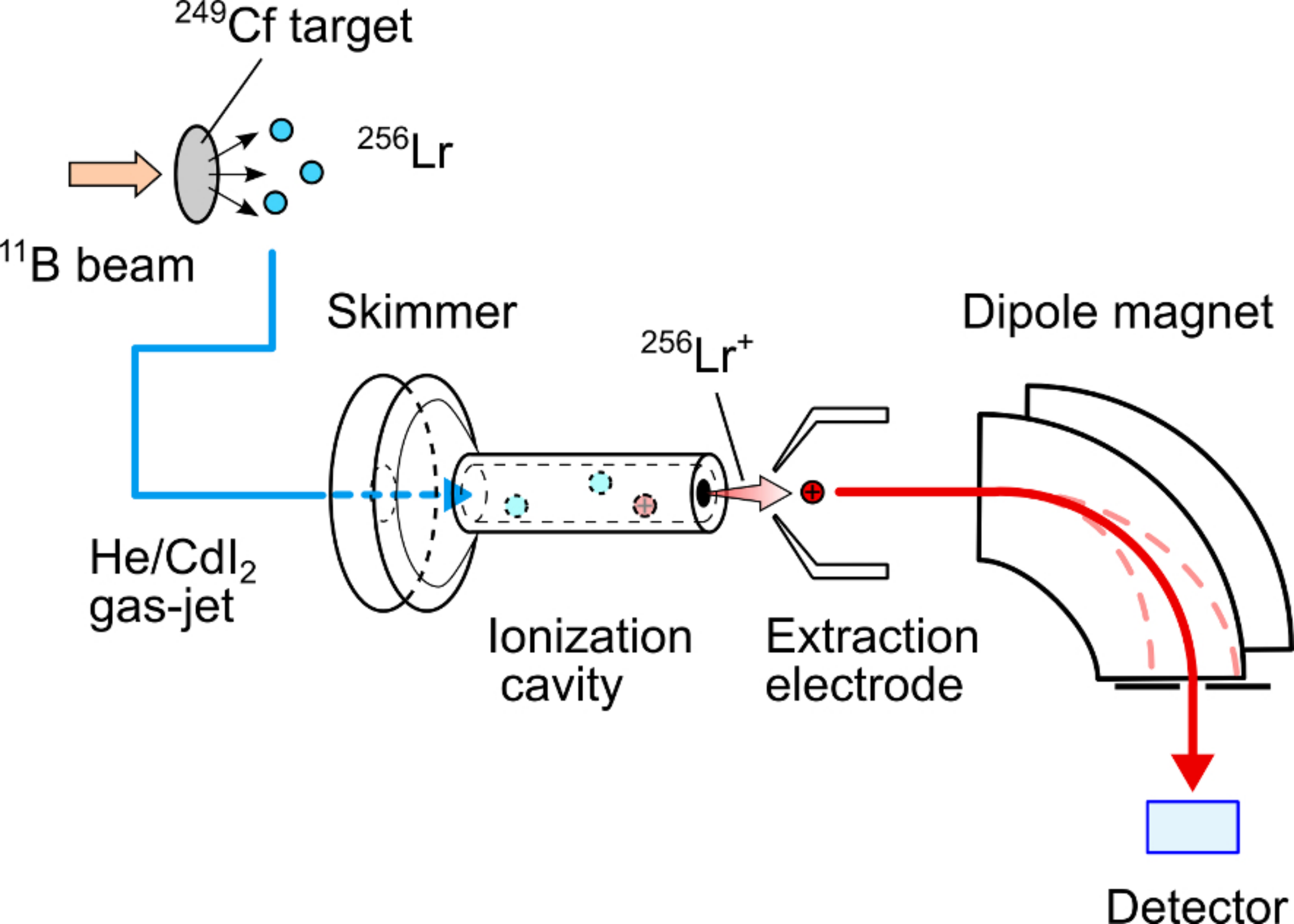
Author	Year	IP_1/eV	method
E. Eliav[15]	1995	4.887	DCB+FSCC[a]
W. Liu[29]	1998	5.28	RECP+CASSCF+ACPF+Δ_{SO}[b]
X. Cao[30]	2003	4.80	RECP+CASSCF+ACPF+Δ_{SO}[b]
A. Borschevsky[17]	2007	4.893	DCB+FSCC[a]
V. A. Dzuba[18]	2014	4.934	CI+all-order[c]
This work		4.963(15)	DC CCSD(T)+Breit+Lamb shift[d]
This work		$4.96^{+0.08}_{-0.07}$	Experimental

