

Review

Recent Progress in Atom-at-a-Time Chemistry of Superheavy Elements with State-of-the-Art Techniques

Yuichiro Nagame^{1,*} and Tetsuya K. Sato²
¹ Advanced Science Research Center, Japan Atomic Energy Agency (JAEA), Tokai 319-1195, Japan

² Institute for Integrated Radiation and Nuclear Science, Kyoto University, Kumatori 590-0458, Japan

* Correspondence: nagame.yuichiro@jaea.go.jp

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Abstract: Chemical studies of superheavy elements (those with atomic numbers of ≥ 101) advance our understanding of the properties of matter at the limits of existence, clarify the influence of relativistic effects on atomic electrons, and expand the periodic table. These elements are synthesized by bombarding heavy actinide targets with heavy ions in accelerators and thus feature extremely low production rates and are usually available in quantities of several or often one atom at a time with their half-lives ranging from several minutes to fraction of a second. The need for chemical experiments to be performed on an atom-at-a-time basis imposes stringent procedural limits. Herein, we review chemical experiments recently conducted on superheavy elements using state-of-the-art techniques and discuss the related future prospects focusing on the identification of superheavy element-containing molecules in liquid and gas phases and the reactivity and other properties of individual superheavy atoms.

Keywords: superheavy element; atom-at-a-time chemistry; relativistic effects; molecular formation; atomic property; state-of-the-art technique

1. Introduction

The expansion of the periodic table and classification of newly discovered heavy elements are important milestones in chemistry and physics. Elements 113 (nihonium, Nh), 115 (moscovium, Mc), 117 (tennessine, Ts), and 118 (oganesson, Og), were officially recognized in 2016 [1], completing the seventh row of the periodic table. The United Nations Educational, Scientific and Cultural Organization (UNESCO) proclaimed 2019 as the International Year of the Periodic Table to commemorate its 150th anniversary [2]. Numerous related ceremonies were held in various countries, and special issues were featured in several journals [3]. The latest periodic table approved by the International Union of Pure and Applied Chemistry (IUPAC) is shown in Figure 1. The actinide series begins with Ac (atomic number $Z = 89$) and ends with Lr ($Z = 103$), representing the filling of 5f orbitals [4,5]. This series is followed by 6d transition elements, which range from Rf ($Z = 104$) to Cn ($Z = 112$), and 7p elements, which range from Nh ($Z = 113$) to Og ($Z = 118$). Elements beyond actinides starting from Rf ($Z \geq 104$) are called transactinide or superheavy elements and exist because of the stabilization provided by the nuclear shell structure. Unlike elements up to Fm ($Z = 100$), which can be produced in nuclear transmutation processes involving neutron capture followed by β^- decay in high-flux nuclear reactors, transfermium elements ($Z \geq 101$) can only be produced through heavy-ion nuclear reactions in accelerators. Herein, the term “superheavy elements” refers to elements with $Z \geq 101$.

Given that the atomic electronic structure changes periodically with increasing Z , the periodic table can be used to infer the chemical properties of a given element based on its position. However, the electronic structure of heavier elements may deviate from periodicity because of relativistic effects, which scale with Z^2 [6–12]. In other words, the periodic law may not hold for such elements. The discovery of new elements and their rational



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classification have drawn considerable attention as the core challenges of chemistry and physics [3,13–23], as reflected by ongoing efforts to upgrade heavy-ion accelerators and related devices [24–26].

1																	18	
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	57 ~ 71	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	89 ~ 103	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og
Lanthanides			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
Actinides			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Figure 1. Latest version of the periodic table approved by IUPAC. Heavy actinides and transactinides are highlighted in blue and red, respectively.

Superheavy elements are produced in accelerators by bombarding targets with heavy ions and identified by measuring their nuclear decay or that of their known daughter isotopes. The amounts of the thus produced elements are extremely small, and all synthesized isotopes are short-lived, decaying in tens of seconds or fractions of second. Thus, experiments with superheavy elements require “extreme chemistry”, i.e., the handling (e.g., chemical separation, detection, and identification) of their single atoms at timescales on the order of the corresponding half-lives.

The last two decades have witnessed considerable progress in the experimental and theoretical chemical studies of superheavy elements. At the dawn of the chemical study of unknown heavy elements in the 20th century, experimental research aimed to identify their position in the periodic table. Since the beginning of the 21st century, the influence of relativistic effects on the chemistry of superheavy elements has been vigorously studied through high-precision chemical experiments, and our understanding of this phenomenon continues to deepen. The related experimental investigations generally compare the chemical properties of superheavy elements with those of their lighter homologs to evaluate relativistic effects. Another important aspect is clarifying the basic chemical properties of superheavy elements, such as oxidation states, ionic radii, redox potentials, chemical compound formation, and ground-state electronic configurations. The chemical studies of superheavy elements published up to around 2015 have been reviewed elsewhere [27–32].

This review briefly introduces the relativistic effects and atom-at-a-time chemistry characterizing the chemical studies of superheavy elements and outlines the chemical experiments at an atom-at-a-time scale. Subsequently, we discuss recent chemical studies involving state-of-the-art techniques, focusing on the determination of the isolated chemical (molecular) species of Rf and Db in liquid and gas phases, respectively; the formation of an exotic Sg-containing molecule; the direct identification of No and Ac molecules; the chemical reactivity (adsorption behavior) of Cn through Mc atoms; and the atomic properties of superheavy elements. A part of this review is based on the modification of our previous works [33–36].

2. Characteristics of the Chemistry of Superheavy Elements

2.1. Relativistic Effects

As the atomic number increases, the positive charge of a nucleus at the center of the atom increases, resulting in stronger interactions with electrons moving around it. In particular, s and $p_{1/2}$ (inner shell) electrons have a considerable probability of being found near the nucleus and are strongly attracted to the same, thus featuring velocities sufficiently high for relativistic effects to be considered. A qualitative understanding of this phenomenon can be conveniently gained using the Bohr model, according to which the energy E_n , orbital radius r_n , and velocity v_n of an electron moving around a nucleus with Z protons are expressed as

$$E_n = -\frac{me^4 Z^2}{8\epsilon_0^2 h^2 n^2}, \quad (1)$$

$$r_n = \frac{\epsilon_0 h^2 n}{\pi m e^2 Z}, \quad (2)$$

$$v_n = \frac{e^2 Z}{2\epsilon_0 h n} \approx \frac{1}{137} \frac{Z}{n} c, \quad (3)$$

where m is the electron mass, e is the elementary charge, h is Planck's constant, c is the speed of light in vacuum, ϵ_0 is the dielectric constant, and n is the principal quantum number, with $n = 1, 2$, and 3 corresponding to K, L, and M shells, respectively. According to the theory of relativity, matter in motion with velocity v and rest mass m_0 has m :

$$m = \frac{m_0}{\sqrt{1 - (v/c)^2}}. \quad (4)$$

In Ni ($Z = 28$), the $1s$ electron has a velocity of $0.2c$ and a mass 2% greater than its rest mass, whereas in U ($Z = 92$), the electron has a velocity of $0.67c$ and a mass of 135% of its rest mass. For U, the orbital radius is 75% of the value determined without considering relativistic effects. This contraction and stabilization of the s and $p_{1/2}$ electron orbitals is called the direct relativistic effect. The relativistic contraction results in a more efficient screening of the nuclear charge, so that the outer $p_{3/2}$, d , and f orbitals become more spatially expanded and energetically destabilized. This expansion of outer electrons is called the indirect relativistic effect. The third relativistic effect is the strong spin-orbit splitting of energy levels with $l > 0$ ($p, d, f, \dots$) into two levels with $j = l \pm 1/2$, where l and j are the angular momentum quantum number and azimuthal quantum number, respectively. The spin-orbit splitting for the same l decreases with increasing number of subshells, i.e., it is much stronger for inner shells than for outer shells, and decreases with increasing l for the same n quantum number, i.e., the $np_{1/2}$ – $np_{3/2}$ splitting is larger than the $nd_{3/2}$ – $nd_{5/2}$ and both are larger than the $nf_{5/2}$ – $nf_{7/2}$. This can be explained by the fact that the orbital density near the nucleus decreases as l increases [9].

Relativistic effects are present in all elements but are particularly pronounced for high- Z elements. Figure 2 shows relativistic and non-relativistic calculations of the energy levels of the valence electrons of Sg ($Z = 106$), and its homologs, Mo and W. As can be seen in the figure, as the atomic number increases, the $s_{1/2}$ orbital becomes more stable, the d orbital becomes less stable, and position reversal occurs for Sg [37].

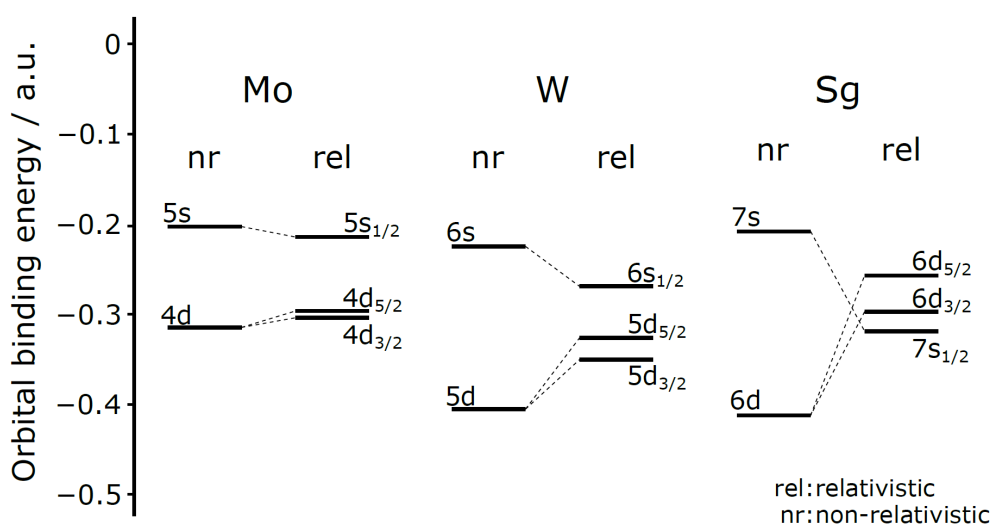


Figure 2. Relativistic (rel) and nonrelativistic (nr) energy levels of the valence ns and $(n - 1)d$ electrons of Mo, W, and Sg. Data are taken from [37].

Owing to relativistic effects, a drastic rearrangement of ground-state electron configurations is expected for heavier elements. Given that electron configurations are responsible for chemical behavior, such relativistic effects can lead to unexpected chemical properties, e.g., substantial deviations from those based on extrapolation from lighter homologs. For example, in the case of transactinide elements with ground-state electronic configurations of $6d^x 7s^2$ ($x = 1$ – 10), the valence $6d$ and $7s$ atomic orbitals are involved in chemical bonding. Relativistic effects cause the $7s$

orbitals to become stabilized and contracted, and the 6d orbitals to become destabilized and expanded, which affects the chemical properties of compounds of these elements. Differences between the chemical properties of superheavy elements and those of their homologs are predicted from the differences in the corresponding atomic (ionic) radii and the energies and radial extensions of the valence orbitals. Table 1 lists the calculated ground-state electronic configurations, stable oxidation states, and first ionization potentials (IP₁ values) of transactinide elements ($Z \geq 104$), as well as the predicted ionic radii of Rf–Hs in their highest oxidation states [9]. The mutual proximity of the relativistic energy levels of the 7s and 6d electrons is expected to stabilize the maximum oxidation states.

Table 1. Predicted ground-state electronic configurations, stable oxidation states, and first ionization potentials of Rf–Og and predicted ionic radii of Rf–Hs in their maximum oxidation states with a coordination number of six [9].

Element	Electronic Configuration	Stable Oxidation State	First Ionization Potential (eV)	Predicted Ionic Radii (Å)
Rf	6d ² 7s ²	4 , 3	6.01	0.79 (Rf ⁴⁺)
Db	6d ³ 7s ²	<u>5</u> , 4 , 3	6.9	0.74 (Db ⁵⁺)
Sg	6d ⁴ 7s ²	<u>6</u> , 4	7.8	0.65 (Sg ⁶⁺)
Bh	6d ⁵ 7s ²	7, <u>5</u> , 4 , <u>3</u>	7.7	0.58 (Bh ⁷⁺)
Hs	6d ⁶ 7s ²	8 , <u>6</u> , <u>4</u> , <u>3</u>	7.6	0.45 (Hs ⁸⁺)
Mt	6d ⁷ 7s ²	3, <u>6</u> , <u>1</u>	8.7	
Ds	6d ⁸ 7s ²	6, <u>4</u> , <u>2</u> , <u>0</u>	9.6	
Rg	6d ⁹ 7s ²	5 , 3, −1	10.6	
Cn	6d ¹⁰ 7s ²	4 , <u>2</u> , 0	11.97	
Nh	7s ² 7p ¹	1, 3	7.306	
Fl	7s ² 7p ²	2	8.626	
Mc	7s ² 7p ³	1, 3	5.579	
Lv	7s ² 7p ⁴	2, 4	6.881	
Ts	7s ² 7p ⁵	3, 1, <u>5</u> , −1	7.638	
Og	7s ² 7p ⁶	4, <u>2</u> , <u>6</u>	8.914	

Underline: most stable state in solution; bold: most stable state in the gas phase.

