December 07, 2018

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

The Scientific Article

The article **"First Ionization Potentials of Fm, Md, No, and Lr: Verification of Filling-Up of 5f Electrons and Confirmation of the Actinide Series"** was submitted on September 07, 2018 and published in the Journal of the American Chemical Society (JACS) on October 25, 2018 (J. Am. Chem. Soc. 140, 14609-14613 (2018).

The experiment was conducted at the Japan Atomic Energy Agency, Tokai, Japan, in collaboration with our groups at GSI Darmstadt , HIM Mainz, and JGU Mainz. The first author is Dr. Tetsuya K. Sato, staff scientist at Japan Atomic Energy Agency, Tokai, Japan. In 2017, he was a visiting scientist at HIM Mainz for an extended period.

Protons, Neutrons, Atoms, Elements... The Basic

Matter around us consists of atoms. Every atom consists of a small atomic nucleus, which comprises almost the total mass of the atom, and an extended electron shell. The nucleus is built up from (positively charged) protons and (neutral) neutrons, whereas the shell consists of (negatively charged) electrons. The electrons surround the nucleus in certain orbitals. Atoms with the same number of protons belong to the same element. The elements up to uranium (element 92) exist in nature (except technetium). The elements heavies than uranium are man-made. All these elements are arranged in the periodic table of the elements. Their positions in the periodic correspond to their proton number and electron shell structure and thus provide information on their chemical behavior. In neutral atoms, the proton number and the electron number is the same.

Atoms with the same number of protons belong to the same element. Atomic nuclei with the same number of protons and different numbers of neutrons are called isotopes. The elements up to uranium (element 92) exist in nature (except for technetium). The elements heavier than uranium are man-made.

All elements are arranged in the periodic table of the elements. Their positions in the periodic table correspond to their proton number; elements in the same column (i.e., in the same group) feature similar and electronic shell structure, which characterizes the chemical behavior of an element. An element's position in the periodic table and thus provides information on its chemical behavior, e.g., as a metal or an inert gas.

The electron configuration characterizes the chemical behavior of an element. Thus, it behaves e.g. like a metal or like an inert gas.

The Radioactive Decay

If atomic nuclei have too many protons (all of which repel each other) or have an this ratio is unfavorable proton to neutron ratio, the nuclei are not stable but undergo radioactive decay.

- One important decay mode is α decay, where an α particle consisting of two protons and two neutrons is emitted.
- Spontaneous fission is α decay in which the nucleus splits into two fragments.
- In β-decay, a neutron is converted into a proton (under emission of an electron; β^--decay) or a proton converts into a neutron (under emission of a positron, the positively charged antiparticle of the electron; β^+-decay). Thus, the number of nucleons remains the same in β-decay processes. Both β-decay processes are accompanied by the emission of a (anti)neutrino.

Production and Stability of the Heaviest Elements

The elements heavier than uranium are man-made. The elements up to the element fermium (which has atomic number 100) can be produced at research reactors by irradiating a target of a heavy element with neutrons. The target atoms capture a neutrons and subsequently decay through β^--emission, thus forming an element with the next higher proton number. This process can be repated, up to fermium.

As there are no isotopes of fermium which decay through β^--emission, no elements with higher proton number can be synthesized by this method.

Heavy ion induced fusion reactions give access to yet heavier elements. Target foils containing the element to be irradiated are bombarded with ions from an accelerator such as the Tandem Accelerator at JAEA Tokai

If a projectile at the right energy hits an atomic nucleus of the target centrally, the two nuclei may fuse, forming an excited compound nucleus. Ideally, if this compound nucleus deexcites by the evaporation of neutrons, an atom of anew heavy element is formed. Most often, though, the nucleus fissions into two lighter fragment. Therefore, the production rates for the heaviest elements are very small: typically between a few atoms minute or per hour down to a single atom per month.

The heavier an atom is, the more protons are contained in its nucleus. With increasing proton number, the repulsive force of these protons will eventually lead to immediate disintegration of the nucleus. The elements with a proton number higher than 103 can only exist due to nuclear shell effects and are called the superheavy elements. A topic of intense research concerns the question of the heaviest possible element. To date, all elements up to element 118 officially recognized as discovered.. It is currently not clear, which element is the heaviest one that can exist.

In our work, we studied the elements with atomic numbers 100 (fermium, with chemical symbol Fm), 101 (mendelevium, Md), 102 (nobelium, No), and 103 (lawrencium, Lr). The following isotopes were synthesized in nuclear fusion reactions:

