

# CHEMISTRY OF THE HEAVIEST ELEMENTS

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*Chemical studies of the heaviest elements with atomic numbers  $Z \geq 101$  provide not only crucial and challenging opportunities to advance our understanding of properties of matter at the limits of existence but also those to elucidate the influence of relativistic effects on atomic electrons and to architect the periodic table of the elements at the farthest reach. These elements are all man-made ones synthesized at accelerators using nuclear reactions of heavy-ion beams with heavy element target materials. As both half-lives and production rates of these nuclides are rapidly decreasing, they are usually available in quantities of only a few atoms or often one atom at a time. Here, we briefly introduce recent highlighted chemistry experiments conducted by state-of-the-art rapid chemical separation apparatuses.*

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## Introduction

Presently, we know 26 artificial transuranium elements. According to the actinide concept by Seaborg<sup>1</sup>, the 5f electron series ends with element 103, lawrencium (Lr), and a new 6d electron transition series is expected to begin with element 104, rutherfordium (Rf). The elements with atomic numbers  $Z \geq 104$  are called transactinide elements. The present Periodic Table of the elements is shown in Figure 1. The currently known transactinide elements, elements 104 through 112, are placed in the periodic table under their respective lighter homologues in the 5d electron series, hafnium (Hf) to mercury (Hg). Elements from 113 to 118 synthesized would be in the successive 7p electron series, although the elements with  $Z = 113, 115, 117$  and 118 have not yet fully been authenticated and named.

Searching for and producing new elements are very challenging subjects in recent advanced nuclear chemistry. How many chemical elements may be synthesized on earth? How can they be produced? How long can they survive? Which properties do determine their stability? What are their chemical and physical properties? And how are the

orbital electron configurations affected in the strong electric field of heavy atoms? These are the most fundamental questions in science.

Chemical characterization of the heaviest elements at the farthest reach of the Periodic Table is extremely fascinating and challenging subjects not only in nuclear chemistry but also general chemistry<sup>2-9</sup>. Very important and interesting aspects are to clarify basic chemical properties of these newly synthesized elements, such as ionic radii, redox potentials, or their ability to form chemical compounds as well as to elucidate the influence of relativistic effects on valence electrons of heavy elements and the impact on chemical properties of these elements. The contraction and stabilization of the s and  $p_{1/2}$  electron orbitals is known to be due to the direct relativistic effect<sup>10-12</sup>. Although this effect was thought to be large only for the electrons in inner shells of heavy atoms, it has been indicated that this stabilization is still large even for the outer s and  $p_{1/2}$  electrons. For example, it is calculated that the 7s orbital of element 105, dubnium (Db), is contracted by about 25% due to the relativistic effect. As this contraction results in a more efficient screening of the nuclear charge, the outer d and f orbitals become more expanded and energetically destabilized. This expansion of outer electrons is called the indirect relativistic effect. Spin-orbit splitting of the p, d, and f electron energy levels may

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Fig. 1 Current Periodic Table of the elements. The elements with  $Z \geq 104$  are called transactinide elements, while those with  $Z \geq 93$  transuranium elements.

also occur with the lower angular momentum orbitals such as  $p_{1/2}$  being strongly stabilized. Relativistic effects scale approximately with  $Z^2$ . Therefore, it is expected that heavier elements show a drastic rearrangement of electrons in their atomic ground states, and accordingly surprising chemical properties. The heaviest elements with atomic numbers  $Z \geq 101$ , however, are all man-made elements synthesized at accelerators using nuclear reactions of heavy-ion beams with heavy element target materials and they can only be identified by measuring their characteristic nuclear decay or that of their known daughter nuclei with sensitive detection techniques. As both half-lives and cross sections of these nuclides are rapidly decreasing, they are usually available in quantities of only a few atoms or often only one atom at a time.

Here, we demonstrate recent highlighted studies of the chemical separation and characterization experiments with the heaviest elements in liquid-phase chemistry, gas-phase chemistry and in studies of atomic properties. The more comprehensive reviews on chemical investigations of the heaviest elements including the concept of single-atom chemistry as well as newly developed rapid chemical separation apparatuses are reported in the references<sup>2-6</sup>. Detailed and general experimental techniques in liquid- and gas-phase chemistry including development of apparatuses for chemical investigation of single-atoms with short half-lives are summarized in ref.<sup>13</sup>.

### Liquid-phase Chemistry

The chemical characterization of the heaviest elements in liquid-phase experiments has been accomplished by partition methods with single atoms, e.g., liquid-liquid extraction, ion-exchange chromatography, and reversed-phase extraction chromatography<sup>14-16</sup>. The ultimate goal of these atom-at-a-time scale partition experiments is to

determine the so-called distribution coefficient,  $K_d$ , as a function of ligand concentration. The  $K_d$  value is given in its simplest definition as the ratio of the number of atoms - determined by its radioactivity - either in the organic phase (in liquid-liquid extractions) or in the stationary phase (in column chromatography) to that in the aqueous liquid phase. In order to get statistically significant results, it is indispensable to repeat the same experimental procedure several hundred or even several thousand times with cycle times of about the lifetime of the nuclide under investigation. In these processes, the behavior of the heaviest elements is compared with that of its lighter homologues under identical conditions.

The liquid-phase experiments with the heaviest elements are carried out on the basis of the following steps: i) synthesis of a specific isotope of the heaviest elements, ii) rapid transport of this nuclide to chemical separation devices by a gas-jet transport technique, iii) fast chemical characterization that includes dissolution in an aqueous solution containing inorganic/organic ligands for complex formation, iv) preparation of a sample suitable for nuclear spectroscopy ( $\alpha$ -spectroscopy) which usually requires the evaporation of aqueous solution to dryness, and v) detection of nuclides through their characteristic nuclear decay properties for unambiguous identification. For characterization of the heaviest elements, recent partition experiments have been conducted using the automated rapid ion-exchange separation apparatus ARCA II (automated rapid chemistry apparatus) with a miniaturized computer-controlled liquid chromatography system<sup>17</sup> and AIDA (automated ion-exchange separation apparatus coupled with the detection system for alpha spectroscopy)<sup>18</sup>; AIDA consists of ARCA II and an automated on-line  $\alpha$ -particle detection system. AIDA enables cyclic discontinuous column chromatographic separations of short-lived nuclides in liquid phases and automated detection of  $\alpha$ -particles within a typical cycle time of 60 s.

