

EXISTENCE OF LONG-LIVED ISOTOPES OF A SUPERHEAVY ELEMENT IN NATURAL Au*

A. MARINOV^{†,§§}, I. RODUSHKIN[‡], A. PAPE[§], Y. KASHIV[†], D. KOLB[¶],
R. BRANDT^{||}, R. V. GENTRY^{**}, H. W. MILLER^{††}, L. HALICZ^{‡‡} and I. SEGAL^{‡‡}

[†]*Racah Institute of Physics, The Hebrew University of Jerusalem, Jerusalem 91904, Israel*

[‡]*Analytica AB, Aurorum 10, S-977 75 Luleå, Sweden*

[§]*IPHC-UMR7178, IN2P3-CNRS/ULP, BP 28, F-67037 Strasbourg cedex 2, France*

[¶]*Department of Physics, University GH Kassel, 34109 Kassel, Germany*

^{||}*Kernchemie, Philipps University, 35041 Marburg, Germany*

^{**}*Earth Science Associates, P.O. Box 12067, Knoxville, TN 37912-0067, USA*

^{††}*P.O. Box 1092, Boulder, CO 80306-1092, USA*

^{‡‡}*Geological Survey of Israel, 30 Malkhei Israel St., Jerusalem 95501, Israel*

^{§§}*marinov@vms.huji.ac.il*

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Evidence for the existence of long-lived isotopes with atomic mass numbers 261 and 265, and abundance of $(1-10) \times 10^{-10}$ relative to Au, has been found in a study of natural Au using inductively coupled plasma-sector field mass spectrometry. The measured masses match the predictions for the masses of ^{261}Rg and ^{265}Rg ($Z = 111$), and those of some isobars of nearby elements. Based on chemical arguments, it is proposed that they are most probably isotopes of Rg. It is deduced that long-lived isomeric states exist in these isotopes. The hypothesis that they belong to a new class of long-lived high spin super- and hyperdeformed isomeric states is discussed.

Keywords: Atomic mass measurements; long-lived isomeric states; superheavy elements.

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Long-lived isomeric states of ^{211}Th , ^{213}Th , ^{217}Th , and ^{218}Th have been reported recently in natural Th, with abundances of $(1-10) \times 10^{-11}$ relative to ^{232}Th .¹ The estimated half-lives of the isomeric states, of $\geq 1 \times 10^8$ y are about 16–22 orders of magnitude longer than the known half-lives of their corresponding g.s.¹ (The half-life of the isomeric state in ^{180}Ta ($> 10^{15}$ y), the only one formerly known to occur naturally, is longer than the half-life of its g.s. by more than 18 orders of magnitude.²) Evidence for the existence of isomeric states in the Th nuclei was obtained by accurate mass measurements using a high resolution inductively coupled plasma-sector field mass spectrometer (ICP-SFMS). These results motivated us to search for a similar phenomenon in the region of superheavy elements. If, for instance,

*Dedicated to the late G. W. A. Newton, a colleague and a friend.

Rg ($Z = 111$) exists in nature, it might be found with Au, its closest chemical homologue.³ Unlike Th, where the g.s. masses of the neutron-deficient isotopes are known,⁴ in the case of the relevant superheavy elements, one has to rely on mass predictions. One finds, however, that the various predictions^{5–7} for the atomic masses of the Rg isotopes with mass numbers between 259 and 269 (the mass region studied here) differ by 0.003 u at most. This value is small compared to the experimental uncertainty in our measurements. Also, the average prediction^{5–7} for the mass of the g.s. of, for example, ²⁶¹Rg is 261.154 u and for the g.s. mass of ²⁶¹Au^{5,6} is 261.331 u, values well separated by the ICP-SFMS. Furthermore, the binding energy per nucleon (BE/u) of stable nuclei has a broad maximum near $A \simeq 60$ with a value $BE/u \simeq 8.7$ MeV/u which falls monotonically to about 7.6 MeV/u at Th and U.^{4,8} The predicted BE/u for Rg isotopes is about 7.2 MeV/u.^{5–7} Hence, masses of the Rg isotopes are higher than, and resolvable from, the masses of all molecules with the same mass number, except for multihydrogen-containing molecules. Accurate mass measurements could therefore be an effective tool in searching for naturally existing superheavy elements.

