Heinz W. Gäggeler, Ilya Usoltsev and Robert Eichler*

Reactions of fission products from a ^{252}Cf source with NO and mixtures of NO and CO in an inert gas

<https://doi.org/10.1515/ract-2018-3076>

Received November 2, 2018; accepted December 19, 2018; published online January 17, 2019

Abstract: Fission products recoiling from a ^{252}Cf spontaneous fission source were stopped in various mixtures of inert gases containing CO and NO. For the elements of the transition metal series Mo, Tc, Ru, and Rh previous observations of pure carbonyl complexes were reproduced. However, no formation of volatile mixed nitrosyl-carbonyl complexes or pure nitrosyl complexes for these elements have been observed. Instead, efficient production of volatile nitrosyl compounds for single iodine atoms, presumably nitrosyl iodide, NOI, was detected. This observation is of interest as potential transport path for iodine in nuclear accident scenarios and as a model for radiochemistry with the recently discovered heaviest halogen tennessine ($Z = 117$).

Keywords: Nitrosyl, carbonyl, nitrosyl iodide, fission products, tennessine.

Dedicated to: The memory of Professor Günter Herrmann.

1 Introduction

Chemical studies of transactinide elements require access to fast and *in-situ* separations of volatile molecules formed in gas phase reactions. Given the short half-life for isotopes of currently investigated elements, reaching the below one second regime, the kinetics for formation of suitable compounds has to be fast. This is a prerequisite to study their equilibrium behavior for the determination of thermochemical data. So far, for light transactinides with Z between 104 (rutherfordium) and

108 (hassium) (oxy)halides or oxides have been synthesized at their highest oxidation states (for a current detailed review see [1]). For elements currently under study, $Z = 112$ (Cn), $Z = 113$ (Nh), and $Z = 114$ (Fl) the elemental state was chosen, since these elements appear volatile (for review see [2]). One recent breakthrough was the application of carbon monoxide (CO) as reactive gas in on-line gas-jet experiments [3]. With this technique, products recoiling from heavy-ion-induced nuclear fusion reactions or nuclear fission are stopped in a gas cell containing gas mixtures of CO with inert gases He, Ar, or N_2 or just pure CO. The gas phase complexes are then *in-situ* formed and subsequently transported through thin capillaries to detection setups. It could be shown that d-elements form carbonyl complexes that are gaseous under ambient conditions. Such compounds, e.g. group 6 hexacarbonyls $\text{M}(\text{CO})_6$, are molecules featuring the central atom in its zero-oxidation state that is surrounded by six CO molecules. This means that all metal valence electrons are present. Additionally, the d-orbitals of the transition metal are involved in the formation of the molecular orbitals. These, are subject to secondary relativistic expansion, and are occupied by the electron donation from CO ligands (18-electron rule or EAN-rule). This opens up fascinating perspectives in heaviest element chemistry research, because relativistic effects may be even more pronounced for compounds formed with a central atom in its zero-oxidation state compared to its highest oxidation state in previously investigated compounds [1, 2]. The influence of relativistic effects on chemical properties of heaviest elements is a fascinating topic of current theoretical chemistry as well, for review see [1, 4]. Meanwhile carbonyl complexes have been studied for several 4d and 5d elements [3, 5–9] and even one 6d transactinide element Sg [10]. The thermal stability of some of those carbonyl complexes are under investigation [11, 12] in order to address the binding strength of the M-CO bonds, which is expected to be directly affected by relativistic effects [13–15].

In this study we investigated, whether NO gas can replace CO gas in such *in situ* reactions to form similar volatile complexes, the so-called nitrosyl complex compounds or mixed nitrosyl carbonyl complex compounds.

*Corresponding author: Robert Eichler, Paul Scherrer Institute, 5232 Villigen, Switzerland; and Department for Chemistry and Biochemistry, University of Bern, 3012 Bern, Switzerland, E-mail: robert.eichler@psi.ch

Heinz W. Gäggeler: Paul Scherrer Institute, 5232 Villigen, Switzerland

Ilya Usoltsev: Paul Scherrer Institute, 5232 Villigen, Switzerland; and Department for Chemistry and Biochemistry, University of Bern, 3012 Bern, Switzerland

2 Macrochemical information on nitrosyl complexes and nitrosyl compounds

Nitrogen oxide is an important pollutant in the atmosphere and has large physiological impact [16]. Emission sources are mostly related to car exhaust, predominantly from diesel engines, where NO forms at the high combustion temperatures. A natural source of NO in the atmosphere is also lightning. The nitrogen oxide radical with an unpaired electron is much more reactive compared to carbon monoxide. Therefore, NO is oxidizing, whereas CO has typically reducing character. Depending on the reaction partner NO can exist in three different chemical forms cationic NO^+ , neutral NO, and anionic NO^- ; the latter not only in gas phase but also in solution [17]. If exposed to oxygen, NO is converted into nitrogen dioxide according to equation (1).