In the following, fluoride complex formation of Rf with AIDA and reduction/oxidation (redox) reactions of the heavy actinides, mendelevium (Md) and nobelium (No), with flow electrolytic column chromatography are briefly summarized.

**Fluoride complex formation of rutherfordium (Rf)** : Extensive series of detailed chemical investigations of the heaviest elements were made possible by the development of computer-controlled automated systems that have greatly improved the ability to perform rapidly and reproducibly large numbers of chromatographic separations

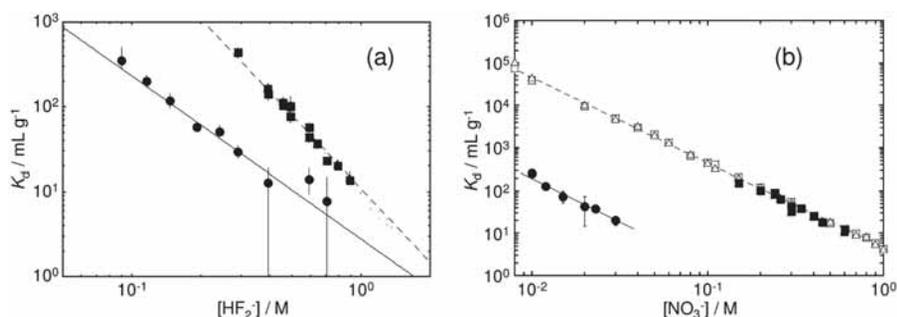
on miniaturized columns and to systematically vary ligand concentrations, thus allowing determining the stoichiometry of the eluted species. The experiments with automated devices have produced detailed and sometimes surprising results that called for a detailed theoretical modeling of the chemical properties with improved quantum-chemical calculations<sup>12,19</sup>.

A typical experimental procedure for studies of the anion-exchange behavior of Rf in hydrofluoric acid (HF) solution with AIDA is described<sup>20</sup>. The nuclide <sup>261</sup>Rf with a half-life ( $T_{1/2}$ ) of 78 s was produced in the <sup>248</sup>Cm(<sup>18</sup>O, 5n)<sup>261</sup>Rf reaction at the JAEA (Japan Atomic Energy Agency) tandem accelerator. Reaction products recoiling from the target, attached onto potassium chloride (KCl) particles produced by sublimation of KCl, were transported by a He gas stream to the collection site of AIDA. After collection for about 2 min, the products were dissolved with 240  $\mu$ L HF solution of various concentrations and were fed onto the chromatographic column filled with the anion-exchange resin (particle size of about 20  $\mu$ m) at a flow rate of 0.74 mL min<sup>-1</sup>. The effluent was collected on a tantalum (Ta) disk as fraction 1 and was evaporated to dryness using hot He gas and a halogen heat lamp. Then, the remaining products in the column (stationary phase) were stripped with 210  $\mu$ L of 4.0 M HCl at a flow rate of 1.0 mL min<sup>-1</sup>. The effluent was collected on another Ta disk and was evaporated to dryness as fraction 2. The pair of disks was automatically transported to the  $\alpha$ -spectroscopy station. Each separation was accomplished within 20 s and the  $\alpha$ -particle measurement started about 60 s after end of the collection of the products at the AIDA collection site. The anion-exchange experiments with the lighter homologues, group-4 elements zirconium (<sup>85</sup>Zr) and hafnium (<sup>169</sup>Hf) in the Periodic Table, were conducted under identical conditions as those with <sup>261</sup>Rf.

Figure 2(a) shows the distribution coefficients ( $K_d$ ) for Rf, Zr and Hf as a function of the concentration of HF: the counter anion HF<sub>2</sub><sup>-</sup>, [HF<sub>2</sub><sup>-</sup>]<sup>18,20</sup>. The  $K_d$  values of these elements decrease linearly with [HF<sub>2</sub><sup>-</sup>] in the log  $K_d$  vs. log [HF<sub>2</sub><sup>-</sup>] plot. It should be noted that the slopes for Zr and Hf are clearly -3 (dashed line), while that for Rf is significantly different, i.e. -2 (solid line). According to the equilibration of ion-exchange reactions, the slope in this plot (i.e., logarithm of  $K_d$  against logarithm of the ligand

concentration) indicates the charge state of the metal compounds. Thus, the results<sup>20</sup> demonstrate that Rf is likely to be present as the hexafluoro complex, [RfF<sub>6</sub>]<sup>2-</sup> similar to the well known [ZrF<sub>6</sub>]<sup>2-</sup> and [HfF<sub>6</sub>]<sup>2-</sup> at lower [HF], while Zr and Hf are likely to be present in the form of the heptafluoro complexes, [ZrF<sub>7</sub>]<sup>3-</sup> and [HfF<sub>7</sub>]<sup>3-</sup>.