In principle, native Au is the most promising material to analyze when searching for Rg. However, background was the main obstacle when looking for isotopes with relative abundances of $(1 - 10) \times 10^{-11}$.¹ Therefore, pure natural Au was used in our measurements. It has been shown that the chemical properties of Sg (element 106), Bh (element 107), Hs (element 108), and element 112, are similar to those of their lighter chemical homologues W, Re, Os, and Hg.⁹ Thus, it is expected that the chemical properties of Rg will be similar to those of Au, and if exists in nature, all or most of it will follow Au in the chemical purification process.

In the present work, we have performed accurate mass measurements for masses 254 (for checking the calibration using the ²³⁸U¹⁶O peak) and 259–269. Evidence for the existence of isotopes with masses that fit the predictions for the masses of ²⁶¹Rg and ²⁶⁵Rg was obtained.

The experimental procedure was similar to that described earlier.¹ The ICP-SFMS was an Element2 (Finnigan, 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 produced after the source, mainly by interaction with oxygen and hydrogen ions from the solution. The predefined medium 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 Ref. 10. This setup provided sensitivity for ¹⁹⁷Au in this resolution mode of up to 7×10^7 counts $s^{-1}mg^{-1}l^{-1}$. The sample uptake rate was 60–80 $\mu l \text{ min}^{-1}$. Methane gas was added to the plasma to decrease the formation of molecular ions.¹¹ Oxide and hydride formation (monitored as UO^+/U^+ and UH^+/U^+ intensity ratios) were approximately 0.04 and 1×10^{-5} , respectively. Mass calibration was performed using

the $^{115}\text{In}^+$, $^{232}\text{Th}^+$, $^{235}\text{U}^+$, $^{238}\text{U}^+$, and $^{238}\text{U}^{16}\text{O}^+$ peaks. The ^{115}In peak was used for on-line mass drift correction. Two stock solutions, “A” and “B”, of 1000 mg Au in 1 l of 10% HCl, were obtained from two manufacturers (Customer Grade and Spex, LGC Promochem AB, Borås, Sweden). Complete elemental screening was performed on both solutions. The following concentrations (expressed as ppm of the Au concentration) of certain trace elements that could potentially give rise to spectrally interfering molecular species are given below:

A: U 0.01, Th 0.3, Bi 67, Pb 11, Tl 0.1, Hg 0.3, Pt 104, Os 16, Re 0.2, W 0.3, Gd 0.005, Ba 0.9, Cs 0.05, I 10, Te 0.07, Ag 0.4, Zn 3, Fe 7, Cr 0.1, S 69, Si 51, Al 19, Na 33.

B: U 0.01, Th 0.3, Bi 104, Pb 18, Tl 0.3, Hg 1, Pt 124, Os 25, Re 0.2, W 0.3, Gd 0.005, Ba 0.9, Cs 0.06, I 5, Te 0.1, Ag 0.6, Zn 6, Fe 20, Cr 0.6, S 182, Si 237, Al 36, Na 149.

The solutions were analyzed on September 13, 2006. A range of about 0.4 u, divided into 65 channels, was scanned in each measured spectrum. The masses 254 and 259–269 were analyzed with an integration time per channel of 3 s. Both solutions A and B were diluted to 20 mg Au l⁻¹ of 0.7 M HNO₃, and each was measured twice. Altogether, four spectra were taken with the Au solutions for each mass number studied. Replicate analyses of blank solution (0.7 M HNO₃) were performed. Instrumental sensitivity varied among runs as a result of matrix effects caused by the introduction of highly concentrated solutions into the ICP source.

