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Gas-phase chemistry of element 114, flerovium

Alexander Yakushev[1,2,a] and *Robert* Eichler[3,4]

[1] GSI Helmholtzzentrum für Schwerionenforschung GmbH, 64291 Darmstadt, Germany
[2] Helmholtz-Institut Mainz, 55099 Mainz, Germany
[3] Paul Scherrer Institut, 5232 Villigen PSI, Switzerland
[4] University of Bern, Department of Chemistry and Biochemistry, 3012 Bern, Switzerland

Abstract. Element 114 was discovered in 2000 by the Dubna-Livermore collaboration, and in 2012 it was named flerovium. It belongs to the group 14 of the periodic table of elements. A strong relativistic stabilisation of the valence shell $7s^2 7p^2_{1/2}$ is expected due to the orbital splitting and the contraction not only of the $7s^2$ but also of the spherical $7p^2_{1/2}$ closed subshell, resulting in the enhanced volatility and inertness. Flerovium was studied chemically by gas-solid chromatography upon its adsorption on a gold surface. Two experimental results on Fl chemistry have been published so far. Based on observation of three atoms, a weak interaction of flerovium with gold was suggested in the first study. Authors of the second study concluded on the metallic character after the observation of two Fl atoms deposited on gold at room temperature.

1. Introduction

Man-made superheavy elements (SHE, atomic number $Z \geq 104$) are unique in two aspects. Their nuclei exist only due to nuclear *shell effects*, and their electron structure is influenced by increasingly important *relativistic effects* [1–3]. Recently the synthesis of elements 113, 115, 117 and 118 has been approved, thus, the discovery of all elements of the 7th row in the periodic table of elements with proton number Z up to 118 has been acknowledged [4]. The light transactinides, elements with $Z = 104$–112, are members of the *6d* transition metal series. Element 112, copernicium, Cn, has the closed-shell configuration $[Rn]5f^{14}6d^{10}7s^2$. Subsequently, the filling of the *7p* valence shell is expected starting with element 113 with the electron configuration $[Rn]5f^{14}6d^{10}7s^2 7p^1$ and ending with element 118 with noble gas electron configuration $[Rn]5f^{14}6d^{10}7s^2 7p^6$. Due to the increasing nuclear charge in SHE, the velocity of electrons close to the nuclei approaches the speed of light. This causes a relativistic increase in the electron mass. Hence, the spherical electron shells, having a non-zero electron density at the nucleus, contract in space and become stabilized in energy. This is the so-called direct relativistic effect. As a consequence, the non-spherical atomic orbitals are more efficiently screened from the nucleus, thus undergoing destabilization in energy and expansion in space: the indirect relativistic effect. Finally, the third effect is the spin-orbit splitting of atomic orbitals with $l > 0$. All three relativistic effects scale approximately with Z^2 for valence electron shells, and are thus most pronounced in SHE. The very large spin-orbit splitting in *7p* orbitals results in a quasi-closed-shell $7p^2_{1/2}$ in element 114, flerovium, Fl.

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[a] Corresponding author: `a.yakushev@gsi.de`

This closed sub-shell, being spherical, is strongly stabilized by the direct relativistic effect, similar to the $7s^2$ atomic orbital. Thus, both Cn and Fl are expected to be more inert than their lighter homologues in the groups.

Calculations of the promotion energies for superheavy elements with $Z = 112$, 114, 118 were performed by Pitzer already in 1975 [5]. He concluded that the energy needed to promote electrons from the closed shells $s^2_{1/2}$ and $p^2_{1/2}$ to the valence state electron configurations sp and p^2 in Cn and Fl, respectively, is too high to be compensated by the energy gain from the chemical bond formation. Thus, Cn and Fl should be very inert, like *noble gases* [5]. More recent molecular, cluster and solid-state relativistic calculations on these elements suggest that Cn and Fl are more inert than their lighter homologues in the groups, but still reveal a metallic character [6–9], e.g., upon $M - M'$ interactions ($M =$ Cn or Fl, $M' =$ metal, e.g., Au). In contrast to Pitzer's conclusion, for Cn d-orbitals are expected to be involved in the metallic bonding, whereas Fl is expected to provide both $7p_{1/2}$ and $7p_{3/2}$ atomic orbitals for metal-metal interactions. Therefore, a metal-metal bonding is expected besides pure dispersion forces for either element upon adsorption on metal surfaces [8, 9]. An overview of theoretical predictions for the interaction of Cn and Fl with gold can be found in, for example, Ref. [10]. The absolute values depend on the chosen calculation method and differ from 0.30 to 0.52 eV for Cn and from 0.47 to 0.77 eV for Fl.