Toyoshima *et al.*<sup>21</sup> studied further the fluoride complexation of Rf in mixed HF/HNO<sub>3</sub> solutions using solution of lower HF concentration. The anion-exchange behavior of Rf in the concentration ranges of 0.0054 - 0.74 M HF and of 0.010 - 0.030 M HNO<sub>3</sub> was investigated to clarify the type of an anionic fluoride complex of Rf and to evaluate equilibrium constants of its formation reactions. The  $K_d$  values were systematically measured as a function of the concentration of the fluoride ion [F<sup>-</sup>] and of the nitrate ion [NO<sub>3</sub><sup>-</sup>]. Figure 2(b) shows the variation of the  $K_d$  values for Rf, Zr, and Hf as a function of the counter anion NO<sub>3</sub><sup>-</sup>, [NO<sub>3</sub><sup>-</sup>] at a constant [F<sup>-</sup>] of 3.0  $\times$  10<sup>-3</sup> M. It is found that the  $K_d$  values of Zr and Hf are identical with each other and the logarithmic values of  $K_d$  linearly decrease with the logarithmic increase of NO<sub>3</sub><sup>-</sup> ion concentration with a slope of -2.0  $\pm$  0.1, as indicated by the dashed line. The evaluated  $K_d$  values of Rf are indicated by closed circles. As shown in Fig. 2(b), at any given concentration of NO<sub>3</sub><sup>-</sup> the  $K_d$  values of Rf are much smaller than those of Zr and Hf, and they smoothly decrease with increasing NO<sub>3</sub><sup>-</sup> concentration with the slope of -2.2  $\pm$  0.2, as indicated by the solid line. The results indicate that, at constant F<sup>-</sup> concentration of 3.0  $\times$  10<sup>-3</sup> M, anionic complexes of Rf, Zr, and Hf are present as [MF<sub>6</sub>]<sup>2-</sup> (M = Rf, Zr, and Hf)<sup>21</sup>. The formation of an anionic fluoride complex of Rf is also interpreted in detail by taking into account chemical equilibria of anion-exchange reactions and of formation reactions of fluoride complexes and comparing those with the ones of the homologues Zr and Hf. The upper limit of formation constants for the fluoride



**Fig. 2** (a) Distribution coefficients ( $K_d$ ) for Rf, Zr, and Hf on the anion-exchange resin as a function of HF<sub>2</sub><sup>-</sup> concentration, [HF<sub>2</sub><sup>-</sup>]<sup>18,20</sup>. (b) Distribution coefficients ( $K_d$ ) of Zr and Hf measured under static conditions (open symbols) and those of Zr, Hf, and Rf from column chromatography (solid symbols) as a function of the equilibrated concentration of NO<sub>3</sub><sup>-</sup>, [NO<sub>3</sub><sup>-</sup>], at fixed [F<sup>-</sup>] = 3.0  $\times$  10<sup>-3</sup> M. Linear relationships of the log  $K_d$  vs. log [NO<sub>3</sub><sup>-</sup>] for Rf and the homologues are indicated by the solid and dashed lines, respectively<sup>21</sup>. Adapted from Refs. [18, 20, 21].

complexes of Rf were experimentally evaluated for the first time; the result clearly demonstrates that the formation of the hexafluoro complex of Rf is much weaker than those of the homologues Zr and Hf<sup>21</sup>.

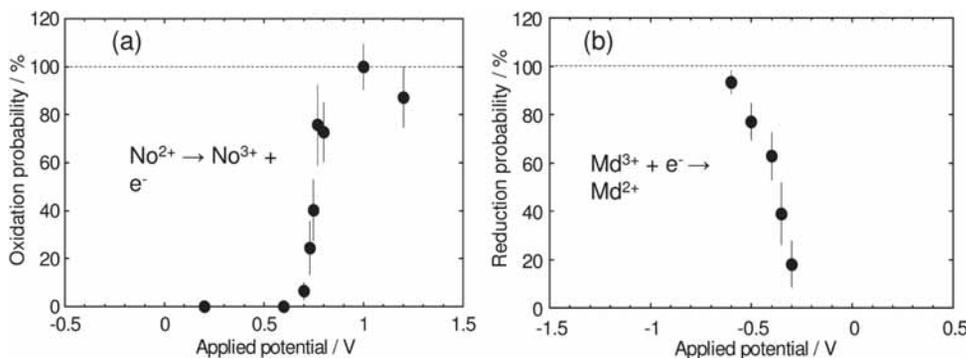
The cation-exchange behaviour of Rf has been thoroughly studied in HF/HNO<sub>3</sub> mixed solution together with its lighter homologues Zr and Hf, and the tetravalent pseudo-homolog Th<sup>22,23</sup>. It is ascertained that at these very low F<sup>-</sup> concentrations the fluoride complex formation of Rf is significantly weaker than that of Zr and Hf, but it is stronger than that of Th. Due to a predominantly electrostatic interaction, a correlation between crystallographic ionic radii<sup>24</sup> and the strengths of the formed complexes appears quite natural. The ionic radii values of the group-4 elements with the coordination number of 6 are as follows<sup>24</sup>: Zr (72) pm ≈ Hf (71 pm) < Rf (76 pm)<sup>19</sup> << Th (94 pm). In this particular case, this nicely correlates with the sequence in the complex formation: Zr ≈ Hf > Rf > Th. Thus, assuming the same kind of interaction for all these elements, the present result is showing that the ionic radius of Rf<sup>4+</sup> is in between those of Zr<sup>4+</sup>/Hf<sup>4+</sup> and Th<sup>4+</sup>. The much weaker complexation of Rf by the fluoride ion is apparent when compared to that of its homologues. A qualitative explanation comes from the Hard Soft Acid Base (HSAB) concept<sup>25,26</sup>. The small fluoride anions are hard donors and prefer the smaller acceptor ions Zr<sup>4+</sup> and Hf<sup>4+</sup>: both having a very similar radius. The larger (softer) Rf acceptor ion tends to prefer larger (softer, more polarizable) donor ligand ions like Cl<sup>-</sup>. The observed large different adsorption behaviour between Rf and its homologues Zr and Hf suggests that the relativistic effect could strongly influence the fluoride complexation of Rf<sup>20</sup>.

**Redox properties of mendelevium (Md) and nobelium (No) :** Redox studies of the heaviest elements are expected to give valuable information on valence electronic states influenced by strong relativistic effects, such as oxidation states and redox potentials. Well established electrochemical approaches like cyclic

voltammetry are, however, not available for the one atom-at-a-time chemistry of the heaviest elements. Thus, one needs to investigate redox properties of the heaviest elements based on the partition behavior of single atoms between two phases instead of measurements of electric currents from redox reactions.

