Enrichment of the Superheavy Element Rg in Natural Au

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Based on the observation of the long-lived isotopes 261Rg and 265Rg (Z = 111, t1/2 ≥ 108 y) in natural Au, an experiment was performed to enrich Rg in 99.999% Au. 16 mg of Au were heated in vacuum for two weeks at a temperature of 1127◦C (63◦C above the melting point of Au). The content of 197Au and 261Rg in the residue was studied with high resolution inductively coupled plasma-sector field mass spectrometry (ICP-SFMS). The residue of Au was 3x10−6 of its original quantity. The recovery of Rg was a few percent. The abundance of Rg compared to Au in the enriched solution was about 2x10−6, which is a three to four orders of magnitude enrichment. It is concluded that the evaporation rate of Rg from an Au matrix in vacuum at 63◦C above the Au melting point is lower than that of Au. This experiment reinforces our first observation of Rg in a terrestrial material. As before it is concluded that a long-lived isomeric state exists in 261Rg and that it probably belongs to a new class of isomeric states, namely high spin super- or hyperdeformed isomeric states.

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In recent years long-lived isomeric states have been reported in several isotopes found in natural material [1–2]. They, for instance, were seen in the neutron deficient 211Th, 213Th, 217Th and 218Th isotopes, with estimated half-lives of ≥ 1x108 y, which is 16 to 22 orders of magnitude longer than the known half-lives of their corresponding g.s. [1, 4]. They were also observed in the superheavy element region [2, 3]. Isotopes with atomic mass numbers 261 and 265 have been reported in natural Au [2] and interpreted as long-lived isomeric states in 261Rg and 265Rg, since Rg (Z = 111) is a chemical homolog of Au [3]. In the superactinides, a nucleus with atomic mass number 292 has been found in purified Th and interpreted as most probably a nucleus with atomic number 122, because element 122 is predicted to be eka-Th [3, 4]. Since all these nuclei were observed in natural materials it was deduced that the lower limit on their half-lives should be about 1x108 y, or otherwise they would have decayed away. The predicted half-lives for 261Rg, 265Rg and 292122 in their normally deformed g.s. are in the region of 10−6 to 10−8 s [5]. Therefore it was concluded that, like in the neutron-deficient Th isotopes, these nuclei are also in long-lived isomeric states. It was hypothesized that they may belong to a new class of high spin superdeformed (SD) or hyperdeformed (HD) isomeric states. Such isomeric states have been seen in 195Hg [6], in 210Fr [7, 10] and in heavy actinide nuclei like 236Am, 236Bk [11], 247Es and 252No [12]. Their character as high spin SD and HD isomeric states has been proven by observation of abnormal α-particle groups in coincidence with γ-rays of SD bands [8, 9].

In the experiments of [2, 3] it was assumed that the chemical procedures used by the purveyors of separated Au and Th were not so specific as to separate the heavy homologs Rg and eka-Th from Au and Th, respectively. The purpose of the present experiment was to try to concentrate Rg in Au. If the evaporation rate of Rg is lower than that of Au from a melt, it may be possible to enrich Rg in Au by keeping the Au in vacuum a little over its melting point. One may thus preferentially evaporate Au relative to Rg. (The melting point of Au is 1064◦C and that of Ag, its lighter homolog, is 961◦C. The corresponding boiling points, under normal pressure are 2866◦C and 2162◦C, respectively.)

As before [1, 3] accurate mass measurements, using ICP-SFMS, have been employed on mass 261 to identify 261Rg. The mass MA of an atom is equal to:

\[ M_A = ZM_H + NM_n - BE \]  

where Z and N are the number of protons and neutrons in the atomic nucleus, MNH and Mnn are the masses of the hydrogen atom and of the neutron, respectively, and BE is the binding energy of the atom. The binding energy per nucleon (BE/u) as a function of A for stable nuclei has a maximum at about A = 60 and then drops monotonically towards higher A [13]. Therefore, the mass of a heavy atom is higher than and separated from the mass of any molecule (except for multi-H, -Li, -Be and -B molecules) with the same mass number.