2. Experimental methods

For short-lived nuclei produced at the one-atom-at-a-time level, on-line gas-solid chromatography is the most rapid and most effective technique, which is usually applied in chemistry experiments with volatile compounds of superheavy elements in two modes: thermochromatography (TC) and isothermal chromatography (IC) [11, 12]. By TC, the deposition temperature of a volatile species in a column is a measure for the strength of the adsorption enthalpy. By IC, the retention time of a volatile species in a column kept at a varying temperature correlates with the adsorption enthalpy value. The most promising chemical separation method seems to be studies of the adsorption of Fl in the elemental state on a gold surface. Fl, as a volatile and a relative inert metal, can be transported to a chemical device by a carrier gas flow. Taking into account the large uncertainty of the predicted adsorption enthalpy values, a wide range of reactivity should be covered by an experimental setup: from the adsorption on gold at room temperature (metallic behaviour) to the deposition at a low temperature (noble gas behaviour).

This challenge calls for the application of the thermochromatograpy method, where the position of each atom in the column contributes chemical information about the investigated species. If a chromatography channel can be formed by position sensitive nuclear decay detectors, the chemical separation and the detection of the characteristic alpha particle energies are fulfilled in one device. The temperature in the column is usually ranging between room temperature and the temperature reachable by a cooling device, such as a liquid nitrogen cryostat. As an example of such thermochromatography detector channel, the open COMPACT detector is shown in Fig. 1. The silicon PIN diodes are covered with a thin layer of gold and form an array of 32 single detectors 1 cm wide and 32 cm long in each channel.

3. Results and discussion

Several studies aimed at the adsorption of Fl on gold were conducted at the FLNR Dubna, Russia by a collaboration led by the PSI group (Villigen, Switzerland) and at the GSI Darmstadt, Germany by the TASCA collaboration.

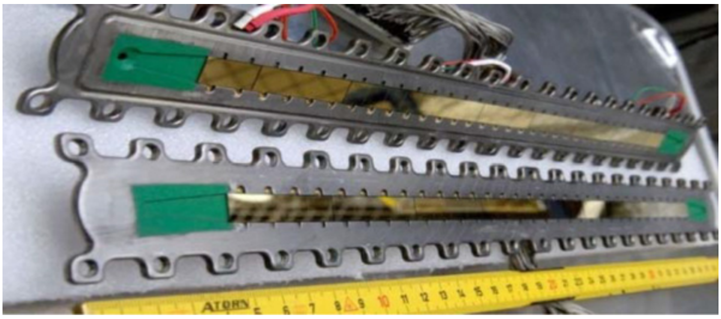

Figure 1. COMPACT detector array – a gas chromatography channel consisting of silicon detectors for α-particle- and SF-fragment spectroscopy.

The first observation of Fl in a chemistry experiment was made in 2007 in Dubna, where Fl isotopes were produced by the irradiation of ^{242}Pu and ^{244}Pu targets with a ^{48}Ca ion beam [13]. Only the long-lived Fl isotopes, ^{287}Fl ($T_{1/2} = 0.48^{+0.16}_{-0.09}$ s), ^{288}Fl ($T_{1/2} = 0.69^{+0.17}_{-0.11}$ s) and ^{289}Fl ($T_{1/2} = 1.9^{+0.7}_{-0.4}$ s) [14] are suitable for the chemical studies. Beam doses of 3.8×10^{18} and 4.5×10^{18} were accumulated during irradiations of ^{242}Pu and ^{244}Pu targets, respectively. The reaction products recoiling from the target were stopped in a recoil chamber made of quartz, which was continuously flushed with a gas flow (He:Ar = 1:1, 1.5 l/min). The species volatile at room temperature were transported through a PFA-Teflon capillary to the detector setup COLD within 2.2 s [13]. Unlike to the detection setup shown in Fig. 1, only one side of the detector channel was covered with gold. The background in the α-particle spectra was caused by other volatile by-products, like Rn and At isotopes, which could be also transported to the detection setup.