A new apparatus for the study of electrochemical properties of the heaviest elements has been developed by Toyoshima *et al.*<sup>27</sup> The apparatus is based on a flow electrolytic cell combined with column chromatography. The working electrode is made of glassy-carbon fibers that are packed in a porous Vycor glass tube (4.8 mm i.d., 7 mm o.d. × 30 mm long), which works as an electrolytic diaphragm. The surface of the carbon fibers was chemically modified with Nafion<sup>®</sup> perfluorinated cation-exchange resin. A platinum (Pt)-mesh counter electrode was placed in the electrolyte pool to surround the glass tube. The potential on the working electrode was controlled using a potentiostat referring to the 1.0 M LiCl-Ag/AgCl electrode placed in the pool.

The apparatus was applied to the oxidation of No<sup>2+</sup> by controlling the applied potential<sup>28</sup>. Toyoshima *et al.* successfully conducted the oxidation of single No<sup>2+</sup> ions to the trivalent state No<sup>3+</sup> in α-hydroxyisobutyric acid (α-HIB) solution. The isotope <sup>255</sup>No with *T*<sub>1/2</sub> = 3.1 min was synthesized in a nuclear reaction between <sup>12</sup>C ions and a <sup>248</sup>Cm target at the JAEA tandem accelerator. Nuclear reaction products recoiling out of the target were attached to KCl aerosols seeded in a He gas stream and then continuously transported to the chemistry laboratory through a Teflon capillary within a few seconds. The transported products were deposited on a collection plate of AIDA for 10 min. Then, the products were dissolved with 1080 μL of 0.1 M α-HIB (pH 3.9) and were subsequently fed through a thin Teflon tube into the electrochemical apparatus at a flow rate of 600 μL min<sup>-1</sup>. The effluent including the fraction of No<sup>3+</sup> from the column electrode was collected on Ta disks. The remaining products in the column that contain No<sup>2+</sup> were stripped with 360 μL of 3.0 M HCl and were collected on additional Ta disks. These samples were evaporated to dryness using hot He gas and halogen heat lamps and were then transferred to the α-spectrometry station of AIDA. The above procedures were accomplished within 3 min and repeated numerous times



**Fig. 3** (a) Oxidation probability of divalent No<sup>28</sup> and (b) reduction probability of trivalent Md<sup>29</sup> as a function of the applied potential. Adapted from Refs. [28, 29].

to obtain sufficient statistics for the  $\alpha$ -decay counts of  $^{255}\text{No}$ .

Figure 3(a) shows the oxidation probability of No as a function of the applied potential. The oxidation reaction begins at about 0.7 V and is complete by 1.0 V. The formal redox potential of the  $\text{No}^{3+} + e^- \rightleftharpoons \text{No}^{2+}$  reaction corresponding to a half of the oxidation probability is evaluated to be approximately 0.75 V under the present conditions<sup>28</sup>. The reduction behavior of mendelevium (Md) was studied using the same flow electrolytic chromatography apparatus. By application of the appropriate potentials on the chromatography column, the more stable  $\text{Md}^{3+}$  is reduced to  $\text{Md}^{2+}$ . The reduction potential of the  $\text{Md}^{3+} + e^- \rightleftharpoons \text{Md}^{2+}$  couple was determined to be  $-0.16 \pm 0.05$  V vs. a normal hydrogen electrode<sup>29</sup>, see Fig. 3(b). This new technical approach will open up new frontiers of the chemistry of the heaviest elements. The results also provide an opportunity to test model calculations based on modern relativistic quantum-chemical treatments.

### Gas-phase Chemistry

Pioneering gas-phase chemistry was carried out using thermo-chromatographic separations in which negative temperature gradient is established along a chromatographic column through which a gas stream is conducted. It contains the volatile species of interest that deposit on the surface of the column according to their volatilities. Later, the deposition zones are determined from fission tracks registered in detectors positioned along the column. These fission events are associated with specific deposition temperature correlating with an adsorption enthalpy ( $\Delta H_{\text{ads}}$ ) of the nuclide under investigation<sup>30</sup>. The advantage of this method is that formation and separation of the detected species takes place very rapidly and species with half-lives as short as a few seconds can be measured. Positions of the deposition, however, are determined only after the experiments are finished; real-time observation of the nuclear decay and determination of the detected species are not possible. Further disadvantage is that it is difficult to identify the products deposited if only spontaneous fission (SF) decay is measured. An improved thermo-chromatographic system has been developed in which volatile species are transported through a chromatographic column where they are deposited on the surface of the pairs of detectors that form the column. Both the radiation from the products and their deposition positions as a function of temperature along the column can be simultaneously determined. This unique technique has been applied for first chemical investigation of element 108, hassium (Hs),

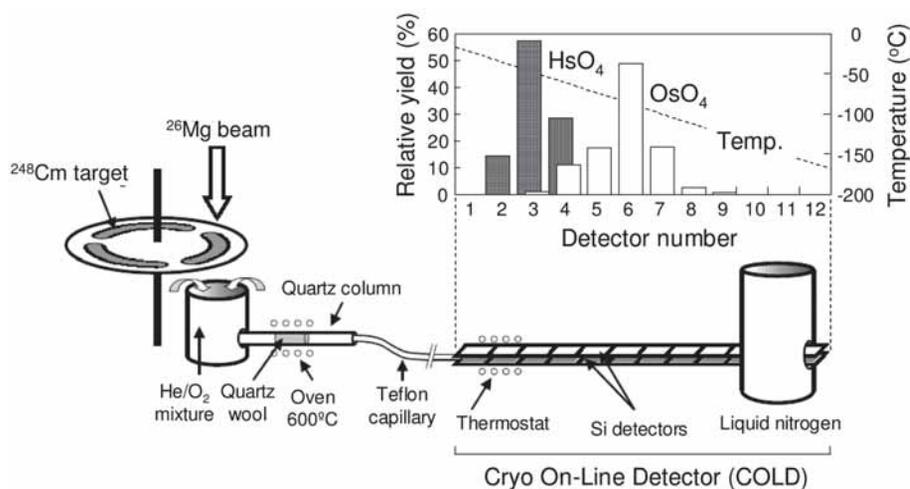
and most recently element 112, copernicium (Cn), element 113 and element 114, flerovium (Fl).