This is seen in Fig. 1, where the systematic behavior of the masses [14] of various M = 261 species, from the quasi-symmetric combination 133Cs128Te to Au-, Bi-, Th- and U-based molecules to the predicted [15] mass of the 261Rg nucleus is displayed. The mass of the very
FIG. 1: Representation of the systematic behavior of the masses of various $M = 261$ species, ranging from the quasi-symmetric combination $^{133}\text{Cs}^{128}\text{Te}$ to $\text{Au}$-$\text{Br}$-, $\text{Th}$- and $\text{U}$-based molecules [14], to the predicted [15–17] mass of $^{261}\text{Rg}$.

neutron-rich $^{261}\text{Au}$ nucleus is predicted to be 261.337 u [15] or 261.324 u [17], values well above the expected mass of the $^{261}\text{Rg}$ nucleus, which is 261.154 u [15–17]. (The calculations [15–17] of the $^{261}\text{Rg}$ mass agree to within 0.002 u.) Thus, as was demonstrated before [2, 3], accurate mass measurements are an effective tool for detecting naturally-occurring superheavy elements.

In the present experiment, an Au solution enriched in $\text{Rg}$ has been produced. Accurate mass measurements in the region of mass 261 were performed using ICP-SFMS with a resolution $m/\Delta m = 4000$. A peak that fits with the predicted mass of $^{261}\text{Rg}$ and does not fit with any known molecule has been observed. The recovery of $\text{Rg}$ was a few percent. An enrichment factor of three to four orders of magnitude has been obtained. It is deduced that under our experimental conditions the evaporation rate of $\text{Rg}$ is lower than that of $\text{Au}$.

16 mg of 99.999% $\text{Au}$ metal, supplied by Leico Industries, were held in a quartz tube in vacuum for two weeks at a temperature of 1127°C (63°C above the melting point of $\text{Au}$). The heating was stopped when the residue could no longer be seen with a magnifying glass. The minute residue was dissolved overnight in aqua regia at 60°C. After evaporating almost to dryness, 3 M HNO$_3$ was added and diluted to obtain a final volume of 20 ml at 0.7 M HNO$_3$. This solution was studied with the ICP-SFMS.

The accurate mass measurements were similar to those described before [1–3]. The ICP-SFMS was a Finnigan Element2 (Thermo-Electron, Bremen, Germany). In this instrument a solution of the material to be studied is introduced into a high temperature (6000 - 8000 K) plasma source. At these temperatures predominantly atomic species are present. Molecular ions are formed after the source, mainly by interaction with oxygen and hydrogen ions from the solution. The predefined resolution mode, $m/\Delta m = 4000$ (10% valley definition), was used throughout the experiments to separate atomic ions from molecules with the same mass number. The sensitivity-enhanced setup of the instrument was similar to that described in [18]. In the present experiment the sample uptake rate was 50 $\mu$l min$^{-1}$ and the sensitivity for $^{197}\text{Au}$ in this resolution mode was 2x10$^7$ counts s$^{-1}$mg$^{-1}$l$^{-1}$. Methane gas was added to the plasma to decrease the formation of molecular ions [19]. Oxide and hydride formation (monitored as UO$^+$/U$^+$ and UH$^+$/U$^+$ intensity ratios) were approximately 0.04 and 1x10$^{-5}$, respectively. Mass calibration was performed using the $^{115}\text{In}$, $^{232}\text{Th}$, $^{235}\text{U}$, $^{238}\text{U}$ and $^{238}\text{U}$O$^+$ peaks.

Complete elemental screening was performed on the enriched $\text{Rg}$ solution to assess the impurity levels. The amount of certain trace elements with relatively high concentrations, expressed as ppb (g/g) of the solution are as follows:

- $\text{Au}$ 4.1, $\text{Ca}$ 140, $\text{Cl}$ 15600, $\text{K}$ 250, $\text{Na}$ 360, $\text{P}$ 150, $\text{S}$ 780, $\text{Si}$ 40, $\text{Th}$ 0.001, $\text{U}$ 0.04.

