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Measurement of the First Ionization Potential of Lawrencium

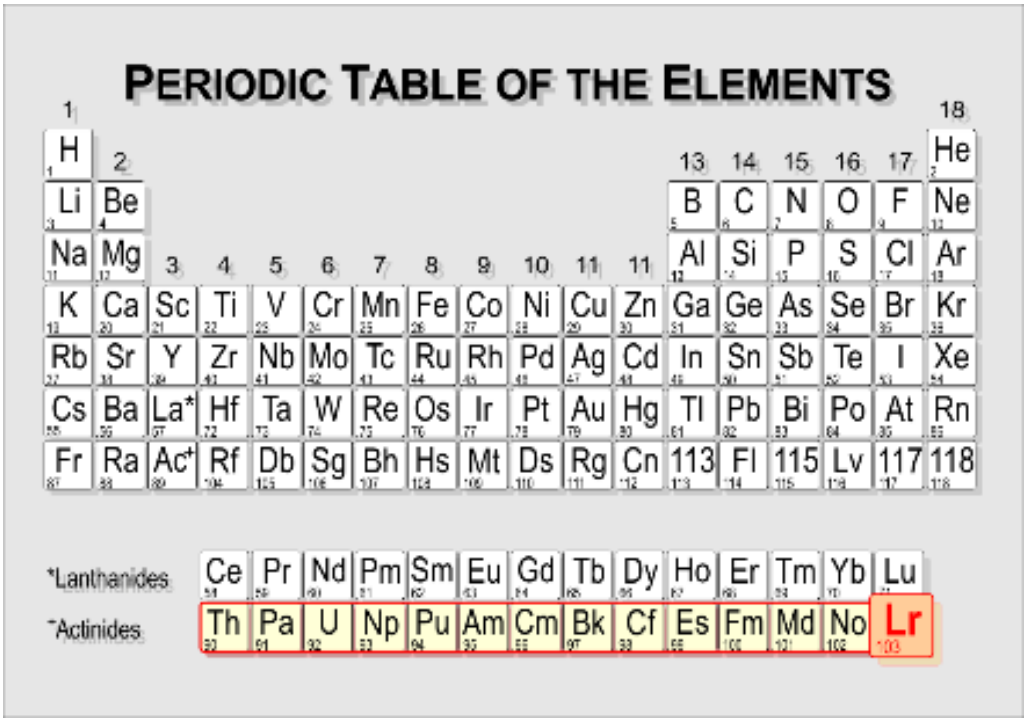
Protons, Neutrons, Atoms, Elements... The Basic

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 112 as well as elements 114 and 116 are officially recognized as discovered, and reports about the observation also of element 113, 115, 117, and 118 are also published. It is currently not clear, which element is the heaviest one that can exist.

In our work, we studied the element with atomic number 103, lawrencium, with chemical symbol Lr. The isotope ^{256}Lr containing 103 protons and 153 neutrons was synthesized in the nuclear fusion reaction

$^{249}Cf + {}^{11}B \rightarrow {}^{260}Lr^* \rightarrow {}^{256}Lr + 4$ neutrons

^{256}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. Identification of Lr 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 $p_{½}$ 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 Lawrencium and its Electron Configuration: Why is this Interesting?

Relativistic effects strongly affect the electron configuration of the heaviest elements. In the actinides, the relativistic expansion of the 5f orbital contributes to the actinide contraction. Together with direct relativistic effects on the 7s and $7p_{½}$ orbitals, this influences the binding energies of valence electrons and the energetic ordering of electron configurations. It is, however, difficult to directly measure energetic levels of the heaviest actinides with Z > 100 by any spectroscopic method as these elements are not available in (weighable) macro

amount.

In comparison with theory, the measurement of the first ionization potential, a fundamental physical property of an element, provides a test of relativistic effects which are significantly noticeable in heavy elements. The ground state electronic configuration of lawrencium is expected to be $[Rn]5f^{14}7s^{2}7p_{½}$, which is different from that of the lanthanide homolog Lu $[Xe]4f^{14}6s^{2}5d$. The reason for this change is the stabilization of the $7p_{½}$ orbital of Lr below the 6d orbital by strong relativistic effects. Lr, therefore, is anticipated to be the first element with a 7p orbital in its electronic ground state.