Furthermore, NO reacts with oxygen and water to form HNO_2 , nitrous acid following the reaction scheme shown in equation (2).

NO forms different types of bonding with other atoms: a) sharing of an electron pair, b) donation of an electron, and c) acceptance of an electron. Only the first option a) is similar to that of CO because it leaves a reaction partner in an unchanged redox state. However, due to the unpaired electron of NO the reaction type a) is rather scarce. Mostly the second type dominates, i.e. NO acts as an electron donor forming the positively charged nitrosyl ion NO^+ that is isoelectronic to CO (see equation 3).

However, it can react also as oxidizer of metals forming oxides and N_2 according to equation (4).

Because of this reactivity pure nitrosyl complexes with metals are very rare. One example is $\text{Ni}(\text{NO})_4$, which obeys the EAN rule (18 electrons). However, quite extensive knowledge exists on mixed nitrosyl-carbonyl metal complexes. Such compounds are typically not volatile at ambient conditions. Examples are mixed nitrosyl-carbonyl complexes with the group 7 metals Tc and Re [18]. For Mn mixed CO-NO complexes have been observed by

matrix isolation methods [19]. Also widely known are organometallic compounds with NO featuring various mostly π -binding organic ligands, both with and without CO [20]. For extensive reviews on nitrosyl complex chemistry we refer to [18, 20] and references therein.

Apart from complex compounds, also known are volatile nitrosyl halides. Nitrosyl fluoride is a colorless strongly fluorinating gas with a melting point of -132.5°C and a boiling point of -59.9°C [21]. Nitrosyl chloride is a very reactive yellowish red gas with the formula NOCl . It has a melting point of -59.6°C and a boiling point of -6.4°C [22]. Its occurrence in aqua regia and its preparation from NO and Cl_2 is known since long times, see e.g. [23]. Nitrosyl bromide is a red liquid melting at -55.5°C and having a boiling point of $\approx 0^\circ\text{C}$ [21], and thus, appears less volatile. NOBr might play a role in the ozone cycle over the arctic [24] as well as nitrosyl iodide, NOI , which is believed to be relevant to the tropospheric ozone cycle [25–27]. No other physical or chemical properties are known for NOI . Mutual correlations of thermodynamic state functions [28] are used here to expose the trends in group 17 of the periodic table for the thermodynamic stability (Figure 1), i.e. the enthalpy of formation of nitrosyl halides from the elements ($\Delta_f H^\circ$) and the reaction enthalpies for the direct reactions of NO with halogen atoms ($\Delta_r H^\circ$), relevant for the *in situ* reaction, as expected for the halogen atoms as recoiling fission products thermalized in a NO containing

Figure 1: The standard formation enthalpy of nitrosyl halides $\Delta_f H^\circ(\text{NOX})$ from the corresponding elemental halogen, nitrogen and oxygen (thermodynamic stability) [29] plotted against the standard formation enthalpy $\Delta_f H^\circ(\text{X atom})$ of single atomic elements (red) and their electron affinity E_a (blue).

The dotted lines show the extrapolated expectations for the stability of nitrosyl halides of At and Ts using predicted stability data for the gaseous elements and electron affinities from [30–32]. Note the expected stability decrease along the elements of group 17.

gas phase (Figure 2, and eq. 2). The stability of nitrosyl halides decreases with increasing atomic number of the halogen atom (data from [29–32]). The reaction between halogens and nitrous oxide (see eq. 5) under inert gas condition is known to be exothermic:

The trends along group 17 elements indicate an increasingly endothermic reaction. Note the escape of the fluorine from the periodic trend.

3 Experimental

An approximately 700 kBq ^{252}Cf target available at Bern University was used as source for fission products [33]. Fragments recoiling from the spontaneous fission were thermalized in a recoil chamber flushed with a carrier gas (He). The advantage of a ^{252}Cf SF-source if compared to a ^{235}U neutron-induced fission source (e.g. available at the SINQ gas-jet facility at Paul Scherrer Institute) is the shift of the light mass peak towards heavier elements. This gives access to higher yields of d-elements like Mo, Tc, Ru, and Rh (see Figure 3). On the other hand, from the halogens only iodine is formed with reasonable fission yield, while, e.g. Br is much depleted.