Figure 1 shows the sum spectrum of the four measurements of mass 254, where the peak of $^{238}\text{U}^{16}\text{O}^+$ is seen. The FWHM of the peak is about 0.030 u. The spectrum shows a shift of 0.021 u in the peak position. A similar shift, of 0.015 u, was observed at mass 265 for the $^{232}\text{Th}^{16}\text{O}_2^+\text{H}^+$ peak (Fig. 3(b)). Based on these shifts, a correction of -0.018 u was applied throughout the measurements. However, shifts of up to about 0.025 u were seen in some of the measurements.

Below are the results for masses 261 and 265. For each mass number, three spectra are presented. The first is the “best” of the four measured spectra. The

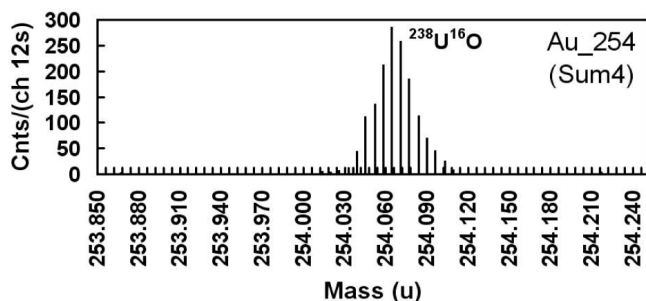


Fig. 1. Measurements of mass 254 obtained with the Au solutions. The sum of four measurements, two with solution A and two with solution B, is displayed. Total measuring time: 780 s. Observed mass position: 254.067 u. Known mass of $^{238}\text{U}^{16}\text{O}$ molecule: 254.046 u.⁴

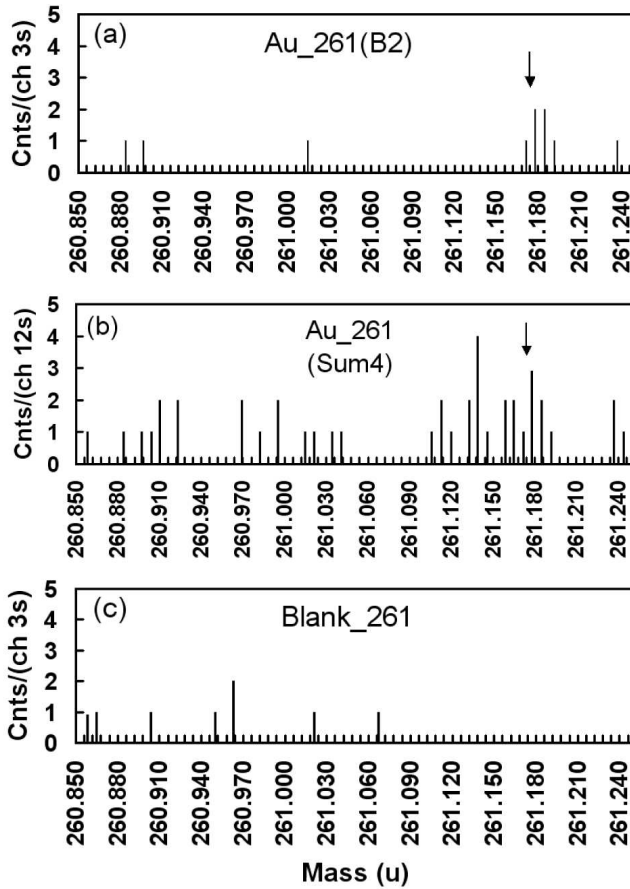


Fig. 2. Measurements of mass 261. Figure 2(a) shows the results obtained in the second measurement with solution B. The sum of four spectra, two with solution A and two with solution B, is displayed in Fig. 2(b). The spectrum of a blank solution is given in Fig. 2(c). Total measuring times: Fig. 2(a) 195 s; Fig. 2(b) 780 s; Fig. 2(c) 195 s. The arrows indicate the position of the predicted ^{261}Rg mass, shifted by the calibration correction of 0.018 u (see text).

second is the sum of the four individual spectra, and the third shows a spectrum of the blank.

