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First Ionization Potentials of Fm, Md, No, and Lr: Verification of Filling-Up of 5f Electrons and Confirmation of the Actinide Series

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Supporting Information

ABSTRACT: We report the first ionization potentials (IP$_1$) of the heavy actinides, fermium (Fm, atomic number $Z = 100$), mendelevium (Md, $Z = 101$), nobelium (No, $Z = 102$), and lawrencium (Lr, $Z = 103$), determined using a method based on a surface ionization process coupled to an online mass separation technique in an atom-at-a-time regime. The measured IP$_1$ values agree well with those predicted by state-of-the-art relativistic calculations performed alongside the present measurements. Similar to the well-established behavior for the lanthanides, the IP$_1$ values of the heavy actinides up to No increase with filling up the 5f orbital, while that of Lr is the lowest among the actinides. These results clearly demonstrate that the 5f orbital is fully filled at No with the $[\mathrm{Rn}]5f^{14}7s^2$ configuration and that Lr has a weakly bound electron outside the No core. In analogy to the lanthanide series, the present results unequivocally verify that the actinide series ends with Lr.

Extending the periodic table and classifying newly discovered heavy elements are among the most fundamental and exciting aspects of the chemical sciences. This leads to architect the periodic table and revise its structure in the heavy element region. The most recent revision of the structure of the periodic table took place in the 1940s when Glenn T. Seaborg introduced the ground-breaking actinide concept,[1,2] placing a new actinide series below the lanthanides. In this new series, the 5f electron shell is filled in a manner similar to the filling of the 4f electron shell in lanthanides. The actinide concept did not only allow for the immediate discoveries of the elements 95, americium, and 96, curium, but was also instrumental for the discovery of heavier ones. Chemical properties of weighable amounts of nuclear-reactor-produced actinides up to Fm have been extensively studied.[3] However, much less is known about the heavier actinides due to stringent limitation on experimental procedures[4] with increasing atomic number as these heavy elements are available in decreasing quantities of only one atom at a time.[5,6]

The first ionization potential (IP$_1$) of an atom is one of the most fundamental chemical and physical quantities of every element. The first measurements of IP$_1$ of actinides were performed by a surface ionization technique.[7] Then laser spectroscopy and resonance ionization mass spectroscopy of macroscopically available actinides up to einsteinium have been conducted to measure accurate IP$_1$ values.[8−11]

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Table 1. IP_1* Obtained from I_{eff} and N at Temperature T

element	T (K)	I_{eff} (%)	N	IP_1* (eV)	$kT \ln(Q_i/Q_0)$ (eV)	IP_1[a] (eV)
^{100}Fm	2900 ± 100	1.3 ± 0.4	71 ± 20	6.39 ± 0.13	0.13 ± 0.02	6.52 ± 0.13
^{101}Md	2900 ± 100	1.2 ± 0.3	71 ± 20	6.43 ± 0.13	0.16 ± 0.01	6.59 ± 0.13
^{102}No	2850 ± 80 3000 ± 100	0.54 ± 0.09 0.77 ± 0.10	43 ± 8 34 ± 7	6.44 ± 0.08 $6.45^{+0.09}_{-0.10}$	0.17 ± 0.01 0.18 ± 0.01	6.61 ± 0.08 $6.63^{+0.08}_{-0.10}$
$_{103}$Lr	2550 ± 50 2850 ± 50	23 ± 5 39 ± 6	35 ± 3 47 ± 3	$5.31^{+0.09}_{-0.06}$ $5.30^{+0.09}_{-0.05}$	$-0.37^{+0.06}_{-0.04}$ $-0.32^{+0.06}_{-0.04}$	$4.99^{+0.10}_{-0.07}$ $4.94^{+0.10}_{-0.07}$

[a]The IP_1* and the temperature-dependent correction factor, $kT \ln(Q_i/Q_0)$, give IP_1 (see text).