2.2. Atom-at-a-Time Chemistry

Table 2 lists superheavy isotopes commonly used in chemical experiments, as well as their half-lives ($t_{1/2}$ values), nuclear reactions required for synthesis, and expected production rates. In the case of Rf, ²⁶¹Rf^a with a relatively long $t_{1/2}$ of 68 s is synthesized via the ²⁴⁸Cm(¹⁸O, 5n) reaction, which produces only several atoms per minute under typical irradiation conditions (target thickness = 800 μg/cm² ($\sim 2 \times 10^{18}$ atoms/cm²), beam intensity = 1.6×10^{12} particles/s). For ²⁶⁵Sg, the production rate is several atoms per hour, and $t_{1/2}$ is ~ 10 s. Owing to the short half-lives and low production rates of superheavy isotopes, each atom produced decays before a new atom is synthesized. Thus, chemistry must be examined on an atom-at-a-time basis, which imposes stringent limits on experimental procedures. Such chemistry is often called “single-atom chemistry” or “extreme chemistry.” Rapid and very efficient radiochemical procedures are required.

Table 2. Superheavy isotopes commonly used in chemical experiments, their half-lives ($t_{1/2}$), typical nuclear reactions required for synthesis, cross-sections, and production rates estimated assuming typical experimental conditions (target thickness = 800 μg/cm², beam intensity = 1.6×10^{12} particles/s).

Element	Isotope ($t_{1/2}$)	Nuclear Reaction	Cross Section ($\times 10^{-9}$ Barn)	Production Rate
Md ($Z = 101$)	²⁵⁵ Md (27 min)	²⁴⁸ Cm(¹¹ B, 4n)	4000	15 s ^{−1}
No ($Z = 102$)	²⁵⁵ No (3.5 min)	²⁴⁸ Cm(¹² C, 5n)	580	2.5 s ^{−1}
Lr ($Z = 103$)	²⁵⁶ Lr (27 s)	²⁴⁹ Cf(¹¹ B, 4n)	122	0.4 s ^{−1}
Rf ($Z = 104$)	²⁶¹ Rf ^a (68 s)	²⁴⁸ Cm(¹⁸ O, 5n)	13	4 min ^{−1}
Db ($Z = 105$)	²⁶² Db (35 s)	²⁴⁸ Cm(¹⁹ F, 5n)	2	0.5 min ^{−1}
Sg ($Z = 106$)	²⁶⁵ Sg (14.4 s/8.5 s)	²⁴⁸ Cm(²² Ne, 5n)	0.24	5 h ^{−1}
Bh ($Z = 107$)	²⁶⁷ Bh (17 s)	²⁴⁹ Bk(²² Ne, 4n)	0.07	1.5 h ^{−1}
Hs ($Z = 108$)	²⁶⁹ Hs (10 s)	²⁴⁸ Cm(²⁶ Mg, 5n)	0.007	2 d ^{−1}
Cn ($Z = 112$)	²⁸³ Cn (4 s)	²⁴² Pu(⁴⁸ Ca, 3n) ²⁸⁷ Fl $\rightarrow$ ²⁸³ Cn	0.0104 [38]	4.5 d ^{−1}
Nh ($Z = 113$)	²⁸⁴ Nh (0.9 s)	²⁴³ Am(⁴⁸ Ca, 3n) ²⁸⁸ Mc $\rightarrow$ ²⁸⁴ Nh	0.017 [39]	8.5 d ^{−1}
Fl ($Z = 114$)	²⁸⁹ Fl (1.9 s)	²⁴⁴ Pu(⁴⁸ Ca, 3n)	0.008 [40]	3 d ^{−1}
Mc ($Z = 115$)	²⁸⁸ Mc (0.2 s)	²⁴³ Am(⁴⁸ Ca, 3n)	0.017 [39]	8.5 d ^{−1}

Considering the following chemical reactions:



The change in Gibbs free energy ΔG can then be expressed as

$$\Delta G = \Delta G_0 + RT \ln \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}, \quad (6)$$

where $[X]$ denotes the concentration or partial pressure of species and ΔG_0 is the standard Gibbs free energy change. If the equilibrium constant K is expressed as,

$$\frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b} = K, \quad (7)$$

for $\Delta G = 0$, where equilibrium holds,

$$\Delta G_0 = -RT \ln K. \quad (8)$$

On the macroscale, this relation is well known as the law of mass action. However, as noted above, the number of superheavy-element atoms synthesized in nuclear reactions is small, and only one or several atoms at a time are available for chemical experiments. In other words, if species A and C in Equation (7) correspond to superheavy-element atoms and their reaction products, respectively, the numerator or denominator equals zero, and K does not have a meaningful value.

Atom-at-a-time chemical studies must be carried out on phenomena that give the same result irrespective of whether single atoms or macro amounts of atoms are used. Hence, one is confronted with the question whether meaningful single-atom chemistry is possible. For single atoms, the classical law of mass action is no longer valid because an atom can exist in only one of the different chemical forms taking part in the chemical equilibrium at given time. Thus, for single atom chemistry, a specific thermodynamic function—the single-particle free enthalpy—is introduced [41,42], and an expression equivalent to the law of mass action where activities or concentrations are replaced with probabilities of finding species in the appropriate phases is derived. According to this expression, the equilibrium constant for the distribution of an atom between two phases (distribution coefficient) is defined in terms of the probabilities of finding this atom in each phase. If a static partition method is exploited, this coefficient must be measured in repetitive experiments. As dynamical partition methods can be considered repetitive static partitions, the displacement of an atom along the chromatographic column gives a statistical result. For short-lived isotopes, the partition equilibrium must be reached during the isotope lifetime, which requires fast reaction kinetics. Thus, chromatographic systems with fast reaction kinetics are ideally suited for single-atom separation, as they enable the fast and multiple sampling of adsorbed or mobile chemical species [28,43].

3. Outline of Chemical Experiments Performed at an Atom-at-a-Time Scale

The detailed and general experimental techniques used in liquid- and gas-phase chemistry, including the development of equipment for the chemical study of single atoms, are summarized elsewhere [44]. Chemical experiments with superheavy elements require an accelerator facility capable of supplying heavy-ion beams with sufficient energy and intensity to synthesize superheavy elements and experimental facilities capable of handling highly radioactive actinide targets, such as ^{244}Pu , ^{243}Am , ^{248}Cm , ^{249}Bk , and ^{249}Cf . Therefore, few research facilities are available worldwide. The preparation of actinide targets requires sufficient nuclear and radiochemistry experience and techniques because of the rare and highly radioactive materials involved [45,46].

Chemical experiments typically involve the (i) synthesis of a specific superheavy isotope, (ii) its rapid transport to chemical separation devices using a gas-jet transport system, (iii) rapid chemical isolation of the desired isotope, (iv) preparation of a sample suitable for nuclear spectrometry, and (v) detection and identification of isotopes based on their decay properties (mainly α decay). The chemical characterization of superheavy elements has been accomplished using fast chemical separation methods, such as gas-phase [47–49] and liquid-phase [50–52] chromatography. Below, we briefly describe steps (i)–(iii).

3.1. Synthesis of Superheavy Elements and Transport of Reaction Products to Chemical Separation Devices

The neutron-rich isotopes of superheavy elements are predicted to be relatively long-lived. Therefore, neutron-rich heavy-actinide targets and neutron-excess incident particles are used to obtain isotopes that are even slightly closer to the neutron-excess side and exhibit the longest possible lifetime suitable for chemical experiments. Targets are prepared by electrodeposition on thin films, such as Be and Ti films [46].

Aerosol gas-jet transport systems are commonly used to deliver nuclear reaction products at the target position in an irradiation cave to chemical equipment in a chemistry laboratory located away from the target-recoil chamber. The reaction products recoiling from the target are stopped in the volume of carrier gas, such as He, which is loaded with cluster materials, such as KCl, NaCl, CdI₂, PbI₂, carbon cluster, and MoO₃ (Figure 3). Then, the products attached to the surface of the cluster materials are swept out of the target-recoil chamber with the carrier gas flow and transported through a capillary tube to chemical separation apparatuses.

However, the gas-jet transport method has several drawbacks. A large amount of side-reaction products is introduced into chemical separation devices along with the target superheavy elements, interfering with isotope radiation measurements. In recent years, intense heavy-ion beams exceeding 6.2×10^{12} particles/s have become available. Thus, the plasma effects caused by the introduction of high-intensity ion beams into the gas catcher section of the target-recoil chamber are leading to problems such as the decomposition of aerosol particles and chemical reagents introduced into the chamber. To address these issues, an electromagnetic separator can be used to pre-separate the injection beam and byproducts from the target isotope as outlined in Section 4.3 [53–55].

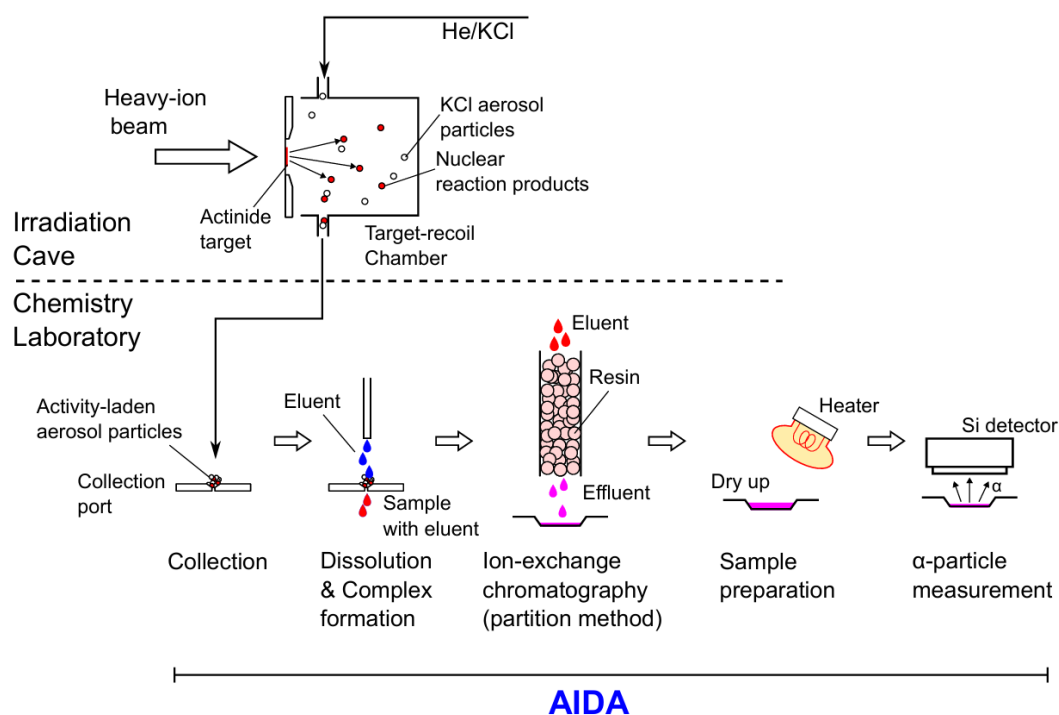


Figure 3. Flowchart of typical liquid-phase experimental procedures showing a schematic representation of the target-recoil chamber connected to a gas-jet transport system. The series of procedures from collecting nuclear reaction products to α -particle measurement is conducted using an Automated Ion-exchange separation apparatus coupled with the Detection system for Alpha spectroscopy (AIDA). Chemical separation was accomplished within 20 s, and the α -particle measurement was started within 60 s after the collection of products. Reproduced from [36]. Copyright 2024 The Japan Academy.

3.2. Chemical Separation and Characterization

Most experiments are conducted in the liquid and gas phases using liquid- and gas-chromatographic techniques, respectively. To compare the chemical properties of superheavy elements with those of their lighter homologs, experiments with Rf, Zr and Hf were conducted under identical conditions, whereas those with Db were performed alongside those with Nb and Ta. Liquid-phase partition studies aim to determine the distribution coefficient (K_d , mL/g) as a function of ligand concentration (M). In its simple definition, K_d is the ratio of the number of atoms (determined by activity) in an organic phase in liquid-liquid extraction or in a stationary phase in column chromatography to that in the liquid phase.