Another recent highlighted gas-phase experiment is the formation and detection of the volatile seaborgium (Sg) compound  $\text{Sg}(\text{CO})_6$  which has been conducted with cryo-thermo-chromatography coupled to a physical recoil separator. The result demonstrates that the short-lived atoms ( $^{265}\text{Sg}$ ,  $T_{1/2} \sim 10$  s) still form a carbonyl compound in single-atom quantities.

Recent reviews on gas-phase chemistry of the heaviest elements are reported in the references<sup>31-33</sup>. Here we make summaries of the experiments on the formation of the Hs tetroxide<sup>34</sup> and the Sg carbonyl complex<sup>35</sup> together with new technical approaches that have been developed for each study. Then, adsorption behaviors of Cn through Fl<sup>36-40</sup> in gas-phases will be briefly introduced.

**Formation of hassium tetroxide,  $\text{HsO}_4$  :** Hassium is expected to be chemically similar to its lighter homologues in group-8 elements, ruthenium (Ru) and osmium (Os), which are known to form highly volatile tetroxides. The unique experimental set-up that has been developed is shown in Figure 4. To produce the nuclides  $^{269}\text{Hs}$  ( $T_{1/2} = 9.7$  s) and  $^{270}\text{Hs}$  ( $T_{1/2} = 3.6$  s),  $^{248}\text{Cm}$  targets on a rotating wheel were bombarded with a  $^{26}\text{Mg}$  beam delivered from the GSI (Gesellschaft für Schwerionenforschung) UNILAC (universal linear accelerator), Germany<sup>34</sup>. The reaction products recoiling from the target were thermalized in the gas volume of the IVO (*in situ* volatilization and on-line detection) device flushed with dry  $1.2 \text{ L min}^{-1}$  helium and  $100 \text{ mL min}^{-1}$  oxygen. The reaction products were transported with the carrier gas through a quartz column (4 mm i.d.  $\times$  30 cm length) containing a quartz-wool-plug at a distance of 6.5 cm from the recoil chamber. This plug was heated to  $600^\circ\text{C}$  and served as a filter for aerosol particles and provided a surface to complete the oxidation reaction of Hs to their tetroxides, which were further transported through a perfluoroalkoxy (PFA) Teflon capillary (2 mm i.d.  $\times$  10 m length) to the detection system.

Using gas-phase adsorption thermo-chromatography, the temperature at which  $\text{HsO}_4$  deposits was measured with a chromatographic column along which a stationary negative temperature gradient was maintained. The chromatographic column, the cryo on-line detector (COLD), served as a detection system for the identification of decaying nuclides of  $^{269,270}\text{Hs}$ . The COLD device consists of 12 pairs of silicon PIN (positive-intrinsic-negative)-photodiodes of  $1 \times 3 \text{ cm}^2$  active area mounted at a distance of 1.5 mm via two spacers made from silicon. A



**Fig. 4** Schematic diagram of IVO-COLD system for the study of gas-phase properties of HsO<sub>4</sub> and the lighter homologue Os. Observed thermo chromatograms of HsO<sub>4</sub> and of OsO<sub>4</sub> are also depicted as a function of the temperature<sup>34</sup>. Adapted from Ref. [34].

temperature gradient from  $-20^{\circ}\text{C}$  to  $-170^{\circ}\text{C}$  was established along the detector array.

As shown in Figure 4,  $\alpha$ -decay of one Hs atom was registered in detector 2, the decay of four atoms in detector 3 and that of two atoms in detector 4. The maximum of the Hs distribution was found at a temperature of  $(-44 \pm 6)^{\circ}\text{C}$ , while the deposition distribution of the homologue, OsO<sub>4</sub>, revealed a maximum in detector 6 at  $(-82 \pm 7)^{\circ}\text{C}$ . The adsorption enthalpy of the compound, HsO<sub>4</sub>, on the detector surface (silicon nitride) was evaluated to be  $\Delta H_{\text{ads}} = -46 \pm 2 \text{ kJ mol}^{-1}$ . On the other hand, the adsorption enthalpy of OsO<sub>4</sub> on silicon nitride deduced from this experiment was  $-39 \pm 1 \text{ kJ mol}^{-1}$ . The observed formation of a very volatile Hs molecule, presumably HsO<sub>4</sub>, in a mixture of oxygen and helium, thus provides strong qualitative evidence that Hs is an ordinary member of group 8 of the Periodic Table that behaves similarly to its lighter homologue Os.

The successful experiment with Hs set a milestone in chemistry of the heaviest elements, making chemical studies of isotopes with half-lives of seconds produced with cross sections of a few picobarn possible. A chemical reaction with O<sub>2</sub> was carried out *in situ* in the recoil chamber. This allowed a fast and efficient transport of chemically pre-separated HsO<sub>4</sub> to a newly developed thermochromatography apparatus.

**Formation of seaborgium carbonyl complex, Sg(CO)<sub>6</sub>** : Even *et al.*<sup>35</sup> conducted the challenging experiments to form a carbonyl complex with Sg using the cryo-online multidetector for physics and chemistry of transactinoides (COMPCT)<sup>40</sup> system coupled to GARIS (gas-filled recoil ion separator) at RIKEN. The nuclide

<sup>265</sup>Sg ( $T_{1/2} = 8.5 \text{ s}$  and  $14.4 \text{ s}$ )<sup>41</sup> was produced via the reaction of <sup>248</sup>Cm(<sup>22</sup>Ne, 5n) and separated from the primary beam and from other reaction products with GARIS<sup>42</sup> as shown in Fig. 5. The development of combination of physical separation of single ions with chemical techniques has paved the way for studies of distinct compound classes<sup>43</sup>.