Figure 2 displays the results for mass 261. The arrows in Figs. 2(a) and (b) indicate the position of the predicted ^{261}Rg mass, corrected for the shift discussed above. This mass is the average of the predictions given in Refs. 5–7. A pronounced group of six events is seen in Fig. 2(a) at the position of the ^{261}Rg mass prediction. In Fig. 2(b) a group of 22 events is seen at a mass that fits the predicted mass of ^{261}Rg . Although this group is somewhat broad, we assume that it is a single group since it is not broader than the $^{232}\text{Th}^{16}\text{O}_2^1\text{H}$ group seen in Fig. 3(b). (The width of the latter is typical for a single group, since the masses of the Th and U molecules are very close to one another, and all the other possible molecules have lower masses

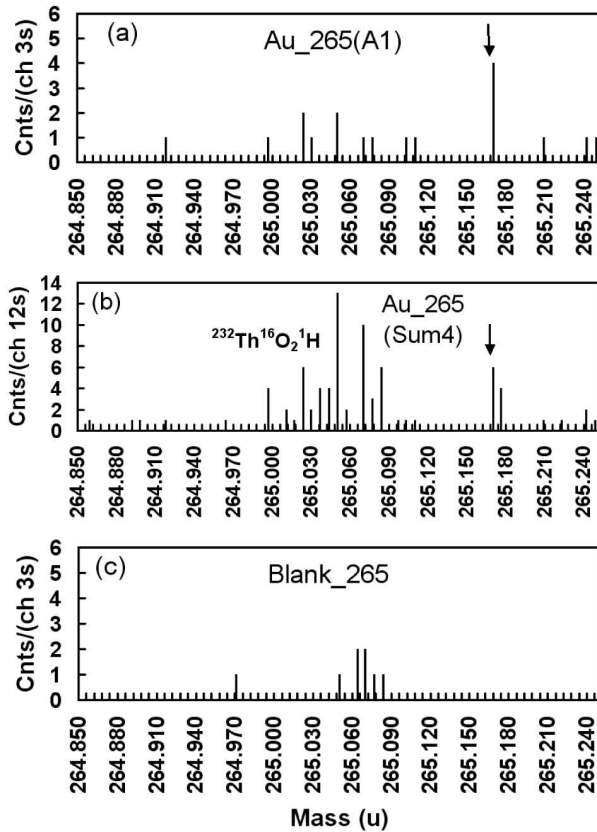


Fig. 3. Measurements of mass 265. Figure 3(a) shows the results of the first measurement with solution A. The sum of four spectra, two with solution A and two with solution B, is displayed in Fig. 3(b). A blank solution spectrum given in Fig. 2(c). Total measuring times: Fig. 3(a) 195 s; Fig. 3(b) 780 s; Fig. 3(c) 195 s. The arrows indicate the position of the predicted ^{265}Rg mass, shifted by a calibration correction of 0.018 u (see text).

(see Table 2.) However, if the four events at the low mass end of this peak are due to background, then 18 events are still seen in this group. (The several events in Fig. 2(b) in the 260.850–261.050 u region could be due to $^{197}\text{Au}^{64}\text{Zn}$ (260.896 u), $^{197}\text{Au}^{16}\text{O}_4$ (260.946 u), $^{232}\text{Th}^{14}\text{N}_2^1\text{H}$ (261.052 u) or background.)

The results obtained for mass 265 are given in Fig. 3. A group of four events is seen in Fig. 3(a) at the predicted mass of ^{265}Rg . The sum of four individual measurements is presented in Fig. 3(b). In addition to the $^{232}\text{Th}^{16}\text{O}_2^1\text{H}$ peak, a group of 10 events, consisting of 4, 3, 2, and 1 counts observed in the four spectra, is seen at the predicted mass of ^{265}Rg . (This peak looks narrow. However, by comparison with Fig. 1, it is estimated that in one channel there should be 1.9 events and in the second channel 1.7 events. The observed 6 and 4 events are not inconsistent with statistical errors.)