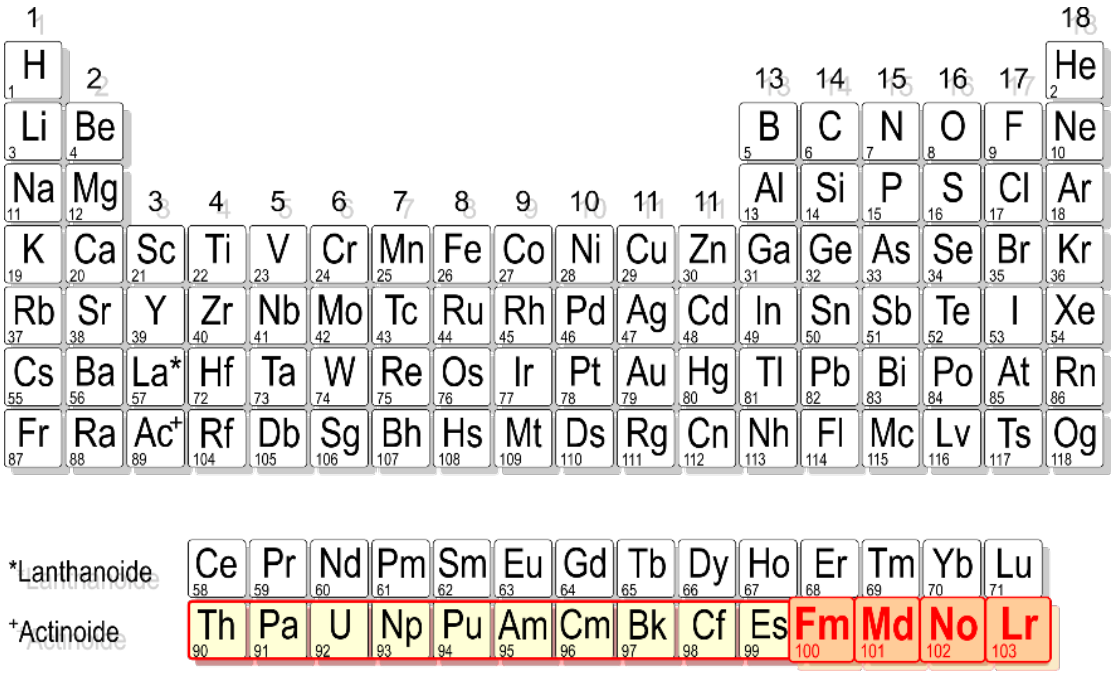
- $^{243}Am + ^{11}B \rightarrow ^{254}Fm^* \rightarrow ^{249}Fm$ + 5 neutrons
- $^{243}Am + ^{12}C \rightarrow ^{255}Md^* \rightarrow ^{251}Md$ + 4 neutrons
- $^{248}Cm + ^{13}C \rightarrow ^{261}No^* \rightarrow ^{257}No$ + 4 neutrons
- $^{249}Cf + ^{11}B \rightarrow ^{260}Lr^* \rightarrow ^{256}Lr$ + 4 neutrons
  - ^{256}Fm decays with a half-life of 2.6 min. In about 15% of all cases, this is through α particle emission into ^{245}Cf, which in turn decays by emission of a further α particle.

- ^{251}Md decays with a half-life of 4 min. In less than 10% of all cases, this is through α particle emission into ^{247}Es.
- ^{257}No decays with a half-life of 24.5 s through α particle emission into ^{253}Fm.
- ^{249}Lr decays with a half-life of 27 s through α particle emission into ^{252}Md, which in turn decays by emission of a further α particle.

Identifcation of the four studied isotopes was facilitated by the detection of these α particles.

Chemical Properties of the Superheavy Elements - The Influence of Einstein's Relativity Theory

In the periodic table of elements, all elements with atomic number ≥ 104 follow the actinide series, which ends with lawrencium (element 103). The first transactinides, up to element 111, are transition metals, while the heaviest known elements belong to the main groups with element 118 standing in the group of the noble gases.



The heavier an element, the higher theo positive charge of its nucleus, which attracts the negatively charged electrons in the electron shells. The velocities, with which electrons move, are directly related to this force, meaning that electrons which are near the atomic nucleus of a superheavy element are accelerated to high velocities – to about 80% of the speed of light. Here is where the influence of the special theory of relativity comes in: according to this theory, objects that are moving become heavier than if they are at rest. While the effect is too small in daily life where velocities are typically very small compared to the speed of light, this is different for the electrons in superheavy elements, and the mass increase is of the order of 50% of the rest mass. This is called the "direct relativistic effect", which acts most pronouncedly on electrons in orbitals with a high probability density near the atomic nucleus, e.g., electrons in s orbitals. These orbitals are therefore relativistically contracted in space and energetically stabilized by the direct relativistic effect.

As a consequence of the contraction of, e.g., the s orbitals, electrons occupying d or f orbitals, which are never near the atomic nucleus, are better screened from the latter, thus feeling less attraction. They thus expand in space and are energetically destabilized by this "indirect relativistic effect". Finally, a third effect, the "spin-orbit splitting" lifts the energetic equivalence of orbitals in a single subshell (like the 6 electrons that can occupy a p orbital) and splits each such subshell into two different levels. The best example is the p orbital, which, in a relativistic description, falls into a p½ and a $p_{3/2}$ orbital, which accommodate 2 and 4 electrons, respectively.

As the influence of relativistic effects increases roughly with the square of the atomic number, the transactinide elements are the best suited laboratory for the study of their influence on chemical properties.