Nuclear reaction products were separated from the primary beam within the first dipole magnet (D), focused in a doublet of quadrupole magnets (Q) and guided by another dipole magnet (D) to the GARIS focal plane. Sg ions passed through windows and were thermalized in a recoil transfer chamber (RTC). The RTC was flushed with a He/CO mixture at 500 to 750 mbar. Volatile species, which formed in the RTC, were transported by the gas stream through a Teflon capillary (2 mm i.d.  $\times$  10 m length) to the COMPCT device which serves as a gas thermochromatography detector with the chromatography column consisting of 32 pairs of Si semiconductor detectors suitable for registering time- and energy-resolved fission fragments and  $\alpha$ -particles emitted in the nuclear decay of <sup>265</sup>Sg and its daughter nuclides. The detectors form a channel with a rectangular cross section. The surface of the detectors was covered with a 50-nm-thick SiO<sub>2</sub> layer. Along the channel, a negative temperature gradient was applied by using a liquid nitrogen cryostat.

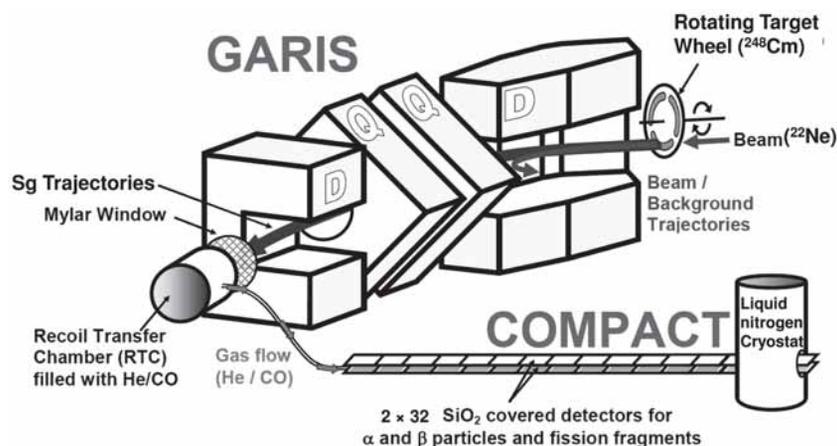
The volatile seaborgium complex showed the same volatility and reactivity with a silicon dioxide surface as those of the hexacarbonyl complexes of the lighter homologues molybdenum (Mo) and tungsten (W). Comparison of the product's adsorption enthalpy with theoretical predictions and data for the lighter homologues supported a Sg(CO)<sub>6</sub> formulation<sup>35</sup>. This result presents the first synthesis of a new class of the heaviest elements. The experiment opens up new perspectives, such as carbonyl formation of other heaviest elements and the route into the new field of organometallic chemistry of the heaviest elements.

**Gas chemistry of copernicium (Cn) through flerovium (Fl)** : So far, no attempts have been made to investigate chemical properties of elements 109 through 111, since extremely low production rates in combination with very short half-lives ( $T_{1/2} < 0.2 \text{ s}$ ) for the nuclides

produced in the cold fusion reactions make it difficult to conduct chemical experiments. The production of longer-lived nuclides beyond elements 110 (darmstadtium, Ds) with half-lives in the range of seconds to minutes has been reported using the  $^{48}\text{Ca}$ -induced nuclear reactions with actinide targets<sup>44-47</sup>. The synthesis of the long-lived isotope of element 112,  $^{283}\text{Cn}$  (SF half-life:  $T_{1/2}^{\text{SF}} \approx 3$  min), through the reaction of  $^{238}\text{U}(^{48}\text{Ca}, 3n)$  with the cross section of about 4 pb triggered the chemical investigation of element 112.

Cn, located below Hg in group 12 of the Periodic Table, is expected to have closed-shell electronic structure with a filled outer s subshell:  $6d^{10}7s^2$ . Based on relativistic calculations which show a strong stabilization of the closed  $7s^2$  shell, it is suggested that Cn would be relatively inert, like the noble gas radon (Rn), or be a very volatile liquid, like Hg. The recent relativistic calculation predicts that the interaction of Cn with metallic surfaces, such as gold (Au) and palladium (Pd), is weaker than Hg on these surfaces.

The experiment on the chemical characterization of Cn was conducted by the group of Paul Scherrer Institute (PSI), Switzerland and Flerov Laboratory of Nuclear Reaction (FLNR), Russia at FLNR<sup>36</sup>. The nuclide  $^{283}\text{Cn}$  ( $\alpha$ -decay half-life:  $T_{1/2}^{\alpha} \approx 4$  s) was produced as the  $\alpha$ -decay daughter of the primary reaction product  $^{287}\text{Fl}$  via the  $^{242}\text{Pu}(^{48}\text{Ca}, 3n)^{287}\text{Fl}$  reaction at a rate of several atoms per week. The cross section through  $^{242}\text{Pu}(^{48}\text{Ca}, 3n)^{287}\text{Fl} \rightarrow ^{283}\text{Cn}$  is expected to be higher than that in the  $^{238}\text{U}(^{48}\text{Ca}, 3n)^{283}\text{Cn}$  reaction. The IVO coupled to COLD system used for the successful experiment in Hs chemistry was modified and significantly improved to enable gas adsorption investigation of Cn atoms on the Au surface. A target of  $^{242}\text{PuO}_2$  with an admixture of  $\text{Nd}_2\text{O}_3$  was irradiated for about three weeks at the U-400 cyclotron of FLNR. The partially  $\alpha$ -decaying nuclide  $^{185}\text{Hg}$  ( $T_{1/2} = 49$  s) was produced through the reaction  $^{142}\text{Nd}(^{48}\text{Ca}, 5n)$  and the nuclide  $^{219}\text{Rn}$  with  $T_{1/2} = 4$  s was also produced in multi-nucleon transfer reactions between  $^{48}\text{Ca}$  and  $^{242}\text{Pu}$ . Here the behavior of Rn and Hg was simultaneously studied with that of Cn during the experiment. The COLD consists of an array of 32 pairs of ion-implanted planar silicon detectors with the 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 gold layer, while the other side retained the original silicon detector



**Fig. 5** Schematic drawing of the experimental set-up for the formation of Sg carbonyl complex<sup>35</sup>. Adapted from Ref. [35].

quartz surface that is chemically inert for the chemical state of most elements. The temperature gradient between  $35^\circ\text{C}$  and  $-186^\circ\text{C}$  was established along this chromatographic channel by a thermostat heating at the inlet and a liquid-nitrogen cryostat cooling near the outlet.