Figure 2: The standard reaction enthalpy $\Delta_r H^\circ(\text{NOX})$ of the formation reaction of the nitrosyl halide from the corresponding gaseous halogen atoms and NO (equation 5) [29] plotted against the standard formation enthalpy $\Delta_f H^\circ(\text{X atom})$ of single atomic elements (red) and their electron affinity E_a (blue). The dotted lines show the extrapolated expectations for the reaction enthalpy for the heavier halogens At and Ts using predicted stability data for the gaseous elements and electron affinities [30–32]. Note, for At the reaction is still exothermic.

Prior to entering the recoil chamber, reactive gases such as CO and/or NO could be added to the inert carrier gas He at variable flow rates. At the exit of the recoil chamber a Perfluoroalkoxy-(PFA®)-Teflon capillary with an inner diameter of 2 mm diameter and a length of 2 m was used to guide the volatile products to a charcoal trap mounted in front of a HPGe γ -detector. The set-up enabled therefore continuous detection of volatile fission products with half-lives on the order of seconds and higher. The sampling and counting time chosen for each experiment was 30 min.

4 Results

In order to confirm previous observations with a similar source [6], the first experiment was conducted with 0.5 L/min He purity 99.999 % (He 5.0, Carbogas) and 0.5 L/min CO purity 99.997 % (CO 4.7, Carbogas). Figure 4 shows the γ -spectrum observed during 30 min collection time. As expected, the main lines can be assigned to isotopes of molybdenum, technetium ruthenium and rhodium. Some minor lines are from isotopes Xe (with its decay products Cs and Ba). If the reactive gas is changed from CO to 99.5 % pure NO (NO 2.5, Air Liquide), the spectrum depicted in Figure 5 was observed. No γ -lines from d-elements are identified anymore. Instead, all γ -lines can be assigned to iodine. The ^{137}Cs -line at 662 keV in Figure 4 is due to accumulated ^{137}Cs on the pre-used charcoal trap.

In the following, gas composition parameters were varied. The results are summarized in Table 1. To our surprise, even with only 10 vol-% or 5 vol-% NO added to the carrier gas the yield of iodine transport remained quite high at 62 ± 17 and 71 ± 5 %, respectively. Adding to the NO/He gas mixture also CO did not influence the yield of iodine. On the contrary, no traces of d-elements could be identified with NO added to the transport gas, even at rather low concentration and irrespective of the amount of CO gas admixture. Note the disappearance of the distinct main lines of I isotopes in the experiments without NO (Figure 4).

5 Discussion

Our measurements clearly show that NO gas cannot be used for separation and transport of volatile d-element complexes. The oxidative character of NO obviously leads to an immediate oxidation of atomic d-elements, which are known to form stable higher oxidation states. In NO/CO gas mixtures no formation of volatile compounds with d-elements have been observed. This observation is in line with knowledge from macrochemistry.

Table 1: Relative yields for ^{136}I , ^{137}I , and ^{138}I observed during 30 min accumulation.

Gas mixtures, vol-%	Relative yield ^a $^{136-138}\text{I}$, %	^{104}Mo
50%NO/50%He	100	n.d.
10%NO/90%He	62 ± 17	n.d.
47.5%NO/5%CO/47.5%He	105 ± 23	n.d.
5%NO/5%CO/90%He	71 ± 5	n.d.
50%CO/50%He	n.d.	Transport observed

^aYields are normalized to the experiment with the 1:1 He:NO mixture. n.d. means “not detected”.

assume that bromine would behave similarly to iodine, given the fact that nitrosyl complexes of bromine are more stable than those of iodine (see Figures 1 and 2).

It would be interesting to study the behaviour of At with NO in future experiments. Astatine is the first halogen predicted to be metallic [30]. From the general trend of decreasing stability of nitrosyl compounds with increasing atomic number from Cl to I the compound AtNO is less likely to be formed (see Figures 1 and 2). The same assumption holds true for its superheavy homologue tennesine, (Ts, $Z=117$). However, the reaction of NO with single atomic At in the gas phase seems slightly exothermic. The expected reaction entropy loss might be prohibitive, for a negative Gibbs energy for this reaction, though. The formation of the superheavy TsNO seems quite questionable, making an investigation of Ts along this path a ride for relativistic surprises. Therefore, also predictions from relativistic *ab initio* density functional theory are required. Tennesine was discovered in 2010 (see for review of all related experiments [34]) and the known isotopes are $^{293}, ^{294}\text{Ts}$ with an average life time of about 22 ms and 51 ms, respectively. So far, on-line chemical separations have been performed with nuclides having half-lives down to about 0.5 s, e.g. with ^{287}Fl [35]. It would therefore require a major technological improvement to increase the formation and separation time of molecules by one order of magnitude. The observed reaction might be interesting for developing a chemical system for Ts using a radiofrequency gas stopping cell, e.g. [36]. Preparation of such experiments are under way.