In liquid chromatography experiments (Figure 3), the following processes must be repeated many times: (a) dissolution of reaction products transported by the gas jet, (b) loading of these products on ion-exchange resins, (c) elution of the adsorbed isotopes with a suitable eluent, and (d) collection and drying of the eluate for α -particle measurement. The development of computer-controlled automated systems with a greatly improved ability to rapidly and reproducibly perform numerous chromatographic separations on miniaturized columns and

systematically vary ligand concentrations has enabled detailed chemical investigations and the determination of the stoichiometry of the eluted species [56]. Experiments using automated apparatuses have produced detailed and sometimes surprising results. A computer-controlled high-performance liquid chromatography method based on an Automated Rapid Chemistry Apparatus (ARCA II) [57], developed by the GSI Helmholtzzentrum für Schwerionenforschung GmbH (GSI) and University of Mainz group, and Automated Ion-exchange Separation Apparatus coupled with the Detection System for Alpha Spectroscopy (AIDA) [58], developed by the Japan Atomic Energy Agency (JAEA) based on ARCA II, were used to perform precise liquid-phase experiments on Rf. The speciation of this element was successfully established by measuring K_d at different ligand concentrations. Figure 4 shows a photograph of AIDA installed in the JAEA tandem accelerator facility [56].

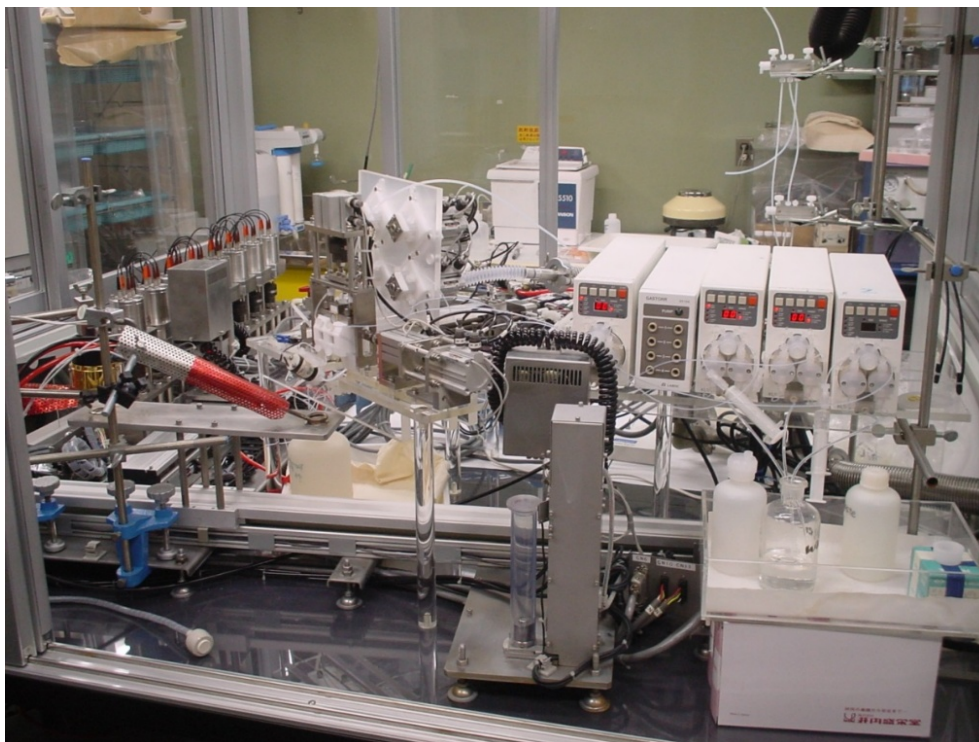


Figure 4. Photograph of AIDA installed in the chemistry laboratory of the JAEA tandem accelerator facility. The design of the ion-exchange part is based on that of ARCA II [57]. On the right side, pumps for feeding eluents to the microcolumns are visible. Eluates collected on Ta disks are evaporated to dryness using a halogen heat lamp and a hot He gas flow. New Ta disks are automatically supplied to the elution position of the effluents by the robotic machine positioned in the front. After evaporation, the samples are automatically transferred to the α -particle detection station shown in the left part and placed in the chambers by a robotic arm. Image reproduced from [56]. Copyright 2019 DeGruyter.

In the gas-phase chemical separation method, (a) nuclear reaction products are transported to a chemical separation apparatus by the gas jet and converted to volatile species, (b) they are continuously introduced into the separation column with carrier gas, and (c) radiation detection is performed either in the column or at the end of the column. Two major types of gas-phase chemical methods are available, namely thermal and isothermal chromatography. The largest difference between the two lies in the temperature profile of the separation column, with the former having a high inlet to low outlet inverse temperature gradient and the latter featuring a constant column temperature. The enthalpy of the adsorption of the volatile species of interest on the surface of the separation column can be determined from the adsorption position in the column in thermal chromatography and from the change in elution volume as the column temperature changes in isothermal chromatography. Gas-phase techniques require little mechanical manipulation, allow continuous separation, and can be applied to isotopes with half-lives of <1 s. However, the scope of these techniques is limited to volatile molecules. The main chemical species for which gas-phase chemical separation methods have been applied are assumed to be halides for Rf and Db, oxyhalides for Db, Sg, and Bh, and oxides for Hs [48,49]. Individual-atom volatility studies have been performed for Cn, Nh, Fl, and Mc [59–67] (see Section 5). A notable recent achievement is the formation and detection of a volatile organometallic compound of Sg [68] (see Section 4.3).

4. Identification of Isolated Molecules

In the early stage of superheavy-element chemistry, the most fundamental challenge was the unknown identity of the corresponding compounds because of the constraints of atom-at-a-time chemistry. Experimental studies conducted so far have generally assumed that these superheavy elements form the same chemical species as their lighter homologs, as no chemical comparison can be performed if this assumption does not hold. Although the identification of chemical species at one atom-at-a-time scale is extremely difficult, overcoming this challenge will lead to breakthroughs. The determination of the molecular species of Rf in an aqueous solution using AIDA [69–71] and the formation of a volatile oxychloride of Db [72] and a hexacarbonyl of Sg [68] in the gas phase are notable achievements, as is the direct identification of No and Ac molecules using a mass analyzer [73].

4.1. Determination of the Molecular Species of Rf in an Aqueous Solution Using AIDA

This section describes the identification of Rf molecular species (fluorides) in the liquid phase and their properties [69–71]. The ground-state electronic configuration of Rf is expected to be $[Rn]5f^{14}6d^27s^2$, which makes Rf a Group 4 element alongside Zr and Hf. Figure 5 depicts the anion-exchange behavior of Rf, Zr, and Hf, showing their K_d values as a function of the initial hydrofluoric acid concentration $[HF]_{ini}$ [69]. The linear negative correlations between $\log K_d$ and $\log [HF]_{ini}$ plot were interpreted as the displacement of metal fluorides from the binding sites of the resin by the counter anion [69]. For Zr and Hf, the above plots had -3 (dotted line), while for Rf, the slope was -2 (solid line). According to the equilibration of ion-exchange reactions, the plot slope indicates the charge state of the metal compounds. Thus, the Rf was likely present as $[RfF_6]^{2-}$, while Zr and Hf were likely present as, $[ZrF_7]^{3-}$ and $[HfF_7]^{3-}$, respectively. The formation of $[RfF_6]^{2-}$ was observed even at low F^- concentrations [70]. The formation of an anionic fluoride compound of Rf was interpreted by considering the chemical equilibria of the anion-exchange reactions and fluoride-compound formation reactions and comparing them with those for Zr and Hf. The formation constant of $[RfF_6]^{2-}$ was at least one order of magnitude smaller than those of $[ZrF_6]^{2-}$ and $[HfF_6]^{2-}$, i.e., the driving force for $[RfF_6]^{2-}$ formation was considerably lower [70]. Although quantitative analysis is still open, this result suggests the contributions of relativistic effects. (Here, we assumed the molecular species of Rf based on those of homologs, but the formation of different compounds, e.g., $[RfF_6(H_2O)]^{2-}$ and $[RfF_{6-x}(OH)_x]^{2-}$, cannot be fully excluded.)

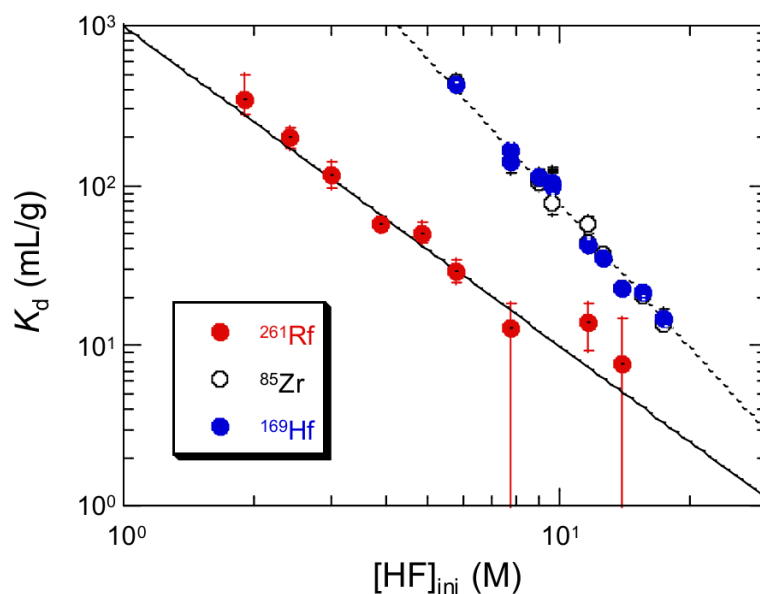


Figure 5. Distribution coefficients (K_d) of Rf, Zr, and Hf on the anion-exchange resin as a function of the initial HF concentration, $[HF]_{ini}$. The solid and dotted lines indicate linear fits with slopes of -2.0 ± 0.3 for Rf and -3.0 ± 0.1 for Zr and Hf, respectively. Reproduced from [69]. Copyright 2004 The American Chemical Society.

The cation-exchange behavior of Rf was studied in dilute F^- solution together with those of Zr, Hf, and the tetravalent pseudohomolog Th [71]. At very low F^- concentrations, the formation of the Rf compound was remarkably less favored than those of Zr and Hf compounds but more favored than that of the Th compound. Given the predominantly electrostatic interaction between metal cations (M^{4+} ; $M = Zr, Hf, Rf$, and Th) and F^- , a correlation between the crystallographic ionic radius [74] and driving force for fluoride compound formation was

expected. The crystallographic ionic radii of the Group 4 elements with a coordination number of six follow the order of Zr^{4+} (72 pm) $\approx$ Hf^{4+} (71 pm) $<$ Rf^{4+} (76 pm) [9] $\ll$ Th^{4+} (94 pm). The relative tendency for fluoride compound formation follows the inverse order of the ionic radii. The above result indicates that the ionic radius of Rf^{4+} is in between those of $\text{Zr}^{4+}/\text{Hf}^{4+}$ and Th^{4+} [71]. The K_d values of Rf and its homologs were also measured at different hydrogen ion concentrations $[\text{H}^+]$ in the range of $[\text{F}^-] = 0.529\text{--}3.17\ \mu\text{M}$. Based on the above, these elements are likely to form the same chemical species; a mixture of $[\text{MF}]^{3+}$ and $[\text{MF}_2]^{2+}$ compounds was present and adsorbed on the cation-exchange resin [71].

Kasamatsu et al. reported hydroxide formation for Rf and its homologs (Zr and Hf) [75] using $\text{Sm}(\text{OH})_3$ as the coprecipitating substrate. In the $\text{Sm}(\text{OH})_3$ coprecipitation method, the tracer element coprecipitates with $\text{Sm}(\text{OH})_3$ only if its hydroxide forms a precipitate under the employed conditions. The authors experimentally observed the coprecipitation behavior of Rf and confirmed the formation of hydroxide precipitates, which was also observed for Zr and Hf. At high hydroxide ion concentrations, Zr and Hf combined with excess hydroxide ions and ceased to form precipitates, whereas no such behavior was observed for Rf. This finding was ascribed to the fact that the ionic radius of Rf in aqueous solution exceeds those of Zr and Hf because of relativistic effects, resulting in a smaller surface charge density and smaller driving force for hydroxide formation. Thus, Rf was less prone to hydroxide ($\text{Rf}(\text{OH})_4$) formation than Zr and Hf [75].

Relativistic density functional calculations of the electronic structures of $[\text{MF}_6]^{2-}$ were carried out to evaluate their stability [76]. The overlap populations between the valence (d) orbitals of M^{4+} and those of F^- followed the order of $\text{Zr} \approx \text{Hf} > \text{Rf}$, suggesting that $[\text{RfF}_6]^{2-}$ is less stable than its Zr and Hf analogs. This behavior can be rationalized using the hard–soft acid–base theory [77]. The small fluoride and hydroxide anions are hard donors and prefer hard (i.e., small) acceptor ions, Zr^{4+} and Hf^{4+} . The much larger (softer) Rf^{4+} prefers larger (softer, more polarizable) donor ligand ions such as Cl^- . In fact, the stability of chloride compounds followed the order of $\text{Rf} \geq \text{Zr} > \text{Hf}$ [78,79]. Although the results of calculation qualitatively agree with those of experiments, further theoretical approaches are required to gain a quantitative understanding. These results provided a framework for discussing the effects of relativistic effects in greater detail based on the determination of the chemical species of Rf.

