

Adsorption of ^{220}Rn on dioxygenyl hexafluoroantimonate surface. A model experiment for studies of the chemistry of element 112

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Abstract By comparison of the ionization potentials and ionic radius (estimated in this work) the chemical reactivity of element 112 is predicted. Due to the expected noble gas behaviour of element 112, we propose an investigation of adsorption of ^{220}Rn on a dioxygenyl hexafluoroantimonate thin film surface as a model experiment for the chemistry of element 112.

Key words transactinides • element 112 • relativistic effect

Introduction

In the chemistry of heavy elements, one of the most interesting problems is the degree to which relativistic effects influence their chemical properties. The regularities of the Mendeleev Periodic System suggest that element 112 (E112) should be similar to Zn, Cd, and Hg, a Group 12 element, assuming it has the $d^{10}s^2$ ground state configuration. The relativistic calculation indicates that in the field of the highly charged nucleus of element 112 the s electrons are moving at relativistic velocities, which cause a contraction of the spherical orbitals. This contraction induces energetic stabilization and thus a higher binding energy of the $7s$ electrons [5, 12]. This relativistic stabilization causes that element 112 should be more volatile and chemically inert than mercury. In 1973 Pitzer suggested that the element 112 should have noble gas properties [11]. Other predictions expect a volatile noble metallic character of element 112, therefore alike Hg it should adsorb on metals proved by the formation of quite strong intermetallic bonds [3, 10, 14].

The results of recent experiments, aimed at the synthesis of superheavy elements in the nuclear reactions between ^{48}Ca with ^{238}U , $^{242,244}\text{Pu}$ and ^{248}Cm , point to a substantial increase in the stability of nuclides with $Z = 108\text{--}116$ and $N = 170\text{--}176$ [9]. Relatively long half-lives of these nuclides provide possibilities for chemical identification of the elements 112 and 114, studies of their chemical properties and comparison with theoretical predictions. In addition, chemical identification of the proton number of the new nuclides is especially important, because all members of the decay chains of these nuclides were unknown.

The first experiment related to chemical identification of E112 was performed recently in Dubna [16]. The nuclide

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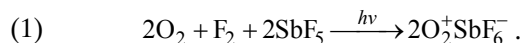
$^{283}112$ ($T_{1/2} = 3$ min) has been synthesised in the nuclear reaction $^{238}\text{U}(^{48}\text{Ca}, 3n)$ with a cross section of about 5 pb [8]. By assuming of “Hg-like” behaviour of element 112, Yakushev *et al.* studied the adsorption of ^{185}Hg and $^{283}112$ on PIPS detectors covered with thin layers of Au and Pd. While about three SF events could be expected, not a single one was detected at an upper limit for the production cross section of about 1 picobarn. In the same experiment, adsorption of ^{185}Hg on the first detector was larger than 95%. The conclusion of the experiment was that E112 is resembling noble gases rather than Hg.

In order to plan the experiment with chemical identification of element 112, we studied in this work chemical properties of Rn as an element with a nearly homologous behaviour compared to the possible noble gas properties of element 112. As a model experiment for studying the chemistry of element 112, we propose adsorption studies of ^{220}Rn on a dioxygenyl hexafluoroantimonate thin film surface. Dioxygenyl compounds of hexafluoroplatinate, hexafluoroarsenate and hexafluoroantimonate are well known as very effective oxidants and adsorbants for xenon and radon [1, 15].

Experimental

Synthesis of dioxygenyl hexafluoroantimonate thin film surface

Dioxygenyl hexafluoroantimonate was synthesized in the form of a thin film surface. In the dry atmosphere, one drop of antimony pentafluoride was placed on a stainless steel disk and reacted with fluor and oxygen from a gas mixture in the following reaction:



Due to the high reactivity of fluorine, we used a gas mixture 20% F_2 + 20% O_2 + 60% N_2 (Messer Griesheim GmbH, Krefeld, Germany). All elements of the installation were made from a Monell alloy, teflon and Pyrex glass. Before reaction, all gases were dried. Non reacted fluorine was absorbed on a solid sodium hydroxide column. After less than 1 min we obtained a white solid film, which is stable at room temperature. The obtained product was highly sensitive to humidity.