References

1. Türler, A., Pershina, V.: Advances in the production and chemistry of the heaviest elements. *Chem. Rev.* **113**, 1237 (2013).
2. Türler, A., Eichler, R., Yakushev, A.: Chemical studies of elements with $Z \geq 104$ in gas phase. *Nucl. Phys. A* **944**, 640 (2015).
3. Even, J., Yakushev, A., Duellmann, C. E., Dvorak, J., Eichler, R., Gothe, O., Hild, D., Jäger, E., Khuyagbaatar, J., Kratz, J.-V., Krier, J., Niewisch, L., Nitsche, H., Pysmenetska, I., Schädel, M., Schausten, B., Türler, A., Wiehl, N., Wittwer D.: Rapid synthesis of radioactive transition-metal carbonyl complexes at ambient conditions. *Inorg. Chem.* **51**(12), 6431 (2012).
4. Pershina, V.: Electronic structure and properties of superheavy elements. *Nucl. Phys. A* **944**, 578 (2015).
5. Even, J., Yakushev, A., Duellmann, C. E., Dvorak, J., Eichler, R., Gothe, O., Hild, D., Jäger, E., Khuyagbaatar, J., Kratz, J.-V., Krier, J., Niewisch, L., Nitsche, H., Pysmenetska, I., Schädel, M., Schausten, B., Türler, A., Wiehl, N., Wittwer D.: In-situ formation, thermal decomposition, and adsorption studies of transition metal carbonyl complexes with short-lived radioisotopes. *Radiochim. Acta* **102**, 1093 (2014).
6. Wang, Y., Qin, Z., Fan, F. L., Fan, F. Y., Cao, S. W., Wu, X. L., Zhang, X., Bai, J., Yin, X. J., Tian, L. L., Zhao, L., Tian, W., Li, Z., Tan, C. M., Guo, J. S., Gaggeler, H. W.: Gas-phase chemistry of Mo, Ru, W, and Os metal carbonyl complexes. *Radiochim. Acta* **102**, 69 (2014).
7. Wang, Y., Qin, Z., Fan, F. L., Haba, H., Komori, Y., Wu, X., Tan, C., Zhang, X.: Gas-phase chemistry of technetium carbonyl complexes. *Phys. Chem. Chem. Phys.* **17**(20), 13228 (2015).
8. Even, J., Ackermann, D., Asai, M., Block, M., Brand, H., Di Nitto, A., Düllmann, Ch. E., Eichler, R., Fan, F., Haba, H., Hartmann, W., Hübner, A., Heßberger, F. P., Huang, M., Jäger, E., Kaji, D., Kanaya, J., Kaneya, Y., Khuyagbaatar, J., Kindler, B., Kratz, J.-V., Krier, J., Kudou, Y., Kurz, N., Laatiaoui, M., Lommel, B., Maurer, J., Miyashita, S., Morimoto, K., Morita, K., Murakami, M., Nagame, Y., Nitsche, H., Ooe, K., Qin, Z., Sato, T. K., Schädel, M., Steiner, J., Sumita, T., Takeyama, M., Tanaka, K., Toyoshima, A., Tsukada, K., Türler, A., Usoltsev, I., Wakabayashi, Y., Wang, Y., Wiehl, N., Yamaki, S.: *In situ* synthesis of volatile carbonyl complexes with short-lived nuclides. *J. Radioanal. Nucl. Chem.* **303**, 2457 (2015).
9. Cao, S., Wang, Y., Qin, Z., Fan, F. Y., Haba, H., Komori, Y., Wu, X., Tan, C., Zhang, X.: Gas-phase chemistry of ruthenium and rhodium carbonyl complexes. *Phys. Chem. Chem. Phys.* **18**, 119 (2016).
10. Even, J., Yakushev, A., Düllmann, C. E., Haba, H., Asai, M., Sato, T. K., Brand, H., Di Nitto, A., Eichler, R., Fan, F. L., Hartmann, W., Huang, M., Jäger, E., Kaji, D., Kanaya, J., Kaneya, Y., Khuyagbaatar, J., Kindler, B., Kratz, J.-V., Krier, J., Kudou, Y., Kurz, N., Lommel, B., Miyashita, S., Morimoto, K., Morita, K., Murakami, M., Nagame, Y., Nitsche, H., Ooe, K., Qin, Z., Schädel, M., Steiner, J., Sumita, T., Takeyama, M., Tanaka, K., Toyoshima, A., Tsukada, K., Türler, A., Usoltsev, I., Wakabayashi, Y., Wang, Y., Wiehl, N., Yamaki, S.: Synthesis and detection of a seaborgium carbonyl complex. *Science* **345**(6203), 1491 (2014).
11. Usoltsev, I., Eichler, R., Wang, Y., Even, J., Yakushev, A., Haba, H., Asai, M., Brand, H., Di Nitto, A., Düllmann, C. E., Fan, F. L., Hartmann, W., Huang, M., Jäger, E., Kaji, D., Kanaya, J., Kaneya, Y., Khuyagbaatar, J., Kindler, B., Kratz, J.-V., Krier, J., Kudou, Y., Kurz, N., Lommel, B., Miyashita, S., Morimoto, K., Morita, K., Murakami, M., Nagame, Y., Nitsche, H., Ooe, K., Sato, T. K., Schädel, M., Steiner, J., Sumita, T., Takeyama, M., Tanaka, K., Toyoshima, A., Tsukada, K., Türler, A., Wakabayashi, Y., Wiehl, N., Yamaki, S., Qin, Z.: Decomposition studies of group 6 hexacarbonyl complexes. Part 1: production and decomposition of $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$. *Radiochim. Acta* **104**, 141 (2016).