The primary product  $^{287}\text{Fl}$  decays with a half-life of about 0.5 s that is too short-lived to be transported to the COLD detector, so that only the decay of the daughter nuclei  $^{283}\text{Cn}$  and its daughter  $^{279}\text{Ds}$  is detectable in this experiment. It was found that Rn was deposited on the ice layer of the detector surfaces below  $-95^\circ\text{C}$ , while deposition of Hg was observed in the temperature range  $-24^\circ\text{C}$  to  $-50^\circ\text{C}$ . During the experiment, two genetically linked decay chains associated with the  $\alpha$ -decay of  $^{283}\text{Cn}$  were observed in the deposition region of Hg on the Au-coated detectors. The strong adsorption interaction of Cn with the Au surface indicates formation of a metal bond, which is typical behavior of group-12 elements.

Further experiments with Cn were conducted and the analysis provided an adsorption enthalpy ( $-\Delta H_{\text{ads}}^{\text{Au}}$ ) of  $52 \text{ kJ mol}^{-1}$  for Cn on Au<sup>37</sup>. These experiments show that Cn is sufficiently volatile for a gaseous transport to the detector and that Cn exhibits a metallic character like Hg, Cn-Au bond, but it is weaker than the Hg-Au bond, indicating that Cn is chemically not as inert as a noble gas.

The elements 113 and 114, located below thallium (Tl) and lead (Pb) in the groups 13 and 14 of the Periodic Table, respectively, mark the beginning of the  $7p$  elements. Because of large relativistic spin-orbit coupling effects on the  $7p_{1/2}$  orbitals, these metals are expected to be more volatile than their lighter homologues. A high volatility and chemical inertness was inferred.

First chemical investigation with element 113 was performed at FLNR<sup>38</sup>. The nuclear fusion reaction of  $^{48}\text{Ca}$

with  $^{243}\text{Am}$  was used in the experiment leading to the production of the nuclide  $^{284}113$  ( $T_{1/2} \sim 1$  s) which is the  $\alpha$ -decay daughter of  $^{287}115$ . The experimental set-up was similar to that exploited in Cn chemistry<sup>36</sup>. The results indicate that element 113 was found volatile; it weakly interacts with Teflon surfaces but reacts much more strongly with the Au surface. The authors tentatively attributed the observed species to either atomic element 113 or its hydroxide  $113(\text{OH})$ . Further investigation is required to get distinct conclusion on element 113.

According to empirical extrapolations and recent theoretical relativistic calculations, Fl is predicted to be much more volatile than Pb but less volatile than Cn. It is also expected that Fl is chemically more inert than Pb but still has a pronounced metallic character, i.e., forms metal-metal bonds with Au. The first pioneering experiments<sup>39</sup> with  $^{287}\text{Fl}$  ( $T_{1/2} \sim 0.5$  s) and  $^{288}\text{Fl}$  ( $T_{1/2} \sim 0.7$  s) produced in the reactions of  $^{242}\text{Pu}$  and  $^{244}\text{Pu}$  with  $^{48}\text{Ca}$  were conducted at FLNR. Identification of three atoms of Fl in thermochromatography experiments and their deposition pattern on the Au surface indicated that Fl is at least as volatile as simultaneously investigated elements Hg, astatine (At) and Cn. The deduced adsorption enthalpy for Fl adsorbed on Au indicates a surprisingly high volatility that would be in contradiction to theoretical prediction. Eichler *et al.*<sup>39</sup> suppose that this behavior is rather unexpected for a typical metal of group 14.

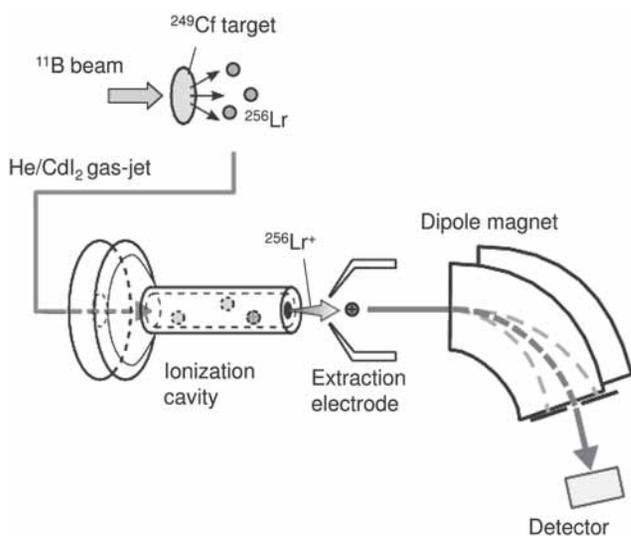
Two further Fl atoms were detected in the experiment at GSI where  $^{288}\text{Fl}$  and  $^{289}\text{Fl}$  ( $T_{1/2} \sim 2$  s) were produced in the reaction of  $^{244}\text{Pu}$  with  $^{48}\text{Ca}$  ions<sup>40</sup>. By using the transactinide separator and chemistry apparatus (TASCA)<sup>48</sup> as a pre-separator, Fl was isolated in-flight from unwanted

nuclear decay products. The gas chromatography and detection system comprised two COMPACT arrays were placed behind TASCA. The adsorption behavior of Fl, its  $\alpha$ -decay daughter Cn, their lighter homologues Pb and Hg and the noble gas Rn were studied simultaneously with two COMPACT detectors. The observed two Fl atoms resulted in that Fl was transported in the flowing gas to the detector, and that Fl is less reactive with Au than Pb. The estimated minimum value of  $-\Delta H_{\text{ads}}^{\text{Au}} > 48$  kJ mol<sup>-1</sup> reveals a metallic character upon adsorption on a Au surface due to the formation of a metal-metal bond, which is at least as strong as that of Cn. The observed behavior is in agreement with results of recent relativistic calculations<sup>19</sup> but disagrees with an observation by Eichler *et al.*<sup>39</sup> To ascertain the chemical characterization of Fl, further investigation is in progress.