Generation of ^{220}Rn and its adsorption on dioxygenyl hexafluoroantimonate thin film surface

Figure 1 presents a scheme of installation for the studies of radon adsorption. The short-lived radon isotope ^{220}Rn ($T_{1/2} = 55$ s) was produced by passing a dried air stream through ^{224}Ra deposited in the first vessel. The air was dried by passing through anhydrous calcium chloride. Next, the gas flow with the generated ^{220}Rn was pumped to the second vessel containing a stainless steel disk coated with a thin film of the dioxygenyl hexafluoroantimonate. After 10 min of adsorption, the installation was disconnected and the disk was removed. The gamma activity of the dioxygenyl hexafluoroantimonate thin film was measured using

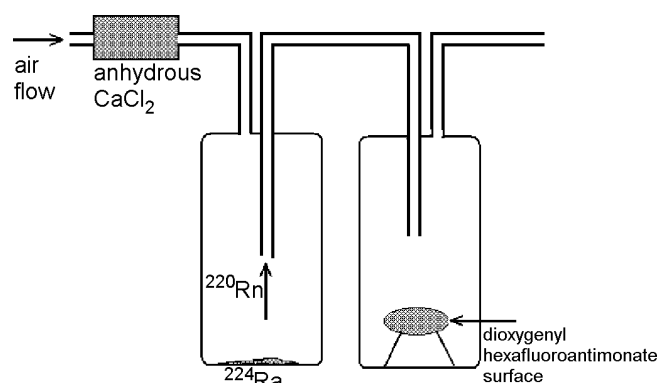


Fig. 1. Installation for ^{220}Rn generation of and its adsorption on film surface.

a gamma ray spectrometer, Ortec, equipped with a high resolution HPGe detector.

Results and discussion

Theoretical prediction of chemical properties of element 112

Table 1 presents ionization potentials and ionic radii of element 112 and for mercury, radon and xenon, for comparison. The data for element 112 and radon are the theoretical values and for xenon and mercury the experimental ones.

The ionization potentials of element 112 and the configuration of cation 112^{2+} were taken from [4], the second ionization potential of Rn from [7] and other values from [6].

The ionic radius of 112^{2+} was estimated by a procedure described by Siekierski [13]. The ionic radius of 112^{2+} has been estimated from the linear dependence of IR on expectation value of orbital radii $\langle r \rangle$ of the outermost orbitals of the lighter homologs. Due to the strong stabilization of the $7s$ orbitals, the 112^{2+} cation has a unique configuration ($[\text{Xe}]6d^87s^2$) in group 12. In the ionization process, the first $6d$ electrons are removed and $7s^2$ pair retained on the cation. It can be assumed that the $7s$ electron lone pair is stereochemically inactive as a result of relativistic stabilization. Therefore, as the outermost orbital in 112^{2+} cation, the $7s$ orbital was considered. As a lighter homolog for the estimation of orbital radius, the Pb^{2+} ($5d^{10}6s^2$) was chosen. Because relevant data for orbital radii are lacking, therefore we used orbital radii in atoms [2] instead of those in ions. For the 112^{2+} cation, due to removing of inner $6d$ electron we assumed that $\langle r_{7s} \rangle$ is smaller by 15 pm than those in atom. Comparison of the outermost $\langle r_{ns} \rangle$ for Pb^{2+} and 112^{2+} gives the ionic radius of 112^{2+} for CN = 6–113 pm.