12. Usoltsev, I., Eichler, R., Türlér, A.: Decomposition studies of group 6 hexacarbonyl complexes. Part 2: modelling of the decomposition process. *Radiochim. Acta* **104**, 531 (2016).
13. Nash, C. S., Bursten, B. E.: Prediction of the bond lengths, vibrational frequencies, and bond dissociation energy of octahedral seaborgium hexacarbonyl, $\text{Sg}(\text{CO})_6$. *J. Am. Chem. Soc.* **121**, 10830 (1999).
14. Pershina, V., Anton, J.: Theoretical predictions of properties and gas-phase chromatography behaviour of carbonyl complexes of group-6 elements Cr, Mo, W, and element 106, Sg. *J. Chem. Phys.* **138**, 174301 (2013).
15. Iliaš, M., Pershina, V.: Hexacarbonyls of Mo, W, and Sg: Metal – CO bonding revisited. *Inorg. Chem.* **56**, 1638 (2017).
16. Monacada, S., Palmer, M. J., Higgs, E. A.: Nitric oxide: physiology, pathophysiology, and pharmacology. *Pharmacol. Rev.* **43**(2), 109 (1991).
17. Shafirovich, V., Lymar, S. V.: Nitroxyl and its anion in aqueous solutions: spin states, protic equilibria, and reactivities toward oxygen and nitric oxide. *PNAS* **99**(11), 7340 (2002).
18. Rattat, D., Verbruggen, A., Berke, H., Alberto, R.: Exploring the nitrosyl approach: “ $\text{Re}(\text{CO})_2(\text{NO})$ ” and “ $\text{Tc}(\text{CO})_2(\text{NO})$ ” complexes provide new pathways for bioorganometallic chemistry. *J. Organometal. Chem.* **689**, 4833 (2004).
19. Wang, X., Zhou, M., Andrews, L.: Manganese carbonyl nitrosyl complexes in solid argon: infrared spectra and density functional calculations. *J. Phys. Chem. A* **104**, 7964 (2000).
20. Richter-Addo, G. B., Legzdins, P.: Recent organometallic nitrosyl chemistry. *Chem. Rev.* **88**, 991 (1988).
21. Hollemann A. F., Wiberg E.: In: *Inorganic Chemistry* 100th ed. (1985). W. de Gruyter, Berlin and New York, p. 597.
22. Beckham, L. J., Fessler, W.A., Kise M. A.: Nitrosyl chloride. *Chem. Rev.* **48**(3), 319 (1951).
23. Gay-Lussac, J. L.: Extrait d’un Mémoire sur l’eau régale. *Compt. Rend.* **26**, 619 (1848).
24. Loock, H.-P., Qian, C. X. W.: Photodissociation studies on nitrosyl bromide: I. Photofragment spectroscopy and electronic structure. *J. Chem. Phys.* **108**, 3178 (1998).
25. Bailleuxa, S., Dufloata, D., Aibab, S., Nakahamab, S., Ozekiba, H.: Nitrosyl iodide, INO : a combined ab initio and high-resolution-spectroscopic study. *Chem. Phys. Lett.* **650**, 73 (2016).
26. O’Driscoll, P., Minogue, N., Takenaka, N., Sodeau, J.: Release of nitric oxide and iodine to the atmosphere from the freezing of sea-salt aerosol components. *J. Phys. Chem. A* **112**(8), 1677 (2008).
27. O’Neill, E., Hinrichs, R. Z.: Production of molecular iodine from the heterogeneous reaction of nitrogen dioxide with solid potassium iodide. *J. Geophys. Res.* **116**, D01301 (2011).