4.2. Identification of a Volatile Compound of Db Using the Isothermal Gas-Chromatography (IGC) Setup

This section describes the experimental identification of a volatile Db oxychloride using an IGC setup [72]. The predicted electronic configuration of Db suggests the formation of stable volatile pentahalides and oxyhalides [9]. So far, gas-chromatographic studies of Db have mainly focused on the synthesis and chemical characterization of chlorides and bromides [47–49], which are more volatile than the corresponding oxychlorides and oxybromides. However, no apparent conclusions were drawn because of the simultaneous formation of halides and oxyhalides ($\text{DbCl}_5/\text{DbOCl}_3$ and $\text{DbBr}_5/\text{DbOBr}_3$) due to traces of oxygen and water in the experimental system and the change of the chromatographic column surface caused by the materials introduced from the aerosol particles used to transport the products of interest from the target-recoil chamber to the chromatographic device. Chiera et al. synthesized the oxychlorides of Db and its homologs (Nb and Ta) and explored their volatilities using a newly developed IGC setup.

Figure 6 shows a schematic of the IGC setup coupled to the target-recoil chamber [80]. IGC is based on volatiles passing through a constant-temperature column and undergoing adsorption/desorption processes on/from its surface. The retention times of volatiles depend mainly on their adsorption interaction with the column surface at the employed temperature and carrier gas velocity. Thus, volatiles with a nuclear lifetime exceeding the retention time pass through the column. The half-life of the examined isotope is used as an internal clock for the chromatographic process to evaluate retention time. Half of the atoms introduced into the column exit from the other end when the time required for an atom to pass through the column (retention time) corresponds to the isotope half-life. Thus, the ratio of the quantity introduced into the column to that detected after the column can be converted into retention time, which is related to the strength of the interaction of a volatile molecule with the column surface.

Prior to performing experiments with Db, Chiera et al. conducted a model experiment with its homologs (Nb and Ta) using IGC and confirmed the formation of oxytrichlorides (NbOCl_3 and TaOCl_3) under the chosen conditions [81]. The molecular species were identified using an empirical correlation between the experimental adsorption enthalpy ($-\Delta H_{\text{ads}}$), which corresponds to the energy of the interaction between the volatile species and stationary chromatographic column, and the standard sublimation enthalpy (ΔH_{subl}^0), which is a measure of volatility. In this case, $-\Delta H_{\text{ads}}$ was determined based on a microscopic adsorption–desorption kinetic model describing the retention behavior and displacement of a molecule through the chromatographic column [82]. The gas-phase experiment with Db was then conducted under conditions strictly identical to those for Nb and Ta.

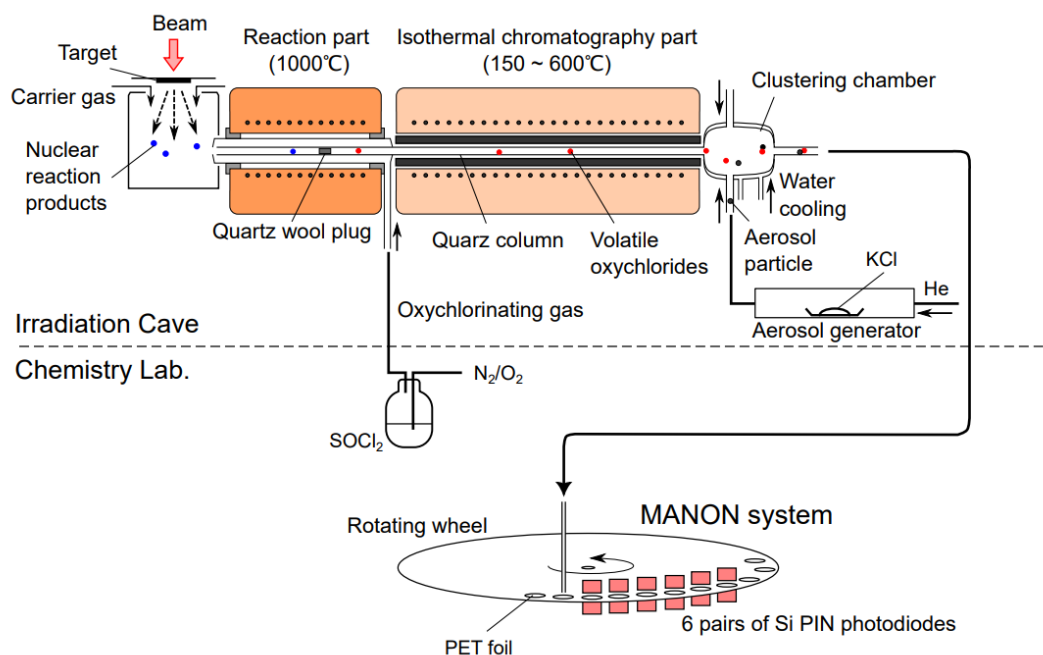


Figure 6. Schematic of the IGC setup. The IGC system is coupled to an α -detection system MANON [83] for studying the volatile DbOCl_3 . PET: polyethylene terephthalate. Reproduced from [36]. Copyright 2024 The Japan Academy.

The ^{262}Db atoms produced in the $^{248}\text{Cm}(^{19}\text{F}, 5n)$ reaction and recoiling out of the target were thermalized using an inert carrier gas (He/N_2 mixture) in the target-recoil chamber and directly injected into the reaction part of a quartz column at 1000°C (Figure 6). Oxychloride compounds were formed in situ in the presence of SOCl_2 – O_2 gas at the reaction part and transported with the gas flow to the isothermal chromatography part (column), where they interacted with the quartz column surface via adsorption–desorption. After exiting the column, the oxychloride molecules were attached to aerosol particles (KCl particles in He gas) and transported to the Measurement System for Alpha-particles and Spontaneous Fission events On line (MANON) [83] for the detection of ^{262}Db and its daughter isotope ^{258}Lr .

The column temperature–yield curve obtained for Db was similar to those obtained for NbOCl_3 and TaOCl_3 (Figure 7). Thus, the authors concluded that only one Db species was formed, assigned it to DbOCl_3 , and determined the corresponding $-\Delta H_{\text{ads}}$. The volatility of the above species followed the order of $\text{NbOCl}_3 > \text{TaOCl}_3 \geq \text{DbOCl}_3$ [72]. Theoretical calculations on Group 5 oxyhalides predicted an increment in the molecular dipole moment with increasing atomic number, which was expected to result in a stronger molecule–quartz surface interaction [84]. Therefore, DbOCl_3 was expected to be less volatile than its lighter homologs. However, the comparable volatilities of DbOCl_3 and TaOCl_3 observed experimentally might indicate that the Db compound features a higher-than-expected degree of covalency, suggesting the importance of relativistic effects for the molecular structure of DbOCl_3 [72].

Qin et al. [85] prepared the pentabromides of Db and its homologs using the isothermal chromatographic method with HBr as the reactive gas at 900°C and determined their adsorption enthalpies ($-\Delta H_{\text{ads}}$ values). The volatility order of $\text{DbBr}_5 > \text{NbBr}_5 > \text{TaBr}_5$ agreed with the results of theoretical calculations [86], which predicted DbBr_5 to be highly volatile because of its lowest effective charge on the metal and highest covalency degree due to relativistic effects.

Pioneering gas-phase chemical experiments with Sg [87–89], Bh [90], and Hs [91] have been conducted to explore the formation of their oxychlorides and oxides, although some uncertainty remains regarding the identification of chemical species. The formation of the oxychloride of Sg (SgO_2Cl_2) was performed at GSI by Türler et al. [89] using the isothermal gas-chromatographic device, On-Line Gas Chromatography Apparatus (OLGA II) [92], and that by Zvara et al. [88] using the thermochromatographic method at Flerov Laboratory of Nuclear Reactions (FLNR), Dubna. OLGA II was also used in the first successful chemical isolation and identification of Bh (BhO_3Cl) at the Paul Scherrer Institute (PSI) in Switzerland [90]. Bh behaved like a typical Group 7 element. Hassium is expected to be chemically similar to its lighter homologs, Ru and Os, which are known to form highly volatile tetroxides. Gas-phase adsorption thermochromatography was used to measure HsO_4 deposition temperatures in a column with a stationary negative temperature gradient [91]. The Cryo On-Line Detector (COLD) was used to identify decaying isotopes.

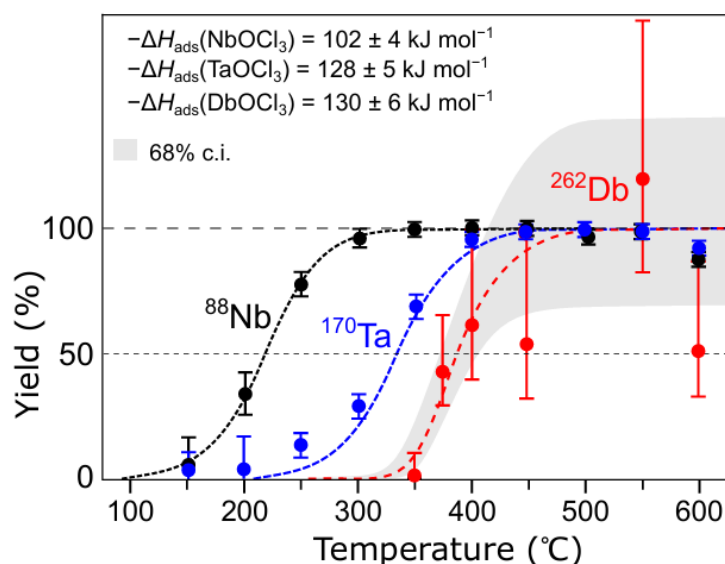


Figure 7. Relative yields of ^{262}Db , ^{88}Nb , and ^{170}Ta oxychlorides at different column temperatures. The column was operated at a reaction part temperature of 1000 °C with SOCl_2 vapor-saturated N_2 (1% O_2) as oxychloride agent (200 mL/min). In general, the column temperature–yield curve moves to the right with decreasing volatility and lifetime. Curve fitting afforded the enthalpies of the adsorption ($-\Delta H_{\text{ads}}$) of the studied species on the quartz surface. Reproduced from [72]. Copyright 2021 Wiley-VCH GmbH.

4.3. Sg Carbonyl Formation Revealed Using a Thermochromatographic Technique Coupled to a Physical Recoil Separator

The formation of an organometallic (carbonyl) compound of Sg was accomplished using the Cryo-Online Multidetector for Physics and Chemistry of Transactinides detector (COMPACT) [65] coupled to the Gas-filled Recoil Ion Separator (GARIS) [93] at RIKEN, Japan [68]. The isotope ^{265}Sg was produced via the reaction of $^{248}\text{Cm}(^{22}\text{Ne}, 5n)$ and separated from the primary beam and other reaction byproducts by the GARIS (Figure 8). This combination of the physical separation of single ions with chemical techniques paved the way for studies of distinct compound classes.

Fusion-evaporation reaction products, including Sg, were separated from the primary beam within the first dipole magnet, focused by a doublet of quadrupole magnets, and guided by another dipole magnet to the GARIS focal plane. Sg ions passed through a Mylar window and thermalized in a Recoil Transfer Chamber (RTC) [54]. The RTC was flushed with a He/CO mixture at 500–750 mbar. The volatiles produced in the RTC were transported by the gas flow through a Teflon capillary to the COMPACT device, which served as a gas thermochromatography detector and featured a chromatography column consisting of 32 pairs of Si semiconductor detectors suitable for registering time- and energy-resolved α -particles and fission fragments emitted in the decay of ^{265}Sg and its daughter isotopes. The detectors formed a channel with a rectangular cross-section, and the detector surface was covered with a 50-nm thick SiO_2 layer. The COMPACT is based on the modification of the COLD device which was used to detect the formation of HsO_4 [91].

After 17 days of beam experiments, highly similar adsorption distributions on the detector surface were obtained for Sg, Mo, and W as shown Figure 9 [68]. Monte Carlo simulation analysis based on the molecular adsorption-desorption model [82] was used to determine $-\Delta H_{\text{ads}}$ for SiO_2 on the detector surface, and the value for the Sg carbonyl was found to be almost equal to that of the Mo and W hexacarbonyls [94–96]. Furthermore, the obtained adsorption enthalpies well agreed with the results of relativistic molecular orbital calculations. Thus, Sg was concluded to form $\text{Sg}(\text{CO})_6$ and thus has chemical properties characteristic of Group 6 elements, which have high melting points but form highly volatile carbonyls. The success achieved using this combination of physical and chemical separation demonstrates the potential of new chemical analytical methods at the single-atom level. This experiment presents the first synthesis of a new class of superheavy-element compounds, opens new perspectives (e.g., the formation of the carbonyls of other superheavy elements), and heralds the era of organometallic chemistry of superheavy elements.

