Chemical investigation of element 114: indication for a massive relativistic effect in chemistry

R.Dressler[1] for a PSI-University of Bern-FLNR-LLNL collaboration*

[1] Laboratory for Radiochemistry and Environmental Chemistry,
Paul Scherrer Institute, CH-5232 Villigen, Switzerland.

The systematic order of the periodic table places element 114 into group 14 together with carbon, silicon, germanium, tin, and lead. The enhancing metallic character with increasing atomic number Z is a typical trend observed along the main groups 13-17 of the periodic table [1]. However, relativistic calculations of the electronic structure of super heavy elements suggest an increased chemical stability of the elemental atomic state for element 114, having an electronic ground state configuration of Rn: $5f^{14}\ 6d^{10}\ 7s^2\ 7p_{1/2}^2$ [2-7]. Therefore, a high volatility and a rather chemical inertness were postulated as a result of the contraction of the outermost s- and p-electron orbital. Modern relativistic calculation models predict atomic properties for element 114, representing a higher chemical inertness but still similarity to the lighter group 14 metal lead [8-10]. Recently, element 112 adsorption on gold was investigated using thermochromatography [11,12]. During these experiments in the irradiation of ^{242}Pu with ^{48}Ca (details see [12]) a decay chain was observed, which is unambiguously attributed to the primary product of the nuclear reaction – the isotope ^{287}114 ($T_{1/2}$=0.5 s). Even more exciting was the observation of this decay chain on detector 19 held at a temperature of -88°C. The lighter group 14 homologues C, Si, Ge, Sn, and Pb are not at all transported at these experimental conditions in their elemental state to the detector. This spectacular first chemical observation of element 114 was confirmed switching to the projectile target combination ^{48}Ca and ^{244}Pu. The production of ^{288}114 ($T_{1/2}$=0.8 s) and ^{289}114 ($T_{1/2}$=2.4 s) are reported in the nuclear reactions ^{244}Pu(^{48}Ca, 4n) and ^{244}Pu(^{48}Ca, 3n), respectively [13]. Indeed, two more decay chains unambiguously attributed to the isotope ^{288}114 were observed, fully confirming the first observation. A kinetic Monte-Carlo based model of gas adsorption chromatography [14] assesses the adsorption enthalpy ($-\Delta H_{ads}^{Au}$) from the observed deposition pattern of element 114 on the gold surface in the Cryo On-Line Detector. This approach reveals an adsorption enthalpy as $-\Delta H_{ads}^{Au}(E114)=35^{+19}_{-3}$ kJ/mol (68% c.i.). Recent relativistic density functional calculations predict a higher reactivity for element 114 compared to element 112 and the formation of a metallic bond between element 114 and gold [10]. A rather rough estimation yields an interval for $-\Delta H_{ads}^{Au}(E114)$ between 100-150 kJ/mol corresponding to a deposition temperature of element 114 on gold of about 150-300°C at the current experimental conditions. A semi-empirical macroscopic metal-metal adsorption model [15,16] predicts an even higher adsorption enthalpy of a metal-like element 114 on gold of $-\Delta H_{ads}^{Au}(E114)$=183 kJ/mol. The adsorption enthalpy of a noble-gas like element 114 on gold surfaces was estimated to $-\Delta H_{ads}^{Au}(E112)=42\pm5$ kJ/mol [17]. The comparison between these theoretical values and our experimental result concludes the formation of a noble-gas like weak physisorption bond between atomic 114 and a gold surface in contrast to the expectations from the relativistic models and from empirical predictions. Element 114 reveals a substantially increased stability of the elemental state compared to its homologues in group 14, which might be explained only with a closed shell electronic structure, as predicted in [2-7] revealing for the first time indication for massive relativistic effects acting on the outermost s- and p-electrons.

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* PSI-University of Bern-FLNR-LLNL collaboration: R. Eichler[1,2], F.Sh. Abdullin[3], N.V. Aksenov[3], A.V. Belozerov[3], G.A. Bozhikov[3], V.I. Chepigin[3], R. Dressler[1], S.N. Dmitriev[3], H.W. Gäggeler[1,2], V.A. Gorshkov[3], R.A. Henderson[4], M.G. Itkis[3], A.M. Johnsen[4], J.M. Kenneally[4], V.Ya. Lebedev[3], Yu.V. Lobanov[3], O.N. Malyshev[3], K.J. Moody[4], Yu.Ts. Oganessian[3], O.V. Petrushkin[3], D. Piguet[1], A.N. Polyakov[3], A.G. Popeko[3], P. Rasmussen[1], R.N. Sagaidak[3], A. Serov[1,2], D.A. Shaughnessy[4], I.V. Shirokovsky[3], S.V. Shishkin[3], A.V. Shutov[3], M.A. Stoyer[4], N.J. Stoyer[4], A.I. Svirikhin[3], E.E. Tereshatov[3], Yu.S. Tsyganov[3], G.K. Vostokin[3], V.K. Utyonkov[3], M. Wegrzecki[5], P.A. Wilk[4], A.V. Yeremin[3]

[2]Departement für Chemie und Biochemie, Universität Bern, CH-3012 Bern, Switzerland.

[3]Flerov Laboratory of Nuclear Reactions, Joint Institute for Nuclear Research, 141980 Dubna, Russia.

[4]Lawrence Livermore National Laboratory, University of California, 94551 Livermore, USA.

[5]Insitute of Electron Technology, 02-668 Warsaw, Poland.