Recently, we reported the successful measurement of IP_1 of Lr in an atom-at-a-time scale experiment using a method based on surface ionization coupled to mass separation and α-particle detection techniques.[12] The result suggested that Lr has the lowest IP_1 value of all actinide elements, although those of other heavy actinides, Fm, Md, and No, have not yet been determined experimentally. According to the systematic variation of the IP_1 values of heavy actinides, an increasing trend is anticipated up to No due to filling electrons up in the 5f orbital.[13−16] Nobelium is expected to have the highest IP_1 among the actinides due to the closed-shell structure of [Rn]$5f^{14}7s^2$. Very recently laser resonance ionization spectroscopy of No, using ^{254}No (half-life, $T_{1/2}$ = 51.2 s) in one-atom-at-a-time quantities, was performed and the IP_1 has been measured to be 6.62621 ± 0.00005 eV,[17,18] supporting the scenario of closed 5f and 7s atomic shells in No. However, to unequivocally confirm the filling of the 5f electron shell in the heavy actinides, it is indispensable to experimentally determine the successive IP_1 values from Fm to Lr.

In the present study, we have applied the earlier developed surface-ionization method[12] to determine the IP_1 values of Fm, Md, and No. In addition, IP_1 of Lr has been also measured to improve the accuracy of the previously reported IP_1.[12] Surface ionization process takes place on a solid surface kept at a high temperature and can be described by the Saha−Langmuir (S-L) equation.[19] The ionization efficiency (I_{eff}) depends on the work function of the ionizing material, ϕ (eV), the temperature of the material surface, T (K), and IP_1 of the element. The detailed experimental setup and the analytical method used in this work have been described in our previous papers.[12,20,21]

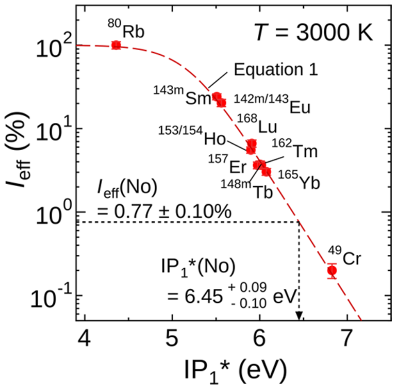

Figure 1. Ionization efficiency (I_{eff}) of various short-lived isotopes as a function of the effective IP_1, IP_1*, at 3000 K. The red-dashed curve is obtained by fitting eq 1 to the experimental data.

Short-lived isotopes ^{249}Fm ($T_{1/2}$ = 2.6 min), ^{251}Md ($T_{1/2}$ = 4.27 min), ^{257}No ($T_{1/2}$ = 24.5 s), and ^{256}Lr ($T_{1/2}$ = 27 s) were produced in nuclear fusion reactions (Supplement Table 1). The produced atoms, recoiling from the target, were transported via a Teflon capillary[20−22] to a surface ion-source installed at the JAEA-ISOL (Isotope Separator Online) by the He/CdI_2 gas-jet transport system.[21] Transported products were injected into the ionization cavity of the ion-source. Metallic tantalum (Ta) was selected as the cavity material in this work. The products were surface-ionized on the hot surface of the Ta cavity kept at a temperature between 2550 and 3000 K. Produced ions are extracted and mass separated in the ISOL. The number of collected ions after the mass-separation was determined by α spectrometry.[12,20] The I_{eff} value was calculated from a ratio of the number of mass-separated ions to that of directly collected atoms transported by the gas-jet system.[20]

The α spectra after surface ionization and following mass-separation are shown in Supplement Figures 1−4. The measured I_{eff} values for ^{249}Fm, ^{251} Md, ^{257}No, and ^{256}Lr are listed in Table 1 with the related surface temperature. On the basis of the S-L equation,[19,23] I_{eff} in a small cavity configuration can be expressed as[12,24]

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

where N is a parameter that depends on the effective number of atom−surface interactions in the cavity, and k is the Boltzmann constant. IP_1*, the effective IP_1, is directly related to the IP_1 as[19,23]

$$IP_1* = IP_1 - kT \ln\left(\frac{Q_i}{Q_0}\right) \qquad (2)$$

where Q_i and Q_0 are the partition functions for the ion and atoms at a given temperature, which can be calculated using excitation energies and statistical weights of their ground and excited states. Thus, IP_1* can be calculated from the experimentally determined I_{eff} value of the isotope of interest via eq 1. Then, IP_1* can be converted to IP_1 using eq 2.