Table 1. Summary of results of mass measurements and comparison with the predicted masses of ^{261}Rg and ^{265}Rg .

Mass no.	Fig. no.	No. of events	$P_{\text{acc.}}$	$M_{\text{c.m.}}^{\text{exp.a}}$	Mass of Rg isotope ^b
261	2(a)	6	8×10^{-7}		
261	2(b)	22(18)	$3 \times 10^{-6\text{c}}$	261.134 ^d	261.154
265	3(a)	4	2×10^{-6}		
265	3(b)	10	3×10^{-9}	265.154	265.151

^aThe uncertainty in mass is estimated to be ± 0.025 u.

^bAverage of predicted values, Refs. 5–7.

^cBecause of the different widths of the lines, the same value is obtained for 22 and 18 events lines.

^dFor 18 counts $M_{\text{c.m.}}^{\text{exp.}} = 261.142$ u.

The statistical significance of the newly observed peaks, that match the predicted masses of the two Rg isotopes, was calculated as described in Ref. 1: The probability $P'_{\text{acc.}}$ that n out of a total number of N randomly distributed counts will occur accidentally in a small mass region r out of a total mass region R is given by¹²

$$P'_{\text{acc.}} = \binom{N}{n} (r/R)^n (1 - (r/R))^{(N-n)}. \quad (1)$$

The total probability that such a group will occur accidentally in a predefined region r out of a total region R is given by

$$P_{\text{acc.}} = P'_{\text{acc.}}(r/R). \quad (2)$$

In calculating the values of $P_{\text{acc.}}$ for the data given in Figs. 2(a) and (b) the value of R was chosen as the whole measured region. For the results displayed in Figs. 3(a) and (b), the region of the molecular ion $^{232}\text{Th}^{16}\text{O}_2^1\text{H}$ was removed from the total region. When the widths of the peaks are narrower than the experimental FWHM of 0.030 u (Figs. 2(a), 3(a) and (b)), the value of r in formula (2) was taken as 0.030 u.

The results are summarized in Table 1. Column 3 gives the number of events with measured masses in accord with the predicted masses of the corresponding Rg isotopes. $P_{\text{acc.}}$ values are given in column 4. Column 5 gives the measured masses of the events in Figs. 2(b) and 3(b), corrected for the 0.018 u shift in mass calibration. Column 6 gives the average predicted g.s. masses^{5–7} of the Rg isotopes with the same mass number.

We were unable to match the signals of the suspected Rg isotopes with any molecular ions. Because of binding energy, masses of the molecules are lower than the masses of the observed peaks. The systematic trend is seen in Table 2 from quasi-symmetrical combinations ($^{133}\text{Cs}^{128}\text{Te}$, $^{138}\text{Ba}^{127}\text{I}$) to U-based molecules. (The same is true for doubly charged ions. For instance m/e of $^{197}\text{Au}_2^{128}\text{Te}^{++}$ ($m = 522$) ion is 260.919 u, as compared to the measured value 261.134 u of the new peak.) On

Table 2. Known masses of several molecules with mass numbers 261 and 265,⁴ and the predicted masses of ²⁶¹Rg, ²⁶⁵Rg,⁵⁻⁷ ²⁶¹Au,^{5,6} and ²⁶⁵Au.⁶

261		265	
Molecular ion	Mass	Molecular ion	Mass
¹³³ Cs ¹²⁸ Te	260.810	¹³⁸ Ba ¹²⁷ I	264.810
¹⁹⁷ Au ⁶⁴ Zn	260.896	¹⁹⁷ Au ⁶⁸ Zn	264.891
²⁰⁹ Bi ⁵² Cr	260.921	²⁰⁹ Bi ⁵⁶ Fe	264.915
²³² Th ¹⁴ N ₂ ¹ H	261.052	²³² Th ¹⁶ O ₂ ¹ H	265.036
²³⁸ U ²³ Na	261.041	²³⁸ U ²⁷ Al	265.032
²⁶¹ Rg	261.154	²⁶⁵ Rg	265.151
²⁶¹ Au	261.331	²⁶⁵ Au	265.360

the other hand, the predicted masses of the extremely neutron-rich nuclei ²⁶¹Au and ²⁶⁵Au are higher than the observed peaks.