Three decay chains were observed (two of them at the temperature of about $-90\,^{\circ}$C) and assigned to Fl isotopes: one to ^{287}Fl and two to ^{288}Fl. The more long-lived ^{289}Fl was also produced with the ^{244}Pu targets, but no unambiguous identification of the decay chains originating from ^{289}Fl was possible [13]. The observed position of Fl decay chains are presented in Fig. 2, on the panels 3 and 4. The distributions of ^{185}Hg, ^{219}Rn and ^{283}Cn decays are also shown on the panels 1 and 2 for comparison. The solid lines represent the deposition pattern obtained by the Monte Carlo simulations. The simulated deposition patterns for Fl isotopes are obtained for the adsorption enthalpy value $-\Delta H_{ads}^{Au}(\text{Fl}) = 34\,\text{kJ} \cdot \text{mol}^{-1}$. This value suggested that the deposition of Fl on gold occurs due to dispersion forces. However, large limits for the 95% confidence interval were determined: $-\Delta H_{ads}^{Au}(\text{Fl}) = 34^{+54}_{-11}\,\text{kJ} \cdot \text{mol}^{-1}$ (95% c.l.) [13].

The reaction $^{244}\text{Pu}(^{48}\text{Ca};3\text{–}4n)^{288,289}\text{Fl}$ was used in the following experiment conducted by the PSI-FLNR group. For background reduction from volatile by-products, a pre-separation with the Dubna Gas-Filled Recoil Separator (DGFRS) was applied prior to the chemical separation.

One decay chain starting from ^{285}Cn was observed during 35 days at a temperature of $-93\,^{\circ}$C [15]. The deposition temperature of the ^{285}Cn event is in a very good agreement with two Fl events from the first experiment (cf. Fig. 2). This chain can be an incomplete decay chain originating from ^{289}Fl, where the first member was missed. Two additional coincident SF events were registered and tentatively assigned to Fl isotopes or their progenies. Considering that both, Cn and Fl, are volatile elements, no unambiguous chemical conclusion on the observed decay chain could be made [15].

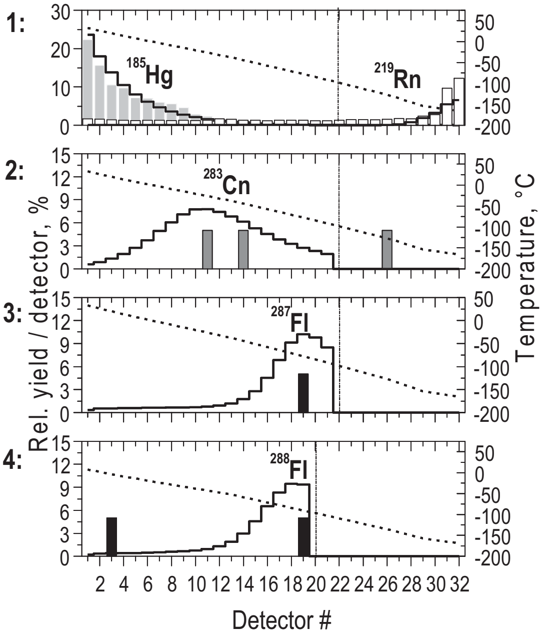

Figure 2. Simulated (solid lines) and measured (bars) deposition patterns of Hg, Rn, Cn, and Fl in COLD (see text for further details). The dotted line depicts the temperature gradient. Adopted from [13].