The First Ionization Potential of the heaviest actinides: Why is this Interesting?

The first ionization potential (IP_1) is a fundamental physical and chemical property of every element and therefore every atom. Information on the IP_1 of the heaviest elements can provide a test and better understanding of relativistic effects which are significantly noticeable for heavy elements. A precise and accurate determination of the IP_1 of the heaviest elements allows challenging modern theoretical calculations on the electronic structure of heavy atoms.

The elements heavier than Fm with atomic number Z = 100, however, 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 only a few atoms at a time. Consequently, beginning with about the end of the actinides properties of the heaviest elements must be studied on an atom-at-a-time scale. The IP_1 values of the heavier actinides with Z > 100, therefore, have not been measured. (Very recently laser resonance ionization spectroscopy of No, using ^{254}No (half-life, $T_{½}$ = 51.2 s) in atom-at-a-time quantities, was performed by a collaboration working at GSI and led by the group of Prof. Dr. Michael Block, and the IP_1 has been measured to be 6.62621 ± 0.00005 eV.)

The ground-state electronic configuration of the heaviest actinide, lawrencium (Lr), is predicted to be [Rn]$5f^{14}7s^2$7p½ which is different from that of the lanthanide homolog Lu, [Xe]$4f^{14}6s^2$5d. The reason for this change in ground-state configuration is because the 7p orbital of Lr is stabilized below the 6d orbital by strong relativistic effects. The weakly-bound outermost electron results in a significantly lower ionization potential (IP_1) of Lr as compared with its neighboring heavy actinides. With an experimentally determined IP_1 value of Lr, we can contribute to a better understanding of shell effects and how relativistic effects play a key role in the electronic structure of heavy atoms.

In the previous paper, we successfully measured IP1 of Lr using a method based on surface ionization coupled to mass separation and α-particle detection techniques. The obtained IP_1 value of Lr was in good agreement with theoretical prediction obtained using relativistic calculations, which favour a 7p½ configuration in the Lr atom. Further, 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 been yet determined experimentally. This 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. 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 contrast to Lr, No (Z = 102) is expected to have the highest IP_1 among the actinide elements due to its fully-filled 5f and 7s orbitals: $[Rn]5f^{14}7s^2$. The IP_1 value of heavy actinides up to No is anticipated to increase with filling electrons up in the 5f orbital in analogy to heavy lanthanides. The presently measured IP_1 values of heavy actinide, Fm to Lr, agree well with those predicted by state-of-the-art relativistic calculations, which are also reported in the current paper. The results obviously indicate that the IP_1 values increase up to No via Fm and Md with filling of the 5f orbital. Therefore, we take this as an indication that the 5f orbital is fully filled at No with the $Rn]5f^{14}7s^2$ configuration. 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 additionally weakly-bound electron in the valence orbital. The result clearly demonstrates that, in analogy to the lanthanide series, the actinide series has been unambiguously confirmed, ending with Lr.

Future Perspectives

The work demonstrates studies with single lawrencium atoms to be possible and that they can be manipulated to extract basic atomic properties – in the present case the first ionization potential. In contrast to previous measurements of this property in lighter elements, some thousands of atoms were sufficient for our measurement. This is many orders of magnitude less than previously used, more conventional techniques. A fascinating next step would be to experimentally determine its ground state electron configuration; such an experiment has to answer the question whether this is $[Rn]5f^{14}7s^27p_{½}$ or $[Rn]5f^{14}7s^26d$.
Ionization potential measurements of yet heavier elements – i.e., with atomic number Z ≥ 104, these then being members of the transactinide series, which follows the actinide series – appear within reach, despite the fact that production rates will be yet smaller than for Lr, and the first ionization potential is predicted to be higher (implying a smaller efficiency of our used method).

The Collaboration

Our collaboration comprises 14 institutions in 5 countries:

- Japan Atomic Energy Agency (JAEA), Tokai, Ibaraki, Japan
- The Van Swinderen Institute for Particle Physics and Gravity, University of Groningen, The Netherlands
- Theoretisch-Physikalisches Institut, Friedrich-Schiller-Universität, Jena, Germany
- Helmholtz-Institut Jena, Jena, Germany
- Graduate School of Science and Engineering, Ibaraki University, Mito, Ibaraki, Japan
- Graduate School of Biomedical Sciences, Tokushima University, Tokushima, Japan
- Graduate School of Science and Technology, Niigata University, Niigata, Japan
- Graduate School of Science, Osaka University, Toyonaka, Osaka, Japan
- Nishina Center for Accelerator-Based Science, RIKEN, Wako, Saitama, Japan

- Institut für Kernchemie, Johannes Gutenberg University Mainz, Mainz, Germany
- Helmholtz-Institut Mainz (HIM), Mainz, Germany
- GSI Helmholzzentrum für Schwerionenforschung GmbH, Darmstadt, Germany
- School of Chemistry, Tel Aviv University, Tel Aviv, Israel
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