Another possibility that has to be considered is the potential presence of hydrocarbon-based molecular ions from pump oil. However, there are no hydrocarbon candidates for masses 261 and 265, and typical hydrocarbon masses lie well above the predicted masses of the Rg isotopes with the same mass number. For instance, the masses of CH₃(CH₂)₁₆CH₃ and CH₃(CH₂)₁₇CH₃ are 254.297 u and 268.313 u,⁴ respectively, whereas the predicted masses of the respective Rg isotopes are 254.164 u⁶ and 268.152 u.⁵⁻⁷ On the other hand, it is evident from the data in Table 1 that the masses of the measured new peaks fit predictions for the g.s. masses⁵⁻⁷ of the corresponding Rg isotopes to within 0.020 u.

Based on mass measurements alone, one cannot conclude whether the newly observed peaks are due to Rg isotopes or to isotopes of nearby superheavy elements. Since the peaks appeared in pure Au solutions, where the concentration of the homologues of the other superheavy elements from W to Pb range from about 100 to 0.1 ppm of Au (see above), it is reasonable to assume that they are due to Rg. It is estimated that the concentration of these proposed Rg isotopes is $(1-10) \times 10^{-10}$ of ¹⁹⁷Au (about $(2-20) \times 10^{-15}$ of the solutions).

The predicted g.s. half-lives of these Rg isotopes are of the order of 1 μ s.¹³ This suggests that the observed events are due to long-lived Rg isomers. (The accuracy of the present experiment is not sufficient to determine the excitation energies of the isomeric states relative to the predicted normal g.s. masses.) If their initial terrestrial concentration was similar to that of ¹⁹⁷Au, then the lower limit on their half-lives would be about 1×10^8 y.

The character of the observed isomers has not been measured directly. They cannot represent high spin isomers that occur near doubly closed shells, since they are far from the nearest predicted^{14,15} spherical doubly closed shells at $Z = 114$ and $N = 184$. Nor can they be related to the actinide fission isomers, since their

lifetimes are in the ns to ms region. As mentioned in Ref. 1, it is also not reasonable to assume that they are normal high spin K-type isomers, since the lifetimes of all the known K-isomeric states in neutron-deficient nuclei with $Z \geq 84$ are not longer than several minutes. One can hypothesize that, as in the case of the Th isomers, the proposed states are aligned high spin superdeformed (SD) and/or hyperdeformed (HD) states,^{16–19} where the high spin, the barriers between the various minima of the potential energy surfaces and the unusual radioactive decay properties contribute to their long lifetimes. A direct indication for the naturally occurring existence of such isomeric states is the low energy and enhanced α -particle group of 4.5 MeV mentioned in three reports^{20–22} and attributed to the decay of Hs. It has been interpreted consistently as an HD to HD α transition.^{23,24}

High spin states in general and such states in the SD and HD minima in particular are preferentially produced by heavy ion reactions.^{19,23} If the observed states turn out to be of the high spin SD and/or HD type, then heavy ion reactions could be involved in their nucleosynthesis.

In summary, evidence for the existence of long-lived superheavy isotopes with $t_{1/2} \geq 1 \times 10^8$ y and atomic mass numbers of 261 and 265 has been found in natural Au. It is proposed that they are isomeric states, most probably in ²⁶¹Rg and ²⁶⁵Rg. The hypothesis that they are high spin SD and HD isomeric states is discussed.

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