A different experiment on Fl chemistry behind a pre-separator was conducted at the GSI Darmstadt. The gas filled separator TASCA was used for the pre-separation. Two COMPACT detectors (Fig. 1) in series were mounted directly to the exit of the Recoil Transfer Chamber (RTC). The silicon detectors of both COMPACT arrays were covered with a thin gold layer [16]. The transport time was determined to be 0.81 s [16]. A short PTFE capillary (2 mm in diameter, 30 cm long) connected the detector arrays. To minimize the transport time, the first detector was connected via a 2-cm long PTFE tube to the RTC with a volume of 29 cm^3. The first detector array was kept at room temperature as an isothermal chromatography channel. The negative temperature gradient, which went down to $-162\,^{\circ}$C, was applied on the second detector array. Again, the nuclear reaction ^{244}Pu(^{48}Ca;3–4n)^{288,289}Fl was used. A beam dose of 4×10^{18} particles was accumulated during 29 days. The chemical yield to the detection setup was measured with short-lived Hg and Pb isotopes. The 100% production rates of Hg and Pb isotopes were determined with a (58×58) mm^2 double-sided silicon strip detector installed in the RTC position. 27% of ^{182,183}Hg atoms and 20% of ^{186}Pb atoms were transported to the first COMPACT detector [16].

Two correlated chains, α–SF and α–α–SF originating from ^{288}Fl and ^{289}Fl, respectively, were observed. Both Fl decays occurred in the first isothermal detector array at room temperature. The positions of these two observed decay chains are presented Fig. 3 in comparison with deposition patterns measured for Pb, Hg, and Rn. Considering the low experimental statistics, a lower limit for the adsorption enthalpy of Fl on gold was determined $-\Delta H_{ads}^{Au} > 48\,\mathrm{kJ \cdot mol^{-1}}$ (95% c.l.) Unlike the first experiment, a stronger interaction of Fl atoms with gold on the detector surface suggested the formation of weak metal-metal bonds. It was concluded that Fl has demonstrated a behaviour typical for a volatile metal in this experiment [16].

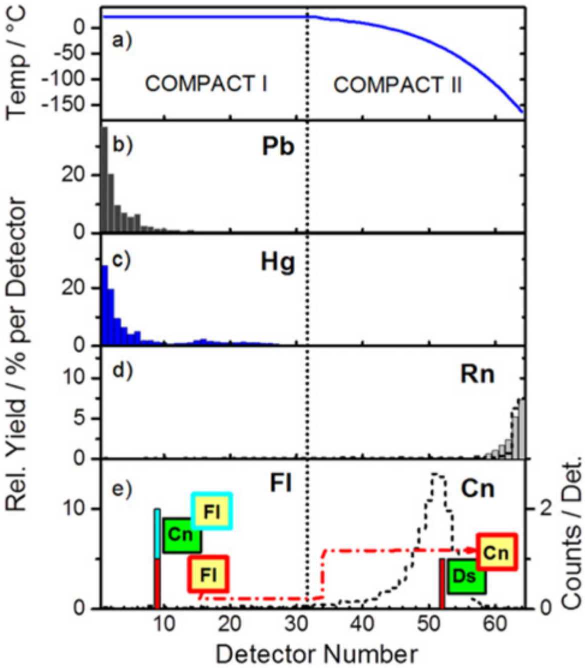

Figure 3. The deposition pattern of Fl decay chains in COMPACT detector arrays in comparison with that of Pb, Hg and Rn. Adopted from [16].

4. Conclusion on chemical properties of Fl and outlook

Two contradicting conclusions on the chemical behaviour follow from the first gas chromatography studies on the flerovium-gold interaction: one suggests weak physisorption of Fl upon the deposition on gold, another suggests a metallic character. The question "is flerovium a metal or a noble gas?" is still waiting for an unambiguous answer. Due to the limited number of observed Fl events so far, the error bars of the determined values of the adsorption enthalpy, representing the interaction strength between flerovium and gold, are very large [13, 16]. Additional experiments with higher statistics are required to obtain an accurate value. Despite the lower overall efficiency, combining the chemistry experiment with a pre-separation stage seems advantageous. Much lower background conditions allow the reliable identification of the decay chains, and thus, increase the sensitivity. Furthermore, the transport time can be reduced by the direct coupling of a chemistry setup to a pre-separator. Most recently, two additional runs were conducted at TASCA resulting in observation of several events from Fl and Cn isotopes. The analysis is being finalized by the TASCA collaboration.

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