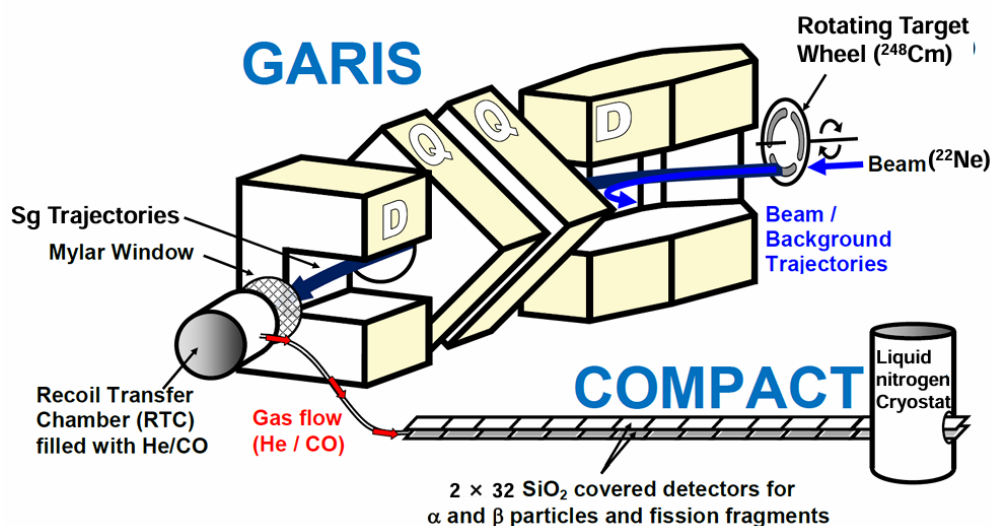


Figure 8. Schematic of the experimental setup used for the synthesis of the Sg carbonyl. Sg separated using the GARIS reacted with CO molecules in the RTC, and the resulting carbonyl molecules were transferred to the COMPACT. D: Dipole magnet and Q: Quadrupole magnet. Reproduced from [68]. Copyright 2014 American Association for the Advancement of Science.

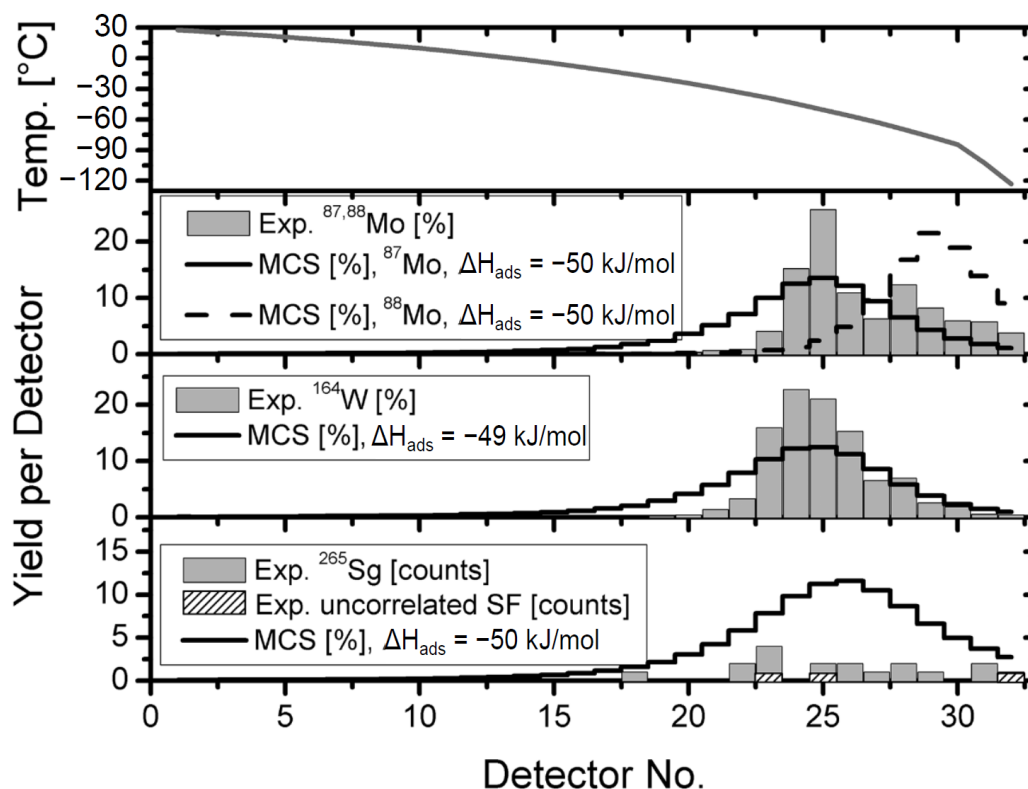


Figure 9. Thermochromatographic behavior of the volatile carbonyls of $^{87,88}\text{Mo}$, ^{164}W , and ^{265}Sg . MCS is the curve obtained using Monte Carlo simulations. The solid line on the top shows the temperature gradient along the detector array. Reproduced from [68]. American Association for the Advancement of Science.

To establish a basis for the future experiments on the formation of heavier-element (Bh and Hs) carbonyls, this process is currently being studied for the corresponding homologs at the Institute of Modern Physics (IMP), China [97–99]. The PSI group is conducting further experiments to establish effective conditions for carbonyl synthesis [100–102]. A novel gas-phase synthesis of carbonyls was developed by Götz et al. [103]. Experiments on carbonyl decomposition will prove the intramolecular bonds between the central metal atom and CO ligands, addressing the influence of relativistic effects [104,105]. Further experiments with not only Sg but also Bh and Hs are required.

4.4. Direct Identification of No and Ac Molecules with the For the Identification Of Nuclide A (FIONA) Setup

Pore et al. produced ^{254}No ($t_{1/2} = 51$ s) and ^{212}Ac ($t_{1/2} = 0.93$ s) by bombarding ^{208}Pb and ^{169}Tm targets, respectively, with ^{48}Ca beams delivered from the Lawrence Berkeley National Laboratory (LBNL) 88-inch cyclotron [73]. The actinide ions were separated from the primary ^{48}Ca beam and reaction byproducts using the Berkeley Gas-filled Separator (BGS) [106] before entering the FIONA spectrometer (Figure 10) [107], which was installed behind the BGS to further study the nuclear and chemical properties of heavy and superheavy isotopes using mass number identification. The corresponding analysis comprised two stages. In the first stage, reaction product ions were selected by the BGS, stopped in a radiofrequency (RF) quadrupole trap, and accelerated across a pulsed drift tube to keV-level energies as a well-defined secondary beam. In the second stage, the reaccelerated ions were separated according to their mass-to-charge ratio, and the separated ions were delivered to a radiation detector. In the experiments, selected ions were introduced into a gas catcher filled with high-purity He gas at ~ 150 Torr. Here, multiply charged ions interacted with the He gas and were reduced to a charge state of $2+$. The traces of H_2O and N_2 in the gas catcher reacted with the $2+$ actinide ions to form actinide-containing molecules based on the supersonic expansion of the gas-ion mixture (see the inset of Figure 10). These charged molecules were transferred to a radiofrequency quadrupole cooler buncher ion trap and confined for up to 50 ms, undergoing collisions with the buffer gas (He) and thus reaching thermal equilibrium. After cooling, the ions were reaccelerated into the FIONA mass spectrometer, where they were directly identified based on mass-to-charge ratios, with notable species including adducts, such as $[\text{No}(\text{H}_2\text{O})]^{2+}$, $[\text{No}(\text{H}_2\text{O})_3]^{2+}$, and $[\text{No}(\text{H}_2\text{O})_4]^{2+}$, an N_2 adduct, $[\text{No}(\text{N}_2)_2]^{2+}$, and a mixed adduct $[\text{No}(\text{H}_2\text{O})(\text{N}_2)_2]^{2+}$ [73]. Molecular species of ^{212}Ac were also detected. Direct molecular identification is crucial for interpreting the usual chemical behavior of superheavy elements. The determination of chemical species in this study provides an important roadmap for future research in superheavy-element chemistry.

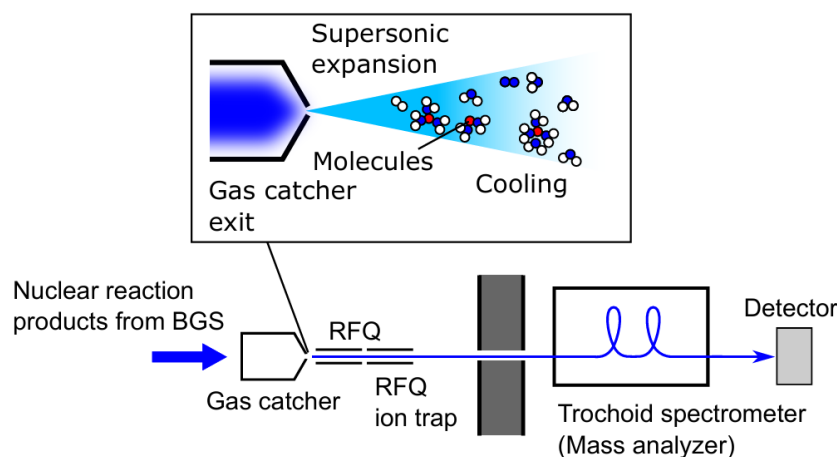


Figure 10. Schematic of the FIONA device at the LBNL 88-inch cyclotron facility. The inset illustrates the supersonic expansion occurring as ions and gases exit the gas catcher and resulting in the formation of molecular species. Reproduced from [73]. Copyright 2025 Springer Nature.

5. Chemical Reactivity (Adsorption Behaviors) of Cn through Mc

To date, no studies have been conducted on the chemical properties of Mt, Ds, and Rg, as the extremely low production rates and very short half-lives (< 0.2 s) of these isotopes, which are produced in the so-called cold fusion reactions, hinder chemical experiments. However, the production of longer-lived isotopes beyond Ds with half-lives in the range of seconds has been reported using the hot fusion reactions with ^{48}Ca beams (see Table 2). Thus, longer-lived isotopes of Mt–Rg can be formed as decay products of heavier isotopes. We hope that research into the chemical properties of these elements will begin in the near future. The synthesis of ^{283}Cn (α -decay half-life: $t_{1/2}^{\alpha} \approx 3.8$ s) through the reaction of $^{238}\text{U}(^{48}\text{Ca}, 3n)$ with the cross section of about 2.5 pb [108–110] served as the catalyst for the chemical study of Cn.

Copernicium, placed below Hg in Group 12, is expected to have a closed-shell electronic configuration with a filled s subshell in its outermost shell ($[\text{Rn}]5f^{14}6d^{10}7s^2$). Relativistic calculations show a strong stabilization of the closed $7s^2$ shell and suggest that Cn should be inert (like the noble gas Rn) or be a very volatile liquid (like Hg). The interaction of Cn with metallic surfaces, such as Au and Pd, was calculated to be weaker than that of Hg.

The first successful experimental characterization of the chemical properties of Cn was conducted by the PSI and FLNR at Dubna, Russia [59,60]. The isotope ^{283}Cn was synthesized as the α -decay daughter of the primary reaction product ^{287}Fl in the $^{242}\text{Pu}(^{48}\text{Ca}, 3n)$ reaction at a rate of several atoms per week. The cross section via $^{242}\text{Pu}(^{48}\text{Ca}, 3n)^{287}\text{Fl} \rightarrow ^{283}\text{Cn}$ is expected to be higher than that in the $^{238}\text{U}(^{48}\text{Ca}, 3n)^{283}\text{Cn}$ reaction. The thermochromatographic COLD detector array was modified and notably improved to enable the investigation of gas-phase Cn atom adsorption on Au. A $^{242}\text{PuO}_2$ target with an admixture of Nd_2O_3 was bombarded for ~ 3 weeks at the U-400 cyclotron of the FLNR. The partially α -decaying ^{185}Hg ($t_{1/2} = 49$ s) was produced via the reaction of $^{142}\text{Nd}(^{48}\text{Ca}, 5n)$ and ^{219}Rn ($t_{1/2} = 4$ s) was produced in multinucleon transfer reactions between ^{48}Ca and ^{242}Pu . The behavior of Rn and Hg was studied simultaneously with that of Cn. The COLD detector comprised an array of 32 pairs of ion-implanted planar Si detectors with active surfaces facing each other to form a rectangular channel. The surface of the detectors on one side of the channel was covered by a 30–50 nm Au layer, whereas the other side retained the original quartz surface that is chemically inert to the atoms of most elements. A temperature gradient of 35 °C to –186 °C was established along this chromatographic channel using thermostat heating at the inlet and liquid N_2 cryostat cooling near the outlet. The primary product ^{287}Fl ($t_{1/2} = 0.5$ s) was too short-lived to be transported to the COLD detector, and only the decay of the daughter isotope ^{283}Cn and its daughter ^{279}Ds was detectable. Rn was deposited on the ice layer of the detector surfaces below –95 °C, while Hg deposition was observed from –24 °C to –50 °C. Two genetically linked decay chains associated with the α -decay of ^{283}Cn were observed in the region of Hg deposition on the Au-coated detectors. The strong adsorption interaction of Cn with the Au surface indicates the formation of metal–metal bonds, which is typical of Group 12 elements. Further experiments with Cn revealed that the enthalpy of its adsorption on Au ($-\Delta H_{\text{ads}}$) is 52 kJ/mol. The above results show that Cn is sufficiently volatile for gaseous transport to the detector and exhibits a metallic character similarly to Hg, forming Cn–Au bonds that are weaker than Hg–Au bonds and thus not being as inert as a noble gas [59,60].