28. Eichler, R., Eichler, B.: Thermochemical data from gas-phase adsorption and methods of their estimation. In: *The Chemistry of Superheavy Elements* (2014). Schädel M.; Shaughnessy D. (eds.). Springer Verlag, Berlin Heidelberg, p. 375.
29. Chase, M. W., Jr.: In: *NIST-JANAF Thermochemical Tables*, Fourth Edition, *J. Phys. Chem. Ref. Data* **9**, 1 (1998).
30. Hermann, A., Hoffmann, R., Ashcroft, N. W.: Condensed astatine: monatomic and metallic. *Phys. Rev. Lett.* **111**, 116404 (2013).
31. Eichler, B.: Das Flüchtigkeitsverhalten von Transactiniden im Bereich um $Z=114$. *Kernenergie* **19**, 307 (1976).
32. Borschevsky, A., Pasteka, F., Pershina, V., Eliav E., Kaldor U.: Ionization potentials and electron affinities of the superheavy elements 115–117 and their sixth-row homologues Bi, Po, and At. *Phys. Rev. A* **91**, 020501 (2015).
33. Düllmann, C. E., Eichler, B., Eichler, R., Gäggeler, H. W., Jost, D., Kindler, U., Piguet, D., Soverna, S., Törle, P., Trautmann, N., Türlér, A.: Miss Piggy, a californium-252 fission fragment source as a generator of short-lived radionuclides. *Nucl. Instr. Meth. A* **512**, 595 (2003).
34. Oganessian, Y. T., Abdullin, F. S., Alexander, C., Binder, J., Boll, R. A., Dmitriev, S. N., Ezold, J., Felker, K., Gostic, J. M., Grzywacz, R. K., Hamilton, J. H., Henderson, R. A., Itkis, M. G., Miernik, K., Miller, D., Moody, K. J., Polyakov, A. N., Ramayya, A. V., Roberto, J. B., Ryabinin, M. A., Rykaczewski, K. P., Sagaidak, R. N., Shaughnessy, D. A., Shirokovsky, I. V., Shumeiko, M. V., Stoyer, M. A., Stoyer, N. J., Subbotin, V. G., Sukhov, A. M., Tsyganov, Y. S., Utyonkov, V. K., Voinov, A. A., Vostokin, G. K.: Production and decay of the heaviest nuclei $^{293,294}117$ and $^{294}118$. *Phys. Rev. Lett.* **109**, 162501 (2012).
35. Eichler, R., Aksenov, N. V., Albin, Y. V., Belozarov, A. V., Bozhikov, G. A., Chepigin, V. I., Dmitriev, S. N., Dressler, R., Gäggeler, H. W., Gorshkov, V. A., Henderson, R. A., Johnsen, A. M., Kenneally, J. M., Lebedev, V. Y., Malyshev, O. N., Moody, K. J., Oganessian, Y. T., Petrushkin, O. V., Piguet, D., Popeko, A. G., Rasmussen, P., Serov, A., Shaughnessy, D. A., Shishkin, S. V., Shutov, A. V., Stoyer, M. A., Stoyer, N. J., Svirikhin, A. I., Tereshatov, E. E., Vostokin, G. K., Wegrzecki, M., Wilk, P. A., Wittwer, D., Yerebin, A. V.: Indication for a volatile element 114. *Radiochim. Acta* **98**, 133 (2010).
36. Neumayr, J. B., Thierolf, P. G., Habs, D., Heinz, S., Kolhinen, S. S., Sewtz, M., Szerypo, J.: Performance of the MLL-IonCatcher. *Rev. Sci. Instr.* **77**, 065109 (2006).