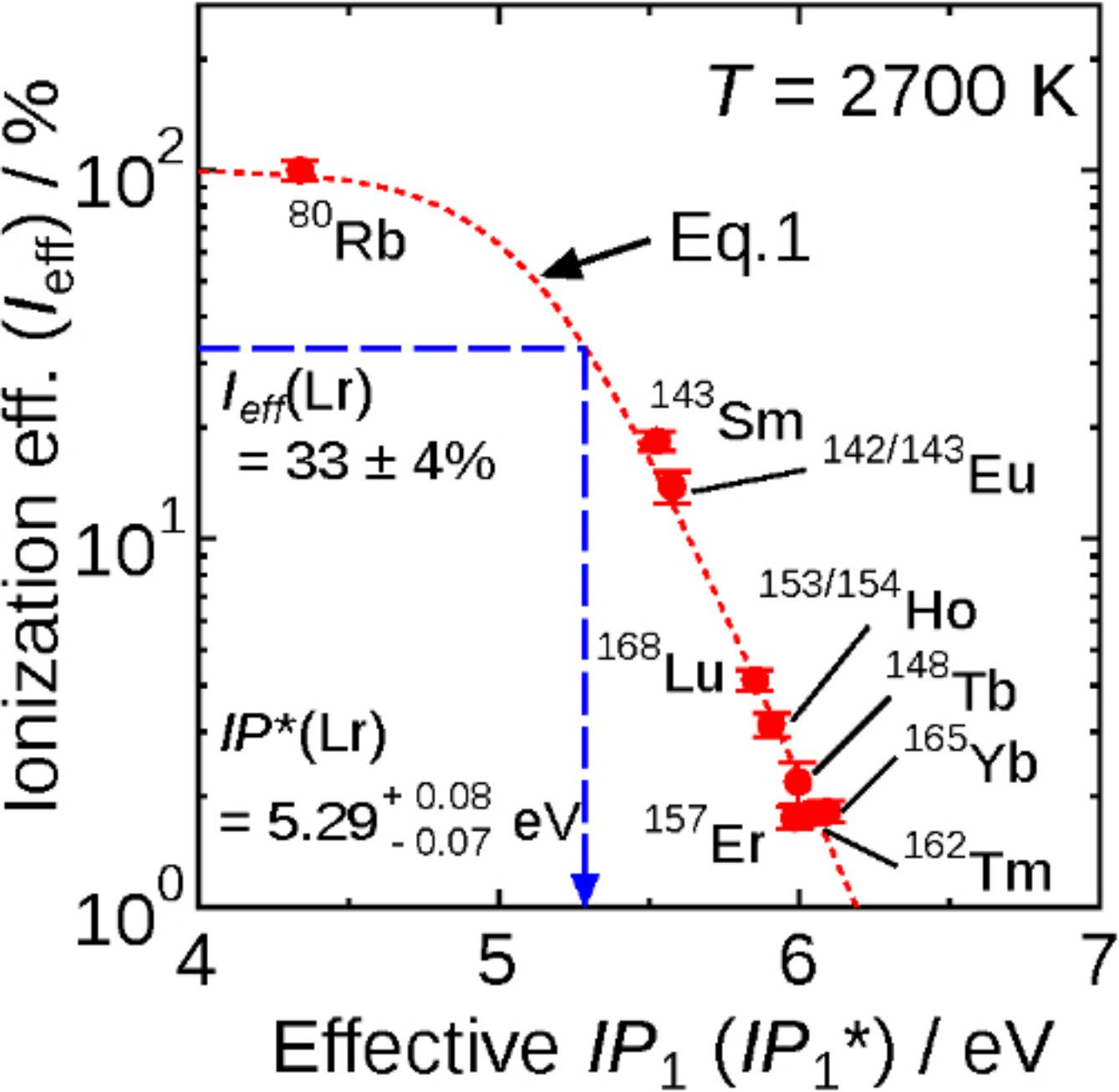
[a]Dirac Coulomb Breit Hamiltonian combined with the Fock space coupled cluster approach; [b]Relativistic effective core potentials (RECP) combined with complete active space SCF (CASSCF) calculations with subsequent multi-reference averaged coupled-pair functional (ACPF) calculations and spin orbit corrections (Δ_{SO}); [c]Configuration interaction method combined with the linearized single-double coupled cluster method; [d]DC Hamiltonian combined with CCSD(T) approach and corrected for the Breit contribution and the Lamb shift.

Figure 1. Schematic experimental setup used to measure the IP_1 of Lr on an atom-at-a-time scale.

For the Lr experiment, a ^{249}Cf target (thickness 260 μg cm^{-2}) in the target-recoil chamber was irradiated with a 67.9-MeV $^{11}B^{4+}$ beam delivered from the Tandem accelerator at the Japan Atomic Energy Agency (JAEA), Tokai. ^{256}Lr atoms, recoiling from the target, attached onto CdI_2 particles produced by sublimation of CdI_2 were transported with a 1.4 L min^{-1} He gas flow through a Teflon capillary (1.5 mmϕ × 8 m) to the ionization cavity of the ion-source installed in the Isotope Separator On-Line (JAEA-ISOL). Before entering the ionization activity, aerosol particles with the attached ^{256}Lr passed through a skimmer structure, installed to remove the He carrier gas to achieve high vacuum conditions at the ion-source (typically 2 × 10^{-2} Pa). In the cavity, the aerosol particles were vaporized and ^{256}Lr atoms were surface ionized. The temperature of the cavity was monitored with a calibrated radiation thermometer with ±50 K accuracy. Ions were extracted and accelerated by an electrostatic potential of 30 kV. $^{256}Lr^{+}$ ions were mass separated in the dipole magnet of the JAEA-ISOL mass separator and were transported to the detection device. The nuclear decay of ^{256}Lr was measured with 8-pairs of Si PIN photodiodes of the rotating catcher wheel apparatus, MANON (**M**easurement system of **A**lpha particle and spontaneous fissio**N** events ON-line)[20] for efficient α-particle measurements.

Figure 2. The ionization efficiency (I_{eff}) of various short-lived isotopes as a function of the effective IP_1 (IP_1*) at 2700 K. The dotted curve is obtained by fitting the experimental data using Eq. (1) for 2700 K. The position of the measured I_{eff} value of Lr, (33 ± 4)%, is also shown.


^{249}Cf target
^{256}Lr
^{11}B beam
Skimmer
^{256}Lr^{+}
Dipole magnet
He/CdI$_2$
gas-jet
Ionization
cavity
Extraction
electrode
Detector


T = 2700 K
Ionization eff. (I_eff) / %
10^2
10^1
10^0
80Rb
Eq.1
I_eff(Lr)
= 33 ± 4%
143Sm
142/143Eu
153/154Ho
168Lu
148Tb
165Yb
157Er
162Tm
IP*(Lr)
= 5.29 +0.08 -0.07 eV
4
5
6
7
Effective IP1 (IP1*) / eV