Flerovium belongs to group 14 similarly to Sn and Pb and is predicted to have an electronic configuration of $[\text{Rn}]5f^{14}6d^{10}7s^27p_{1/2}^2$. Thus, Fl is expected to exhibit high volatility and chemical inertness in the atomic state because of the stabilization of the $7p_{1/2}$ orbital into a quasi-closed-shell structure due to strong relativistic effects. The question of whether Fl is metal or noble gas has been raised [111]. The first challenging experiments with ^{287}Fl ($t_{1/2} \sim 0.5$ s) and ^{288}Fl ($t_{1/2} \sim 0.7$ s) produced in the reactions of ^{242}Pu and ^{244}Pu with ^{48}Ca were conducted by Eichler et al. at FLNR [64]. The identification of three Fl atoms in thermochromatographic experiments and their deposition pattern on the Au surface indicated that Fl is at least as volatile as the simultaneously investigated Hg, At, and Cn. The deduced enthalpy for Fl adsorption on Au indicates a surprisingly high volatility that contradicts the theoretical prediction and is rather unexpected for a typical Group 14 metal [64]. The adsorption properties of Fl on Au were further investigated using COMPACT by GSI and Mainz University. Two further Fl atoms were detected where ^{288}Fl and ^{289}Fl ($t_{1/2} \sim 2$ s) were produced in the reaction of ^{244}Pu with ^{48}Ca ions [62]. The TransActinide Separator and Chemistry Apparatus (TASCA) was used as a preseparator [52] to separate Fl in flight from unwanted nuclear reaction products and thus suppress background levels at the detector station. The gas chromatography and detection system comprised two COMPACT arrays placed behind TASCA, which were used to simultaneously study the adsorption behavior of Fl, its α -decay daughter Cn, their lighter homologs Pb and Hg, and the noble gas Rn. The observation of the two Fl atoms showed that Fl was transported in the flow gas to the detector and was less reactive toward Au than Pb. The estimated minimum value of $-\Delta H_{\text{ads}}^{\text{Au}} > 48$ kJ/mol reveals a metallic character due to the formation of a metal–metal bond at least as strong as that of Cn. The observed behavior agrees with the results of recent relativistic calculations [9,11] but disagrees with the observation of Eichler et al. [61]. Yakushev et al. (2022) examined Fl adsorption on SiO_2 and Au [64]. Figure 11 shows the experimental setup and the deposition distribution of Fl on these surfaces. Five atoms were deposited on the Au surface at room temperature, while three passed the entire Au surface and were deposited in the low-temperature ice region. Thus, Fl exhibits lower reactivity toward Au than the volatile metal Hg but can bond to Au more strongly than the noble gas Rn. Presently, decisive interpretation regarding the two deposition patterns of Fl is lacking [67].

Nihonium, located below Tl in Group 13, marks the beginning of 7p elements. One unpaired electron in the outermost $7p_{1/2}$ subshell of Nh is expected to result in elevated chemical reactivity. The first chemical investigation of Nh was performed at the FLNR [61]. The nuclear fusion reaction of ^{48}Ca with ^{243}Am afforded ^{284}Nh ($t_{1/2} \approx 1$ s), which is the α -decay daughter of ^{288}Mc ($t_{1/2} = 195$ ms). The experimental set-up was similar to that used to probe Cn chemistry [59,60]. The results indicated that Nh is volatile and weakly interacts with Teflon surfaces but is more reactive toward Au surfaces. The observed species were tentatively attributed to the atomic state of Nh or its hydroxide NhOH . To further clarify the chemical behavior of Nh, Aksenov et al. conducted an experiment using a physical recoil separator, the Dubna Gas-Filled Recoil Separator (DGFRS) [112] coupled to COLD detectors at the FLNR [62]. No decays arising from Nh after the chemical separation were observed. Yakushev et al. (2021) studied adsorption of Nh on Au and SiO_2

surfaces using the COMPACT detector arrays behind the TASCA separator at GSI [63], observing no decays of Nh. These results [62,63] suggest that owing to the high reactivity of Nh, it adsorbed onto the surface of the tube connecting the RTC to the detector arrays. Based on these achievements, Yakushev et al. developed an advanced setup, the miniCOMPACT detector array, which does not require any transport line between the RTC and the detector array. This setup was exploited in subsequent Nh and Mc experiments [67].

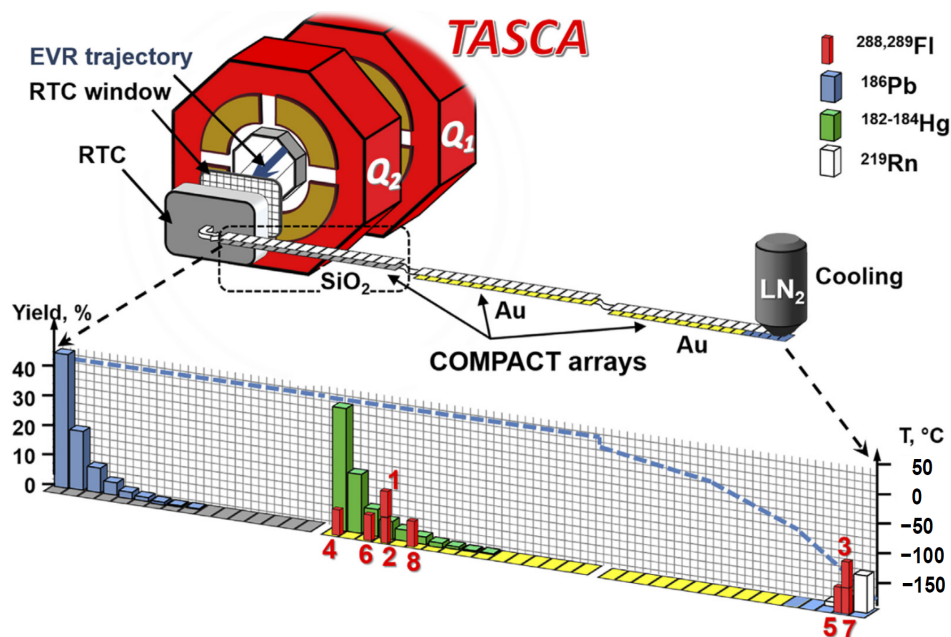


Figure 11. Experimental setup at TASCA and the deposition patterns of $^{288,289}\text{Fl}$, ^{186}Pb , $^{182-184}\text{Hg}$, and ^{219}Rn . The setup allowed the separation of a nonvolatile metal (Pb, blue bars) from a volatile metal (Hg, green bars) and noble gas (Rn, white bars). The positions of Fl decays observed in three TASCA runs [65,66] are shown as red bars. Numbers in red refer to decay chains. The setup comprised two Au-coated COMPACT arrays (yellow) in the first [65] and last Fl experiments. In the second run, a third COMPACT array (indicated by a dashed black rectangle) coated with SiO_2 (gray), was added in front of the two Au-coated (yellow) arrays. A 5 cm long polytetrafluoroethylene (PTFE) tube (inner diameter = 4 mm) connected the first COMPACT with the RTC. The following COMPACT detectors were connected via a 30 cm long PTFE capillary (inner diameter = 2 mm). A negative temperature gradient was applied along the last array via liquid N_2 cooling; the other arrays were kept at room temperature (21 °C). Traces of water caused the formation of a thin ice layer below -80 °C (light blue). The temperature profile along the detection setup is shown by a blue dashed line. For clarity, only 16 detectors are shown per COMPACT array. Reproduced from [66]. Copyright 2022 Frontiersin.org.

Moscovium, which belongs to Group 15, has one unpaired electron in the $7p_{3/2}$ subshell and is therefore expected to have a higher-energy valence atomic orbital and lower IP_1 than the neighboring closed-shell elements, Cn and Fl. Thus, Mc should be more reactive than Cn and Fl. In 2024, the chemical reactivity of Mc and its daughter Nh was simultaneously studied using a gas–solid thermal chromatographic technique based on a new combined chromatography and detection setup [67]. ^{288}Mc was produced in the nuclear reaction of ^{48}Ca ions with an ^{243}Am target at GSI and isolated using TASCA. The adsorption of ^{288}Mc and its α -decay product ^{284}Nh on SiO_2 and Au surfaces was investigated. The enthalpies of Nh and Mc adsorption on SiO_2 were measured $-\Delta H_{\text{ads}}^{\text{SiO}_2}(\text{Mc}) = 54_{-5}^{+11}$ kJ/mol and $-\Delta H_{\text{ads}}^{\text{SiO}_2}(\text{Nh}) = 58_{-5}^{+18}$, respectively. Thus, both elements interacted with the SiO_2 surface more weakly than their homologs (Tl and Bi), which was ascribed to the strong relativistic stabilization of the $7p_{1/2}$ orbital with respect to the $6p_{1/2}$ orbital. However, Nh and Mc were more reactive than Cn and Fl, respectively. Yakushev et al. explained this trend by the influence of strong relativistic effects on the valence electronic orbitals of these elements [67], which was consistent with theoretical predictions [113].

6. Atomic Properties

Technological advancements, such as progress in laser spectroscopy, have allowed the physical and chemical properties of stable elements (e.g., atomic mass, electron affinity (EA), electronegativity, ionization potential, and atomic radius) to be measured with extremely high precision. However, studies on the atomic properties of superheavy elements are extremely limited because of the experimental difficulties encountered at the atom-at-a-

time scale. Chemical studies of superheavy elements have primarily investigated the chemical behavior of their compounds (molecules) and compared it with that of homolog compounds to discuss the impact of relativistic effects on chemical properties [27–32]. Studies of such molecules inevitably face limitations in directly quantifying the influence of relativistic effects on atomic properties. In this sense, atomic property investigation is expected to provide a more direct approach to elucidating the influence of relativistic effects on the electronic configuration of atoms.

This section describes recent progress in the measurement of IP_1 of heavy actinides, EA of At, and atomic mass of heavy elements.

6.1. First Ionization Potential (IP_1) Values of Lr and Heavy Actinides (Fm, Md, and No)

The IP_1 of an atom corresponds to the binding energy of the outermost electrons and is defined as the energy required to remove one electron from a neutral atom in its ground state. Thus, the precise and accurate determination of IP_1 provides information on the binding energy of the most loosely bound valence electron under strong relativistic effects. The IP_1 values of actinides up to Es were measured using Resonance Ionization Mass Spectroscopy (RIMS) [114–116]. However, those of heavy elements with $Z \geq 100$ were not measured experimentally until 2015 owing to the limitation of the one atom-at-a-time condition.

Here, we describe the IP_1 measurement of the heaviest actinide (Lr) using a surface ionization technique and the Isotope Separator On-Line (ISOL) [117,118] installed in the JAEA tandem accelerator facility [119]. In contrast to its lanthanide homolog (the heaviest lanthanide Lu with a ground-state electronic configuration of $[Xe]4f^{14}6s^25d$), Lr is predicted to have a ground-state electronic configuration of $[Rn]5f^{14}7s^27p_{1/2}$ because its $7p_{1/2}$ orbital is expected to lie below the $6d$ orbital owing to strong relativistic effects [120,121]. Thus, by determining the IP_1 of Lr, one can probe the influence of relativistic effects on the electronic configuration of superheavy elements. Surface ionization occurs on a solid surface at a high temperature, as described by the Saha–Langmuir equation. The degree of ionization (β) depends on the work function of the ionizing material (ϕ), its surface temperature (T), and the IP_1 of the element of interest [122]:

$$\beta = \frac{N^i}{N^0} = A \exp\left(\frac{\phi - IP_1}{kT}\right), \quad (9)$$

where N^i and N^0 are the numbers of ions and atoms at the surface, respectively. $A = g_i/g_0$, where g_i and g_0 are the statistical weights for the ions and atoms, respectively, and k is the Boltzmann constant. IP_1 can be determined from the measurement of the ionization efficiency (I_{eff}), $I_{\text{eff}} = N^i/(N^i + N^0) = \beta/(1 + \beta)$.