To confirm the correlation between I_{eff} and IP_1* in the present system, I_{eff} values of short-lived lanthanides, an alkali metal, and a chromium isotope were measured. The short-lived isotopes, ^{143m}Sm, ^{142m,143}Eu, ^{148m}Tb, ^{153,154}Ho, ^{157}Er, ^{162}Tm, ^{165}Yb, ^{168}Lu, ^{80}Rb, and ^{49}Cr were employed. Figure 1 shows the typical plot of the measured I_{eff} values vs IP_1* of these elements at T = 3000 K. The IP_1* values of the above elements were calculated via eq 2 using their known IP_1 values compiled in the National Institute of Standard and Technology (NIST) atomic spectra database (ASD).[25] Low-lying excited states for the calculation of Q_i and Q_0 were also taken from NIST ASD. Values of the parameter N were obtained by a best-fit with eq 1 to the measured I_{eff} values for the isotopes; summarized with the other quantities in Table 1. The determination of IP_1* = 6.45 eV for No from I_{eff} = 0.77% at T = 3000 K is depicted in Figure 1. The I_{eff} vs IP_1* plot at 2900 K for Md and Fm is shown in Supplement Figure 5.

Table 2. Experimental and Theoretical IP_1 Values

		IP_1 (eV)			
ref	method	Fm	Md	No	Lr
		Theoretical			
Sugar[13]	semiempirical	6.50	6.58	6.65	
Rajnak and Shore[14]	semiempirical	6.46	6.57	6.67	
Liu et al.[15]	QRPP-CASSCF+APCF[a]	6.26	6.10	6.14	5.28
Cao et al.[31]	RPP-CASSCF+APCF[b]	6.13	6.23	6.27	4.79
Borschevsky et al.[12,28]	IHFSCC			6.632 ref 28	4.963(15) ref 12[d]
Pantazis and Neese[16]	DKH2-B3LYP[c]	6.45	6.54	6.64	4.56
Dzuba et al.[32]	CI+SD[d]			6.743	4.9
present work	CCSD(T) MCDF	6.469 6.22	6.557	6.638	
		Experimental			
literature		<6.76 ref 33		6.62621(5) ref 18	$4.96^{+0.08}_{-0.07}$ ref 12
present work		6.52 ± 0.13	6.59 ± 0.13	$6.62^{+0.06}_{-0.07}$	$4.96^{+0.05}_{-0.04}$

[a] Quasirelativistic ab initio pseudopotential (QRPP) complete active space self-consistent field (CASSCF) calculations combined with averaged coupled-pair functional (ACPF) and corrected for spin−orbit coupling. [b] Relativistic ab initio pseudopotential (RPP) CASSCF calculations combined with ACPF and corrected for spin−orbit coupling. [c] Second order Douglas−Kroll−Hess approach combined with density functional theory (B3LYP functional). [d] Relativistic configuration interaction (CI) combined with the linearized single−double coupled cluster method.

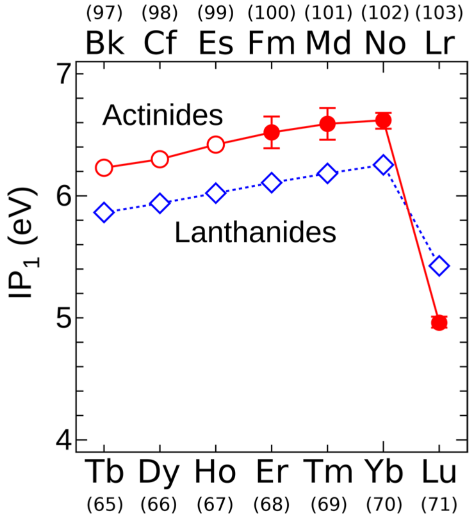

Figure 2. Variation of the experimental IP_1 values of heavy actinides and heavy lanthanides with atomic numbers. Closed circles indicate the values obtained in the present work.