As shown in Table 1, the ionization potentials of 112^{2+} are higher than those for Hg and for Rn, also the ionic radius is greater than for Hg^{2+} . Both factors, the higher ionization potentials ($I_1 + I_2$) and the larger ionic radius indicate that 112^{2+} cation cannot exist in aqueous phase. Therefore, we can conclude that the reactivity of element 112 will be between the reactivity of xenon and radon, probably more similar to xenon and as noble gas reacting only with very electronegative elements and oxidizing compounds like, for example, dioxygenyl hexafluoroantimonate.

Table 1. Comparison of ionization potential and ionic radii of Hg, Xe, Rn and element 112.

	Hg	Xe	Rn	E112
Configuration of M^{2+}	$5d^{10}$	$5p^4$	$6p^4$	$6d^87s^2$
1st ionization potential, eV	10.2	12.1	10.8 (calc.)	12.0 (calc.)
2nd ionization potential, eV	18.8	21.0	18.0 (calc.)	22.5 (calc.)
1st + 2nd ionization potential, eV	29.0	33.1	28.8 (calc.)	34.5 (calc.)
Ionic radius, M^{2+} , pm (CN = 6)	102			113 (estim.)

Adsorption of ^{220}Rn on dioxygenyl hexafluoroantimonate thin film surface

Xenon and radon react spontaneously at room temperature with many solid compounds that contain strongly oxidizing cations such IF_6^+ , O_2^+ , N_2F^+ to form complex fluorides [1, 15]. Dioxygenyl hexafluoroantimonate oxidizes Rn and adsorbs the product in the reaction [1]:

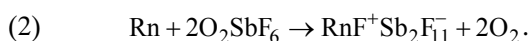


Figure 2 shows a gamma spectrum of the dioxygenyl hexafluoroantimonate thin film surface after exposition to ^{220}Rn . The peaks in the gamma spectrum belong to ^{212}Pb and ^{212}Bi , which are descended from the decay of ^{220}Rn . The reaction of Rn with the dioxygenyl hexafluoroantimonate surface is very rapid and sufficient. When the adsorbed gas mixture contains no water tracers, the film is stable for a long time.

Similarly to the studies of “Hg-like” behaviour of element 112, the possible studies with “Rn-like” behaviour could be performed in a similar equipment [16]. The PIPS detector surfaces should be coated with a thin film of dioxygenyl hexafluoroantimonate. The E112 adsorption experiment will be fulfilled by passing through the parallel coated detectors a gas jet containing the synthesized E112 atoms. The first detectors should be coated by gold films and the next by dioxygenyl hexafluoroantimonate. If element 112 is more similar to Hg it should adsorb on the first detectors, if it is more similar to Rn, it will be adsorbed on the detectors coated with dioxygenyl hexafluoroantimonate. Spontaneous fission of $^{283}\text{112}$ on the surface detectors should be easy to register by the PIPS detector.

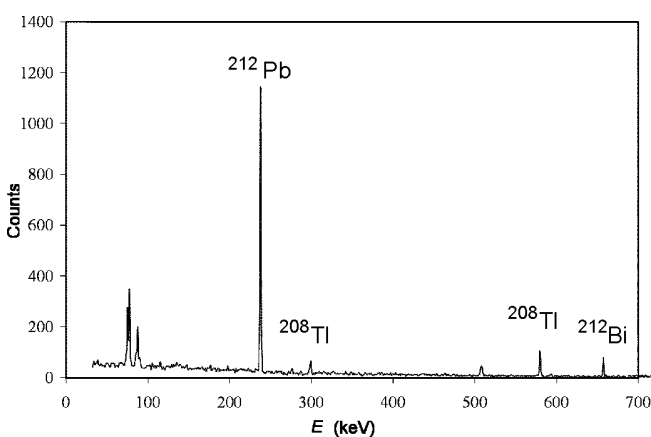


Fig. 2. The gamma spectrum of O_2SbF_6 surface after exposition to ^{220}Rn radioisotope.

The proposed studies should help us in explaining whether element 112 is similar to its lighter congeners in Group 12 as indicates the normal continuation of the Periodic Table, or to the noble gases as suggested by the theoretical predictions based on the relativistic calculation.

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