The experiment was conducted using the ISOL at JAEA as schematically shown in Figure 12. ^{256}Lr ($t_{1/2} = 27$ s) synthesized in the $^{249}\text{Cf}(^{11}\text{B}, 4n)$ reaction [123] was transported by the He/CdI₂ gas-jet method to the ionization site—an ionization cavity made of Ta—via a skimmer [124,125]. The transported products were ionized on the surface of the cavity, and the produced $^{256}\text{Lr}^+$ ions were extracted using a potential of 30 kV, selectively mass-separated by a dipole magnet, and transported to the MANON detection setup [83]. The number of ^{256}Lr ions was measured using α spectrometry at the detector.

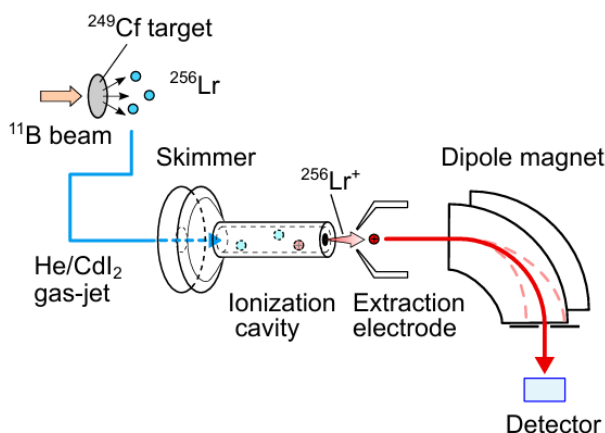


Figure 12. Schematic of the experimental setup used to measure the IP_1 of Lr using the surface ionization method. Reproduced from [119]. Copyright 2015 Springer Nature.

Sato et al. succeeded in ionizing and mass-separating ^{256}Lr using the above system. The I_{eff} of Lr was 33% at $T = 2700\text{ K}$ [119]. Based on I_{eff} values measured at several temperatures, the IP_1 of Lr was determined to be $4.96^{+0.08}_{-0.07}\text{ eV}$, which agreed with the values predicted by modern relativistic theoretical calculations assuming the $[\text{Rn}]5f^{14}7s^27p_{1/2}$ configuration [114]. Thus, the ground-state configuration of Lr is probably $[\text{Rn}]5f^{14}7s^27p_{1/2}$ [119].

Subsequently, Sato et al. measured the IP_1 values of other heavy actinides (Fm, Md, and No) using the same method [126]. ^{249}Fm ($t_{1/2} = 2.6\text{ min}$), ^{251}Md ($t_{1/2} = 4.27\text{ min}$), and ^{257}No ($t_{1/2} = 24.5\text{ s}$) were produced in the $^{243}\text{Am}(^{11}\text{B}, 5n)$, $^{243}\text{Am}(^{12}\text{C}, 4n)$, and $^{248}\text{Cm}(^{13}\text{C}, 4n)$ reactions, respectively, at the JAEA tandem accelerator. The measured IP_1 values agreed with those predicted by state-of-the-art relativistic calculations. In Figure 13, the IP_1 values of heavy actinides with $Z \geq 97$ are plotted together with those of heavy lanthanides (Tb–Lu). The IP_1 values of heavy actinides up to No increase with the filling of the 5f orbital, with the lowest value observed for Lr. These results demonstrate that the 5f orbital is filled at No, which has the closed-shell structure of $[\text{Rn}]5f^{14}7s^2$, with Lr having a weakly bound electron outside the No core. In analogy to the lanthanide series, this finding unequivocally verifies that the actinide series ends with Lr [35,126].

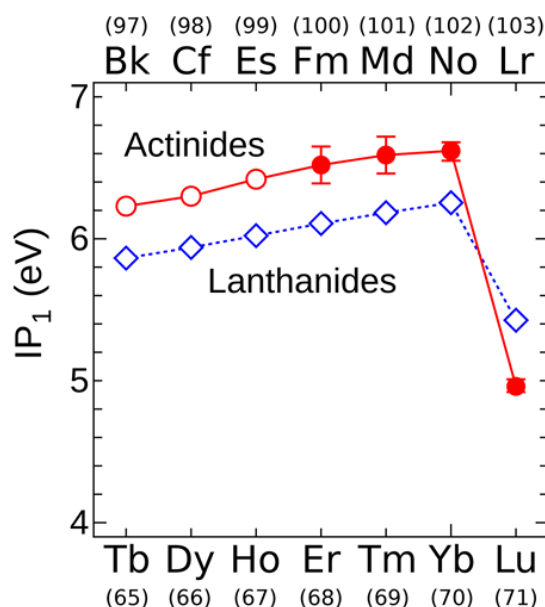


Figure 13. Variation of IP_1 with atomic number for heavy actinides and heavy lanthanides. Filled circles represent values from Sato et al. [126], whereas open circles are values adapted from Kramida et al. [127]. Reproduced from [126]. Copyright 2018 The American Chemical Society.

The successful measurement of the IP_1 of Lr triggered a debate regarding the revision of the periodic table, specifically the place of the last lanthanide (Lu) and last actinide (Lr) [128]. In the current periodic table approved by IUPAC, the lanthanide series begins with La and ends with Lu, and the actinide series starts with Ac and ends with Lr. Both series are placed directly below Group 3 transition metals (Sc and Y) and contain 15 elements (internal transition metals). However, Lu and Lr should be distinguished from lanthanides and actinides and placed in Group 3 with Sc and Y [129,130]. The discussion of the position of Lr in the periodic table is a good test case for how the periodic table should be viewed. An IUPAC task group was established to make a recommendation regarding membership in Group 3 [131–133] and published a brief progress report stating “In the course of many discussions held by the task group we have concluded that there is no objective means to adjudicate between Group 3 consisting of Sc, Y, La, and Ac or as Sc, Y, Lu, and Lr” [134].

Laser spectroscopic methods can also be used to investigate the atomic and ionic-level structures of heavy elements [135–138]. The Radiation Detected Resonance Ionization Spectroscopy (RADRIS) method [139,140], coupled to the Separator for Heavy-Ion reaction Products (SHIP) [141] at GSI, has been used to study the atomic structure of No using ^{254}No ($t_{1/2} = 51.2\text{ s}$) produced in the $^{208}\text{Pb}(^{48}\text{Ca}, 2n)$ reaction [142]. The new elements from Bh to Cn were discovered using the SHIP installed in the Universal Linear Accelerator (UNILAC) facility. A search for the low-lying $^1\text{P}_1$ atomic level in No was conducted [142]. Laatiaoui et al. applied this method to measure the IP_1 of No in one-atom-at-a-time quantities [143]. ^{252}No and ^{254}No were produced in the $^{206}\text{Pb}(^{48}\text{Ca}, 2n)$ and $^{208}\text{Pb}(^{48}\text{Ca}, 2n)$ reactions, respectively. The products were separated from the ^{48}Ca beam by the SHIP and subsequently thermalized inside an optical cell, a buffer-gas stopping cell filled with Ar gas (95 mbar). The cell was separated from the vacuum of the SHIP by a $3.5\text{ }\mu\text{m}$ thick Mylar foil (Figure 14). A fraction of the stopped

reaction products remained in a positive-charge state and were collected onto a catcher filament made of Ta wire. The filament was heated to ~ 1350 K to evaporate neutral No atoms for subsequent laser ionization. The No ions produced through this resonance ionization were immediately transported by electric fields through a drift tube with an applied static voltage and collected on the surface of an α -particle passivated implanted planar silicon (PIPS) detector, where the isotopes were identified through their characteristic decay properties. The IP_1 of No was determined as 6.62621 ± 0.00005 eV [143,144]. The IP_1 values of No obtained by laser resonance ionization spectroscopy and surface ionization agree well with each other, which provides an independent validation of IP_1 . The surface ionization technique helps limit the search regions for precision laser spectroscopy. Recent progress in the laser spectroscopy of actinides at GSI has been summarized by Block et al., who state that Lr will be tackled using the RADRIS method in the near future [137]. These new state-of-the-art techniques will pave the way to the frontier chemistry of superheavy elements.

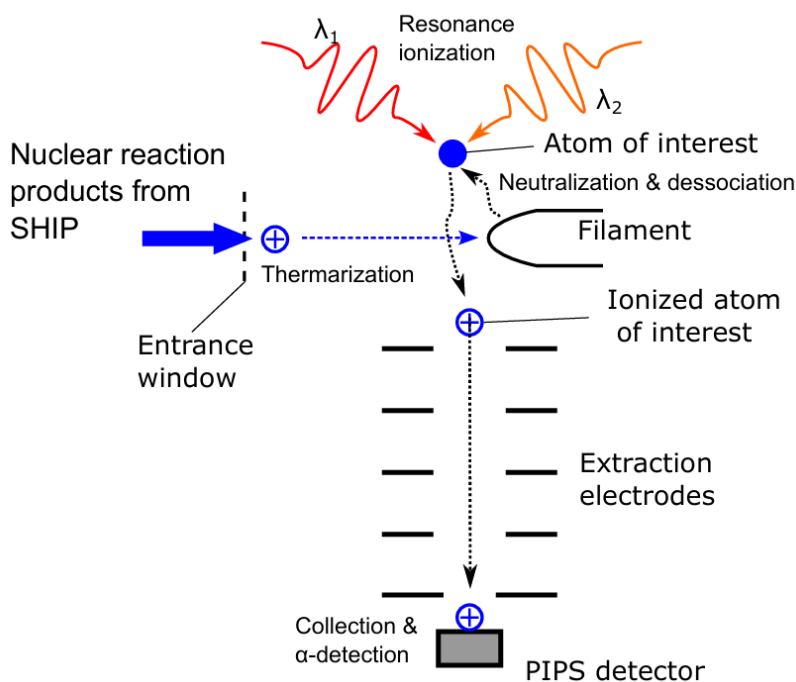


Figure 14. Principle of RADRIS. Laser spectroscopy on radionuclides (spheres) after their production and transmission through the velocity filter SHIP. Reproduced from [143]. Copyright 2016 Springer Nature.

6.2. Electron Affinity (EA) of At

In this section, we briefly introduce the study of the atomic properties of At on a tracer scale. Although At is not a superheavy element, we believe that these experimental approaches will contribute to superheavy-element chemistry in the future.

In 2020, EA of the radioactive ^{211}At ($t_{1/2} = 7.2$ h) produced in a spallation reaction of Th with 1.4 GeV protons at the Isotope Separator On-Line Device (ISOLDE) radioactive ion beam facility at CERN [145] was measured using laser photodetachment threshold spectroscopy [146]. The reaction products were diffused from the target material and effused into a negative surface ion source [147], comprising a hot Ta transfer tube and LaB₆ surface ionizer pellet heated to 1300 °C. Thermionic electrons emitted from the hot LaB₆ surface were adsorbed in a dedicated electron collector. Negative ions produced on the hot surface were accelerated and mass-separated through ISOLDE. The flux of the selectively extracted $^{211}\text{At}^-$ ions was 3.75×10^6 particles/s. The extracted $^{211}\text{At}^-$ ions were superimposed with a laser beam in the Göteborg Anion Detector for Affinity Measurements by Laser Photodetachment (GANDALPH) spectrometer [148,149]. The yield of neutral atoms produced in the photodetachment process, $\text{At}^- + h\nu \rightarrow \text{At} + e^-$, was examined as a function of the photon energy $h\nu$, where ν is the laser frequency.

The experimental EA of At (2.41578(7) eV) agreed with the value predicted by theoretical relativistic calculations, supporting the reliability and accuracy of the theoretical description. The EA of At is an excellent case for benchmarking theoretical models in atomic physics/chemistry, as it requires full relativistic many-body treatment. These theoretical models can be applied to further chemistry of superheavy elements. EA measurements of heavier elements based on this technique are also planned. Rothe et al. (2013) measured the IP_1 of At using

laser ionization spectroscopy. At isotopes were produced at the CERN ISOLDE radioactive ion beam facility by irradiating a thick target of uranium carbide (UC_x) or ThO_2 with a 1.4 GeV proton beam. The observed Rydberg states enabled the determination of the first ionization potential of At IP_1 as 9.31751(8) eV [150]. Based on the EA and IP_1 of a given element, one can determine its electronegativity—a fundamental chemical property for pinpointing chemical behavior.

6.3. Atomic Mass Measurements of Superheavy Isotopes

Atomic mass is one of the most fundamental chemical and physical properties. Accurate mass measurements in the region of superheavy elements are crucial for understanding the structure of heavy nuclei and provide a benchmark for theoretical calculations rationalizing their existence. The limits of the nuclear landscape have been discussed using state-of-the-art nuclear theories [151,152]. Studies probing the properties of superheavy elements lead to the understanding of proton-excess heavy nuclei, such as the limit of nuclear existence and verification of the proton drip line and nuclear (shell) structure of largely deformed nuclei, including multipole deformation, and the spontaneous fission of nuclei in extreme regions [153–160]. The latest atomic mass evaluation, AME2020, which includes detailed information on the experimental input data and the evaluation procedures used to derive the tables of recommended values has been published in [161,162].