### Studies of Atomic Properties

Studies of atomic properties of the heaviest elements are indispensable to understand electronic ground state configurations and other properties, such as first ionization energies, atomic/ionic radii, and stability of oxidation states of the heaviest atoms. From these properties, one can assess the influence of relativistic effects. The first ionization energy ( $\text{IP}_1$ ) is most sensitively reflects the outermost electronic configuration. The  $\text{IP}_1$  values of actinides up to element 99, einsteinium (Es), have been determined by using the technique of resonance ionization mass spectroscopy (RIMS)<sup>49</sup>. However,  $\text{IP}_1$  values of heavy elements with  $Z \geq 100$  have not been measured experimentally due to the limitation of one atom-at-a-time condition.

Sato *et al.*<sup>50</sup> successfully measured the first ionization energy ( $\text{IP}_1$ ) of the heaviest actinide element Lr using a surface ionization technique coupled to a mass separator, JAEA-ISOL (isotope separator on-line)<sup>51</sup>. The ground-state electronic configuration of Lr is predicted to be  $[\text{Rn}]5f^{14}7s^27p_{1/2}$ , in contrast to that of its lanthanide homologue Lu,  $[\text{Xe}]4f^{14}6s^25d$ , as the  $7p_{1/2}$  orbital is expected to be stabilized below the  $6d$  orbital in Lr by strong relativistic effects<sup>52-55</sup>. The isotope  $^{256}\text{Lr}$  ( $T_{1/2} = 27$  s) was produced with a rate of one atom per several seconds in the fusion-evaporation reaction of a  $^{249}\text{Cf}$  target with a  $^{11}\text{B}$  beam. They developed a highly efficient experimental set-up based on the surface ionization and detection of the  $^{256}\text{Lr}^+$  ion to determine the  $\text{IP}_1$  value of Lr. The surface ionization process takes place on a solid surface kept at high temperature, which is coupled to an on-line mass separator; an atom is ionized to the  $1+$  charge state via the interaction with a solid (metal) surface at high temperature and is selectively mass-separated. Figure 6



**Fig. 6** Schematic of the experimental set-up for the measurement of the first ionization energy of Lr<sup>50</sup>. Adapted from Ref. [50].

depicts the experimental set-up schematically. Short-lived  $^{256}\text{Lr}$  atoms recoiling from a  $^{249}\text{Cf}$  target were promptly transported to the ionization site (ionization cavity) by the He/cadmium iodide ( $\text{CdI}_2$ ) gas-jet transport. Here, the transported products were surface-ionized, then, ionized  $^{256}\text{Lr}$  atoms were extracted and mass-separated. The number of  $^{256}\text{Lr}$  ions after the mass-separation was determined by  $\alpha$  spectroscopy<sup>50</sup>.

The ionization experiments were conducted at  $T = 2700$  K and  $2800$  K, and the ionization efficiencies ( $I_{\text{eff}}$ ) of Lr were measured to be  $(33 \pm 4)\%$  and  $(36 \pm 7)\%$ , respectively. Based on these  $I_{\text{eff}}$  values, the  $\text{IP}_1$  value of Lr was determined to be  $4.96$  eV that is in very good agreement with the theoretical calculations which assume the  $7s^2 7p_{1/2}$  configuration<sup>50</sup>. It was found that Lr has the lowest  $\text{IP}_1$  value of all lanthanides and actinides. For the last actinide element, this quantitatively reflects and confirms the theoretically predicted situation of closed  $5f^{14}$  and  $7s^2$  shells with an additional weakly-bound electron in the valence orbital. As discussed above, the surface ionization method, successfully applied to determine the  $\text{IP}_1$  of Lr, can provide experimental data which can benchmark quantum chemical calculations of the heaviest elements. In addition, it opens up new perspectives to determine such a basic atomic property for further heavy elements.

Laser spectroscopic methods are also of potential interest for the investigation of atomic and ionic level structures of the heaviest elements<sup>56</sup>. The apparatus RADRIS (radiation detected resonance ionization spectroscopy) developed by Laatiaoui *et al.*<sup>57</sup> that is coupled to SHIP (separator for heavy ion products) at GSI has been applied to study atomic structure of No. They envisage identifying an atomic level in a No isotope. From a point of an atomic study, successful direct mass measurement of No and Lr isotopes with the Penning trap mass spectrometer SHIPTRAP is also remarkably important achievement<sup>58,59</sup>. These new technical approaches will open up new frontiers of the chemistry of the heaviest elements.

### Perspectives

Combination of atomic physics techniques with the chemical techniques offers a unique opportunity to understand more about relativistic effects that may cause qualitatively new behavior in the chemical properties of the heaviest elements. It might be also useful to study electrochemical properties of the heaviest elements. Experimental redox potentials will give valuable information on valence electronic states, such as binding

energies and oxidation states that would be influenced by relativistic effects.

Chemical techniques will significantly contribute to the nuclear decay study of neutron-rich isotopes and to the characterization of new nuclides. The advantages of chemical techniques compared with physical kinematic separators arise from the possibility of using thicker targets, high beam intensities spread over larger target areas, and in providing access to nuclides emitted under large angles and low velocities that are produced in hot fusion and in multi-nucleon transfer reactions. Chemical techniques are quite feasible for decay studies of relatively long-lived nuclei expected in the region of around  $N = 162$  and  $N = 184$ <sup>60</sup>. Chemistry could also give a clear identification of the atomic number of relatively long-lived spontaneous fission nuclei at the end of  $\alpha$ -decay chains of the heaviest nuclei<sup>61</sup>.  $\square$

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