To calculate the IP_1 values of Fm, Md, No, and Lr from their IP_1* values, excitation energies and statistical weights of the low-lying states of each atom and ion are required. As no experimental data on excited states in the heavy actinides are available, we calculated these values using relativistic computational methods. The intermediate-Hamiltonian Fock space coupled cluster (IHFSCC) method[26] was applied to calculations of the atomic and ionic states of Md and No (for some of the levels the single reference coupled cluster with single, double, and perturbative triple excitations (CCSD(T)) was employed), while the Multi-Configuration Dirac−Fock (MCDF) method, as implemented in the Graps2k code,[27] was used for the Fm atom and its ion. Excited states of No and Lr were taken from refs 28, 29, where they were also calculated within the IHFSCC approach. The methods used here were also applied to the lower excitation energies of the lanthanide homologues of the elements of interest (Er, Tm, Yb, and Lu). For the lighter elements, we can compare our results to the available experimental data, thus assessing the accuracy of our calculations and of our predictions for Fm through Lr. The obtained values are compiled in the Supplement Table 2. Although several low-lying states were found in Fm^+, only one state should be considered for the Fm atom (Supporting Information). There are no excited states in the range of interest for Md, while one state is present for Md^+. In No and No^+, only the ground states are expected to contribute. The errors in the energy of the excited states were evaluated from relative errors of the calculated values compared to the experimental transition energies of the respective lanthanide homologues. The $kT\ \ln(Q_i/Q_0)$ values are presented in Table 1. For the case of Lr, the values were obtained in the same manner in ref 12. The IP_1 values of Fm, Md, and No are determined to be 6.52 ± 0.13, 6.59 ± 0.13, and $6.62^{+0.06}_{-0.07}$ eV, respectively, where IP_1 of No was obtained by taking a weighted average of the IP_1 values listed in Table 1. A more accurate IP_1 of Lr of $4.96^{+0.05}_{-0.04}$ eV was determined by also taking a weighted average of our previous[12] and present values. Errors in IP_1 mainly come from counting statistics, surface temperature, and fitting procedure with eq 1.

In parallel to the measurements, we calculated the IP_1 values of Fm, Md, and No within the relativistic CCSD(T) approach, corrected for the Breit term and the higher order quantum electrodynamic (QED) corrections, using a similar scheme to that employed in ref 30.

The experimental and theoretical IP_1 values obtained in the present work are summarized in Table 2 together with earlier theoretical predictions[12−16,28,31,32] and measurements.[12,18,33] The present experimental values for Md and No agree with the semiempirical values[13,14] as well as with the more recent relativistic calculations[28] for No and the DKH2-B3LYP calculations[16] for both atoms. Our result on IP_1 of No also agrees with the recent value from laser-spectroscopic measurements,[18] thus providing independent validation to our experimental method. The calculated IP_1 of Er, the homologue of Fm, is 5.94 eV as obtained from the present MCDF calculation, that is significantly lower than the experimental value of 6.11 eV. Therefore, the MCDF prediction probably also underestimates the IP_1 value of Fm. The CCSD(T) + Breit + QED calculations of IP_1 agree well with the measurements for all elements investigated here.

The variation of the IP_1 values of the heavy actinides with atomic number in comparison with those of the heavy lanthanides is shown in Figure 2. As expected from the prediction,[13−16] the IP_1 values increase up to No via Fm and Md with filling of the 5f orbital in analogy to the heavy lanthanides. We take this as an indication that the 5f orbital is fully filled at No. The lowest IP_1 value of Lr is confirmed; the ground-state electronic configuration of the Lr atom has closed $5f^{14}$ and $7s^2$ shells with an additional weakly bound electron in the valence orbital. The results unambiguously confirm that the actinide series end with Lr.[34]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b09068.

> Experimental details of the nuclear reactions for the production of the short-lived actinide isotopes, ^{249}Fm, ^{251} Md, ^{257}No, and ^{256}Lr and for production of various isotopes used to determine a relationship between IP_1* and I_{eff} in the present system; alpha spectra of ^{249}Fm, ^{251} Md, ^{257}No, and ^{256}Lr measured after mass-separation; ionization efficiencies of various short-lived isotopes as a function of the IP_1* at 2900 K, which was used for IP_1 calculations of Md and Fm; and summary of computed low-lying level energies for the Fm, Md, and No atoms and ions together with those of respective lanthanide homologues, Er, Tm, and Yb (PDF)

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Notes

The authors declare no competing financial interest.

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