These concentrations are correct to within a factor of two. After these impurity determinations, the solution was spiked to 1 ppb of $\text{U}$. These levels of contamination are higher than those specified in [2] where pure original $\text{Au}$ solution, without processing, was used. (The corre-
FIG. 4: Measurement of mass 254 obtained with the enriched Rg solution which was spiked to 1 ppb U (see text). Total measuring time: 70 s. Observed mass position: 254.084 u. It is shifted from the known mass of $^{238}\text{U}^{16}\text{O}$ of 254.046 u [14] (indicated by an arrow) by 0.038 u.

FIG. 5: Measurements of mass 261 obtained with the enriched Rg solution (a), and with the synthetic solution (b). Figure 5(c) presents the subtraction of spectrum (b) from spectrum (a). A peak of 37±13 counts is seen in Fig. 5(c) at the predicted position of $^{261}\text{Rg}$ [15–17]. The error estimate was calculated according to the formula $\sigma=\left(\frac{N_{total}+N_{back}}{2}\right)^{1/2}$ where $N_{total}$ is the total number of counts in the Rg region taken from Fig. 5(a) and $N_{back}$ is the number of background counts taken from Fig. 5(b).

sponding values there for Na and S were in the region of a few ppb.) A synthetic solution which contains the above-mentioned impurities with their measured concentrations, spiked to 1 ppb of U, was prepared and used for comparison in the experiments.

After a two-hour warm-up, the machine was still unstable. Therefore the measurements were started after nine hours of stabilization. A range of 0.45 u, divided into 70 channels, was scanned in each spectrum. The scanning was performed by changing the acceleration voltage while keeping the magnetic field constant. The mass 261 was analyzed with an integration time per channel of 1 s and run 90 times. The calibration was checked by measuring mass 254 ($^{238}\text{U}^{16}\text{O}$) before and after the long series of measurements on mass 261. A calibration correction of 0.037 u was deduced from these measurements (see below) and applied to the data.

Figure 2 shows the sum spectrum of ten measurements of mass 197 ($^{197}\text{Au}$) taken with a 1 ppb (g/g) Au solution. The FWHM of the peak is 0.038 u.

Figure 3 shows the sum of four measurements of mass 197, taken with a ten-fold diluted sample of the enriched Rg solution. The peak of $^{197}\text{Au}$ is shifted from its known value [14] by −0.022 u. By a comparison of Figs. 2 and 3 it is concluded that the Au concentration in the enriched Rg solution is 2.2 ppb (g/g). It is therefore deduced that the residue of Au in this 20 ml solution is 44 ng which is about 3×10$^{-15}$ of its initial value of 16 mg.

Figure 4 shows the results obtained on mass 254 measured with the enriched Rg solution which was spiked to 1 ppb U. It was taken before performing the measurements on mass 261. The peak of $^{238}\text{U}^{16}\text{O}$ is seen and it is shifted from the known value [14] by 0.038 u. A similar spectrum taken after the mass region 261 measurements were finished gave a shift of 0.036 u. An average correction of 0.037 u was applied to the data.

Figure 5 shows the sum of 90 spectra obtained on mass 261 with the enriched Rg solution (a) and with the synthetic solution (b). Figure 5(c) presents the subtraction of spectrum (b) from spectrum (a). A peak of 37±13 counts is seen in Fig. 5(c) at the predicted position of $^{261}\text{Rg}$ [15–17]. The error estimate was calculated according to the formula $\sigma=\left(\frac{N_{total}+N_{back}}{2}\right)^{1/2}$ where $N_{total}$ is the total number of counts in the Rg region taken from Fig. 5(a) and $N_{back}$ is the number of background counts taken from Fig. 5(b).