As the first ionization potential directly reflects the binding energy of a valence electron under the influence of relativistic effects, its experimental determination provides direct information on the energetics of the electronic orbitals of Lr, including relativistic effects, and a test for modern theories. Note, however, that this measurement cannot answer any question about the electronic configuration itself.

Our Experiment

See the website of the JAEA group for information about the experiment!

The Theoretical Calculations

Alongside the experimental measurements, at the Helmholtz Institute Mainz, together with colleagues from Tel Aviv University, Israel, we have carried out a calculation of the first ionization potential of Lr. In order to capture relativistic effects which are extremely important in this heavy element, the calculation was performed using the relativistic Dirac Hamiltonian. Additionally, to achieve maximal accuracy, it was necessary to account for electron correlations. This means that the instantaneous interaction between the 103 electrons of Lr should be treated explicitly, rather than using a framework where each electron sees the other ones as a “charge cloud”, as is done in more approximate methods. We have used the coupled cluster approach, which is considered the most accurate and complete method for treatment of electron correlation. The combination of the relativistic Hamiltonian with the coupled cluster approach provides us with a state-of-the-art computational tool, which is ideally suited for high accuracy calculations of properties of heavy and superheavy elements. This method is very complex and extremely computationally demanding, which limits its use to atoms and small molecules. The calculated ionization potential of Lr is 4.963 ± 0.015 eV, in excellent agreement with the measured value of 4.96 +0.08/-0.07 eV, providing at the same time support for the experimental results and a confirmation for the validity of the theoretical method.

Another important aim of the calculation was to determine the ground state configuration of Lr (which the present experiment could not provide). It is generally agreed that Lr has 102 electrons arranged in closed shells and a single valence electron, which occupies an open shell. However, there are two possibilities for the type of this open shell for the last electron: some scientists predicted it to be the d orbital, as expected from the trends in the Periodic Table and similar to what we see in its lighter homologue Lu, while other, more recent investigations predict it to be the $p_{½}$ orbital. The current calculations confirm the latter scenario, and also explain it. Lr is an extremely heavy element, and thus experiences very strong relativistic effects, which stabilize the $p_{½}$, and destabilize the d orbital. Thus, the atom

in a $p_{½}$ ground state configuration is more energetically stable, as was shown by our calculations. We have also tested this result by performing calculations that neglect relativistic effects (our programs allow us to change the speed of light in the input; setting it to a very large number simulates a non-relativistic framework). These calculations predict the d ground state configuration to be more stable; this demonstrates that the change is the ground state from the d to the $p_{½}$ orbital is caused by relativistic effects.

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 $[Rn]5f^{14}7s^{2}7p_{½}$ or $[Rn]5f^{14}7s^{2}6d$.
Ionization potential measurements of yet heavier elements – i.e., with atomic number $Z \geq 104$, 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 Scientific Article

"Measurement of the first ionization potential of lawrencium, element 103" was submitted on November 27, 2014 and published in **Nature** on April 08, 2015 (Nature 520, 209-211 (2015)).

It is accompagnied by a **"News & Views" article** written by Prof. Andreas Türler: **"Nuclear chemistry: Lawrencium bridges a knowledge gap"** (Nature 520, 166-167 (2015)).

The experiment was conducted at the Japan Atomic Energy Agency (JAEA), Tokai, Japan, while theory efforts were led by the Helmholtz Institute Mainz. The first author is Dr. Tetsuya K. Sato, staff scientist at Japan Atomic Energy Agency, Tokai, Japan.

Press Releases

- Johannes Gutenberg University Mainz, Germany (german, english)

The Collaboration

Our collaboration comprises 11 institutions in 5 countries:

- Japan Atomic Energy Agency (JAEA), Tokai, Ibaraki, Japan
- Massey University, Massey, New Zealand
- Helmholtz Institute Mainz (HIM), Mainz, Germany
- ISOLDE, CERN, Switzerland
- Ibaraki University, Mito, Ibaraki, Japan
- GSI Helmholzzentrum für Schwerionenforschung GmbH, Darmstadt, Germany
- Johannes Gutenberg University Mainz, Mainz, Germany
- Tel Aviv University, Tel Aviv, Israel
- RIKEN, Wako, Saitama, Japan
- Hiroshima University, Kagamiyama, Higashi-Hiroshima, Japan
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