The first high-precision measurement of atomic masses in the region of $Z > 100$ was achieved at GSI, where the SHIPTRAP apparatus was used to determine the masses of $^{252-254}\text{No}$ [163,164]. This apparatus [165] comprises a Penning-trap mass spectrometer (PTMS) and the SHIP kinematic velocity filter installed at the UNILAC facility of GSI. Block et al. produced the No isotopes by irradiating a Pb target with ^{48}Ca beams. The No ions were separated using the SHIP, thermalized in He gas, and introduced into a PTMS. A PTMS performs high-precision mass analysis by trapping ions in an electrostatic field and measuring their cyclotron frequency. Subsequently, the masses of the $^{255,256}\text{Lr}$ isotopes produced in $^{209}\text{Bi}(^{48}\text{Ca}, xn)$ reactions were measured using the same technique [166]. Kaleja et al. (2022) measured the atomic masses of ^{251}No , ^{254}Lr , and ^{257}Rf using SHIPTRAP [167].

The direct mass measurements of isotopes around $Z = 100$, ^{246}Es , ^{251}Fm , $^{249-252}\text{Md}$, ^{254}No , and ^{257}Db , with a Multireflection Time-of-flight Mass Spectrograph (MRTOF MS) were performed by the KEK (High Energy Accelerator Research Organization) group at the RIKEN facility [168,169]. The MRTOF MS comprises a pair of ion mirrors separated by a field-free drift region. The outermost electrode of each mirror is switched to allow ions to enter and exit. Ions are stored in the MRTOF MS for a time sufficient for them to be reflected a specific number of times and achieve a time focus. Prior to mass measurement, ions are trapped and cooled in an ion trap and then guided to the MRTOF MS. The mass of ions is determined from their flight time. An MRTOF MS combined with a cryogenic He gas cell and ion trap system was installed behind the GARIS-II [170] separator at RIKEN [171,172] (Figure 15). Schury et al. reported the precise mass determination of ^{257}Db produced in the $^{208}\text{Pb}(^{51}\text{V}, 2n)$ reaction using the MRTOF MS [169]. GARIS-II was employed to suppress the primary beam and unwanted transfer reaction products. Ions of fusion-evaporation products including ^{257}Db were delivered to the He gas stopping cell and thermalized therein. Thermalized $^{257}\text{Db}^{2+}$ ions were then transported to the MRTOF MS for mass analysis. An α -particle detector [173,174] embedded in the time-of-flight detector was used to unequivocally identify rare ^{257}Db time-of-flight events by correlation with α decays. The mass excess was determined to be 100,063 keV/ c^2 [169].

Advantageously, the MRTOF MS method can be applied to isotopes with half-lives in the millisecond range and enables the determination of molecular composition through the precise mass measurements of molecular ions.

Direct mass measurements and/or mass spectroscopic methods also provide an alternative for the identification of unknown isotopes and molecules based on their mass-to-charge ratios. The direct measurements of mass numbers of superheavy isotopes, ^{284}Nh and ^{288}Mc produced in the $^{243}\text{Am}(^{48}\text{Ca}, xn)^{291-x}\text{Mc}$ reactions, have been successfully undertaken at LBNL [175]. The isotopes were separated and identified by the combined BGS and FIONA setup as indicated in Section 4.4. Discovery of a new isotope ^{241}U produced in the multinucleon transfer reactions of the bombardment of ^{238}U on a ^{198}Pt target was performed using the MRTOF MS coupled to the KEK Isotope Separation System (KISS) installed at the RIKEN [176]. The KISS is designed to effectively extract neutron-rich isotopes produced in multinucleon transfer reactions [177].

Owing to the experimental challenges, studies of the atomic properties of superheavy elements are in their infancy. Currently, the atomic masses and IP_1 values of only several superheavy isotopes have been experimentally determined. In the future, various approaches, including laser spectroscopic techniques, will reveal the properties of superheavy atoms, enabling the detailed discussions of the influence of relativistic effects on the electronic structure of superheavy elements.

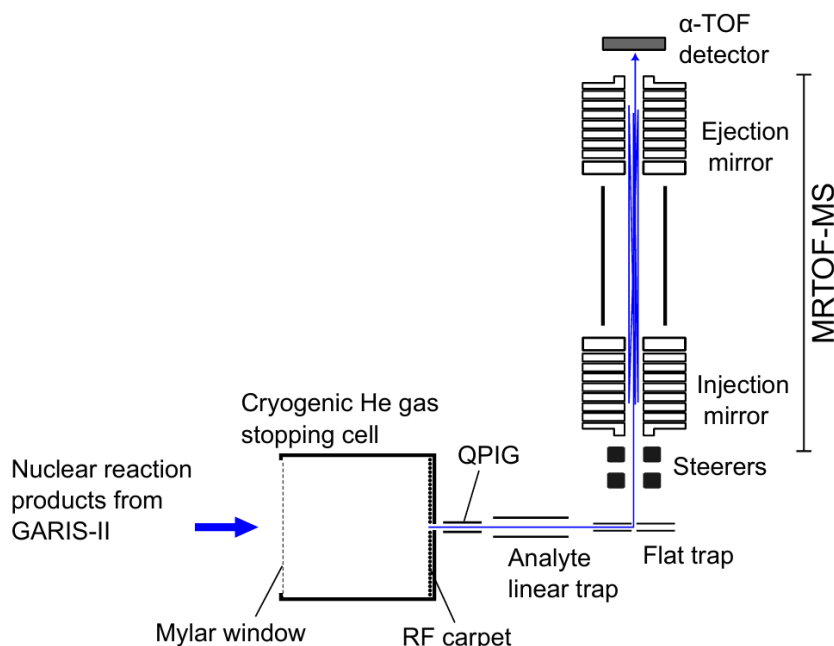


Figure 15. Schematic of the experimental setup used to measure the atomic mass of ^{257}Db produced in the $^{208}\text{Pb}(^{51}\text{V}, 2n)$ reaction. QPIG: Quadrupole RF ion guides. Reproduced with permission from [169]. Copyright 2021 American Physical Society.

7. Future Perspectives

The combination of atomic physics techniques with ion-beam technologies offers a unique opportunity to deeply understand relativistic effects that may endow superheavy elements with unexpected chemical properties. Measurements of ionization potentials, electron affinities, and atomic/ionic radii are indispensable for studying the electronic ground-state configurations of superheavy atoms. The chemical investigations of superheavy elements using state-of-the-art techniques, such as gas-phase ion chemistry [178–182] and ion mobility measurements [135,183], will open new avenues for superheavy-element chemistry.

The gas-phase ion chemistry of Lr was examined using the FIONA mass spectrometer connected to the BGS at the LBNL. After ^{255}Lr ($t_{1/2} = 31.1 \text{ s}/2.54 \text{ s}$) synthesized in the $^{209}\text{Bi}(^{48}\text{Ca}, 2n)$ reaction had been separated by the BGS, the Lr ions were trapped in the ion trap installed in the first stage of the FIONA device (Figure 10). The reaction rate constants for oxide formation were investigated based on changes in the yields of Lr ions and Lr oxide ions produced by adding a small amount of oxygen gas. Given that superheavy-element chemistry is investigated on an atom-at-a-time basis and very short-lived chemical operations are required, ion chemistry approaches, which trap ions and allow chemical reactions to be performed in isolation, are an attractive option in terms of reaction kinetics and efficiency [182]. The contribution of relativistic effects to ion–gas chemical reactions has also attracted attention [179].

Another new endeavor is the mobility measurements of superheavy-element ions. These ions, synthesized in nuclear reactions, are cooled in a radiofrequency gas cell, extracted, excited by laser irradiation, and transported through a drift tube. The ion transport velocity in the drift tube depends on the excited state of the atoms, which can be used to estimate the strength of the interaction between the gas molecules and atomic ions of interest and obtain information such as ion radii. Laatiaoui et al. plan to observe the strong $^1\text{S}_0\text{--}^3\text{P}_1$ transition of Lr^+ ions and eventually aim to elucidate the atomic structure of superheavy elements [183].

Nuclear shell structure determines the stability and existence limits of superheavy isotopes with $Z \geq 100$. Shell effects also affect nuclear size and shape. The RADRIS technique was used to measure nuclear charge radii of Fm and No isotopes [184,185]. High-resolution laser ionization spectroscopy with supersonic gas-jet expansion was used to study the ground- and isomeric-state properties of nuclei at the extremes of stability [186]. In 2017, this technique was used in a measurement on Ac isotopes around the $N = 126$ neutron shell closure [186]. These achievements highlight the potential for further laser spectroscopic measurements of superheavy nuclei.

Redox studies of superheavy elements, such as those probing oxidation states and redox potentials, provide valuable information on valence electronic configurations influenced by strong relativistic effects. However, traditional electrochemical methods, such as cyclic voltammetry, cannot be used for the one-atom-at-a-time chemistry of superheavy elements. Thus, the redox properties of the corresponding single atoms can only be

studied by a partition method to distinguish different oxidation states [187,188]. The reduction of Md(III) and Lr(III), and oxidation of No(II) were studied by several researchers [33]. The determination of the ionic radii of heavy actinides is a topic of particular interest as it will help experimentally assess the magnitude of the contraction influenced by relativistic effects on valence electrons. The measurement of the ionic radius of No^{3+} is essential to understand the contraction of trivalent actinide ions. However, owing to the high stability of the 5f electron shell, the divalent state is most stable for No in aqueous solution. To determine the ionic radius of No^{3+} , No^{2+} has to be oxidized to No^{3+} , and the +3 oxidation state should be preserved during the experiment. A new experimental approach of measuring the ionic radius of No^{3+} was conducted by Bilewicz who used H_5IO_6 as a strong oxidizing agent [189].

Spectroscopic approaches are also of interest for proving superheavy-element chemistry. The ionic radii of the trivalent actinides (An), U^{3+} – Cf^{3+} , in aqueous solution were derived from the accurately determined ion–water distances obtained by combining extended X-ray absorption fine structure data with molecular dynamics calculations [190]. A contraction of the actinide–O distance along the series was demonstrated. The coordination of an Es compound was studied using complementary X-ray absorption and luminescence spectroscopy. In this experiment, <200 ng of ^{254}Es ($t_{1/2} = 275.7$ d) was used [191]. Laser spectroscopic studies of molecules containing radioactive isotopes, which are typically produced at rates below 10^6 molecules (RaF) per second, were performed, and energetically low-lying electronic states were proved [192]. Spectroscopic methods will be attractive tools for characterizing molecules containing superheavy elements in future.

Studies proving the chemistry of superheavy elements do not only examine the chemical properties of these elements but also provide clean samples for nuclear investigations. Experiments performed in the liquid phase and gas phase have markedly contributed to the nuclear decay studies of neutron-rich isotopes and the characterization of new isotopes, such as ^{263}Rf [193], ^{263}Db [194], $^{265,266}\text{Sg}$ [68,87,89], $^{266,267}\text{Bh}$ [90], $^{269,270,271}\text{Hs}$ [91,195,196], ^{283}Cn [59,60], ^{284}Nh [61,67], $^{288,289}\text{Fl}$ [65], and ^{288}Mc [67]. Liquid-phase techniques were also used in the characterization of long-lived α -decaying daughter isotopes that undergo spontaneous fission [197], showing the potential for the unique identification of the atomic number in liquid-phase experiments involving superheavy elements. As discussed in Section 3, it takes 20–30 s for sample preparation for α -particle measurement due to drying eluate in the liquid-phase experiments. A new approach combining sample preparation and α -particle detection in an aqueous solution is being performed [198]. The active surface of commercially available α -particle Si detectors was modified with sulfonic acid groups to enable cation exchange. Ion-exchange separation could be performed on the surface of the Si detector in solution, which is of interest for studies examining the liquid-phase chemistry of short-lived isotopes.

Experimentally determined chemical properties of superheavy elements are currently required not only for property comparison among homologs but also for providing benchmarks against theoretical calculations and theoretical verification. Some approaches, such as IP_1 measurements, provide results directly comparable with those of theoretical calculations. So far, the question of how relativistic effects manifest themselves in the chemical properties of superheavy elements has not been fully answered. New state-of-the-art techniques have been introduced, and superheavy-element chemistry has entered a new era. The frontier of the periodic table is being steadily explored. In the future, an experimental design closely linked to theoretical calculations should be developed to investigate how the chemical properties of superheavy elements are determined and elucidate the roles of relativistic effects.

Author Contributions

Y.N.: conceptualization and writing—original draft preparation. T.K.S.: conceptualization and writing—reviewing and editing. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement

No data were created or analyzed in this study.

Conflicts of Interest

The authors declare no conflict of interest.

Use of AI and AI-Assisted Technologies

During the preparation of this work, the authors used DeepL to provide English proofreading. After using this tool, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

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