The 90 measured spectra are independent of one another. Each measurement used a different sample of the solution. At low statistics at an abundance level of about $10^{-15}$ of the solution (see below) it is possible that in some spectra the peak of $^{261}\text{Rg}$ will be more pronounced than in others.
Such behavior has been seen by us for instance in a study of the known molecule $^{232}$Th$^{40}$Ar$^{16}$O at 0.1 ppm of Th, where in one spectrum 12 counts were seen and in the spectrum measured immediately afterward, one count was observed. In the spectrum of Fig. 5(a) 130 counts are seen in the region of interest (ROI) of ±0.044 u around the predicted position of $^{261}$Rg. In the region out of interest (OROI) from 260.815 to 261.147 u (3.8 times larger than the ROI) there are 420 counts. If the group of events around the predicted position of $^{261}$Rg is due to background, then the ratio $N_{OROI}/N_{ROI} = 3.23$ should be the same, within statistics, in each individual spectrum. In 26 spectra events were seen at the predicted mass of $^{261}$Rg. In 11 spectra it was found that this ratio is statistically different from 3.23, between 0.2 and 1.4 with an average value of 0.6. These spectra are dominated by counts around the predicted position of $^{261}$Rg. The data are as follows: (Spectrum number; $N_{ROI}$; $N_{OROI}$; $N_{OROI}/N_{ROI}$; P): (1; 2; 1; 0.5; $1x10^{-2}$), (2; 1; 6$x10^{-4}$), (27; 2; 1; 0.5; $1x10^{-2}$), (57; 6; 4; 0.7; $2x10^{-5}$), (63; 6; 2; 0.3; $7x10^{-7}$), (69; 4; 3; 0.8; $9x10^{-4}$), (70; 7; 2; 0.3; $4x10^{-6}$), (79; 5; 7; 1.4; $5x10^{-3}$), (84; 4; 4; 1.0; $3x10^{-3}$), (89; 5; 1; 0.2; $2x10^{-6}$). P is the Poisson probability of observing $N_{OROI}$ events when $N_{ROI} \times 3.23$ are expected. As seen these probabilities are between $1x10^{-2}$ to $4x10^{-8}$ for each of these individual spectra. These results are displayed in Figs. 6 and 7.

In Fig. 6, six out of the 11 mentioned spectra are seen. In these as well as in most of the 11 spectra, more events are seen in the high mass region, around the predicted $^{261}$Rg position, than in the rest of the measured region.

In Fig. 7 the sum of the 11 spectra is shown. A pronounced peak of 48 counts is seen at mass 261.144±0.020 u (taking into account the calibration shift). The total number of events OROI is 28 as compared to 155 (48 x 3.33) deduced if the ratio of $N_{OROI}/N_{ROI} = 3.23$ of
Fig. 5(a) is respected. (The probability of seeing 28 counts when 155 are expected is extremely small.) The observed mass of this peak fits, within 0.010 u, with the predicted mass \[15–17\] of \(^{261}\)Rg of 161.154 u. It is larger than the mass of any molecule with \(M = 261\) (except for multi-H, -Li, -Be and -B molecules) as seen in Fig. 1. By a comparison with Fig. 3 the average intensity of this peak in the 90 spectra, compared to \(^{197}\)Au is about \(2 \times 10^{-6}\) \((4 \times 10^{-15}\) of the solution). It is about a factor of ten larger in the 11 spectra mentioned above, about \(4 \times 10^{-14}\) of the solution. Thus, an enrichment of three to four orders of magnitude, compared to the earlier determined abundance of \((1-10) \times 10^{-10} \[2\], has been achieved in this experiment. The recovery of Rg from the initial Au is estimated to be a few percent. The high enrichment factor shows that the evaporation rate of Rg in a matrix of Au is lower than that of Au.

In summary, the present results strengthen the first observation \[2\] of the superheavy element Rg (\(Z = 111\)) in nature. As was argued in \[2\], if its terrestrial concentration about \(4.5 \times 10^9\) y ago was similar to that of Au, then the half-life of the observed \(^{261}\)Rg nucleus is \(\geq 10^8\) y. Since the half-life of the normally deformed g.s. of \(^{261}\)Rg \[7\] is predicted to be about 1 \(\mu\)s, it was concluded \[2\] that the observed nucleus is in an isomeric state, probably unrelated to high-spin states near closed shells, fission isomers or K-isomers at normal deformations. It is therefore hypothesized \[2\] that it belongs to a new class of high spin isomeric states in the SD or HD minimum of the nuclear potential energy \[8–10, 12\]. This work also shows that it is possible to enrich Rg in purified Au by evaporating the Au in a vacuum at about 63\(^\circ\) C above its melting point.

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