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Comparing the fluorination of Pb^+ and Po^+ : insights into p-block relativistic effects for superheavy elements

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Abstract

It is expected that the chemical properties of the heaviest of the superheavy elements (SHEs, $Z = 113 - 118$) do not align with what is suggested by their current positions on the periodic table. Specifically, the onset of significant relativistic effects, including increased spin–orbit splitting of the p -orbitals may lead to enhanced stability of low-oxidation states. Notably, it is predicted that flerovium ($Z = 114$) may exhibit pseudo-noble gas behavior from a $7p_{1/2}^2$ electron configuration that acts as an ‘inert pair’. Even though it is expected that the $p_{1/2}$ – $p_{3/2}$ splitting becomes pronounced toward the end of the p -block’s sixth row, there is currently limited experimental evidence to confirm its extent or impact. Here, the production of gas-phase lead ($Z = 82$) and polonium ($Z = 84$) fluoride cations (PbF_n^+ and PoF_n^+) were compared to elucidate differences in accessible oxidation states. The PoF_n^+ and PbF_n^+ species were produced and identified with the FIONA spectrometer at the Lawrence Berkeley National Laboratory 88-Inch Cyclotron Facility. Polonium showed notably different fluorination chemistry than lead, producing PoF^+ and PoF_3^+ as primary products compared to lead’s PbF^+ and PbF_2^+ . The distribution of PoF_n^+ products observed offer insights as to the role of spin–orbit splitting for polonium. Similar studies of superheavy elements would elucidate the accessibility of their low-oxidation states as well as to inform chemical predictions for eighth-row elements not yet discovered.

1. Introduction

The onset of large spin–orbit splitting is expected to significantly influence the chemical properties of the heaviest elements [1, 2]. This effect may lead to the emergence of new pseudo-shell closures that would disrupt the established chemical trends of the periodic table. Presently, the difficulties in performing measurements on rare radioactive species, has limited experimental studies of heavier elements. Therefore most studies trying to understand the extent and impact of spin–orbit splitting for these elements have been theoretical [3–11]. The calculated spin–orbit splitting of the $p_{1/2}$ and $p_{3/2}$ pair for elements in the fifth, sixth and seventh rows of the periodic table’s p block is presented in figure 1. Here, the separation of these orbitals is shown to increase with higher Z , starting to become prominent in the sixth row around polonium. As efforts are being made to better understand the chemical properties of seventh-row superheavy elements (SHEs, $Z > 103$) and to predict the properties of elements that may exist beyond the limits of today’s periodic table ($Z > 118$) [12–17], a better understanding of spin–orbit splitting in the lighter sixth-row elements will be immensely useful.

Polonium, which is studied here, is one of the rarest elements on Earth. Despite being discovered over a century ago by Marie Curie [18], its chemical properties still remain poorly understood. All of its isotopes are radioactive and difficult to study with traditional chemistry techniques [19]. Even

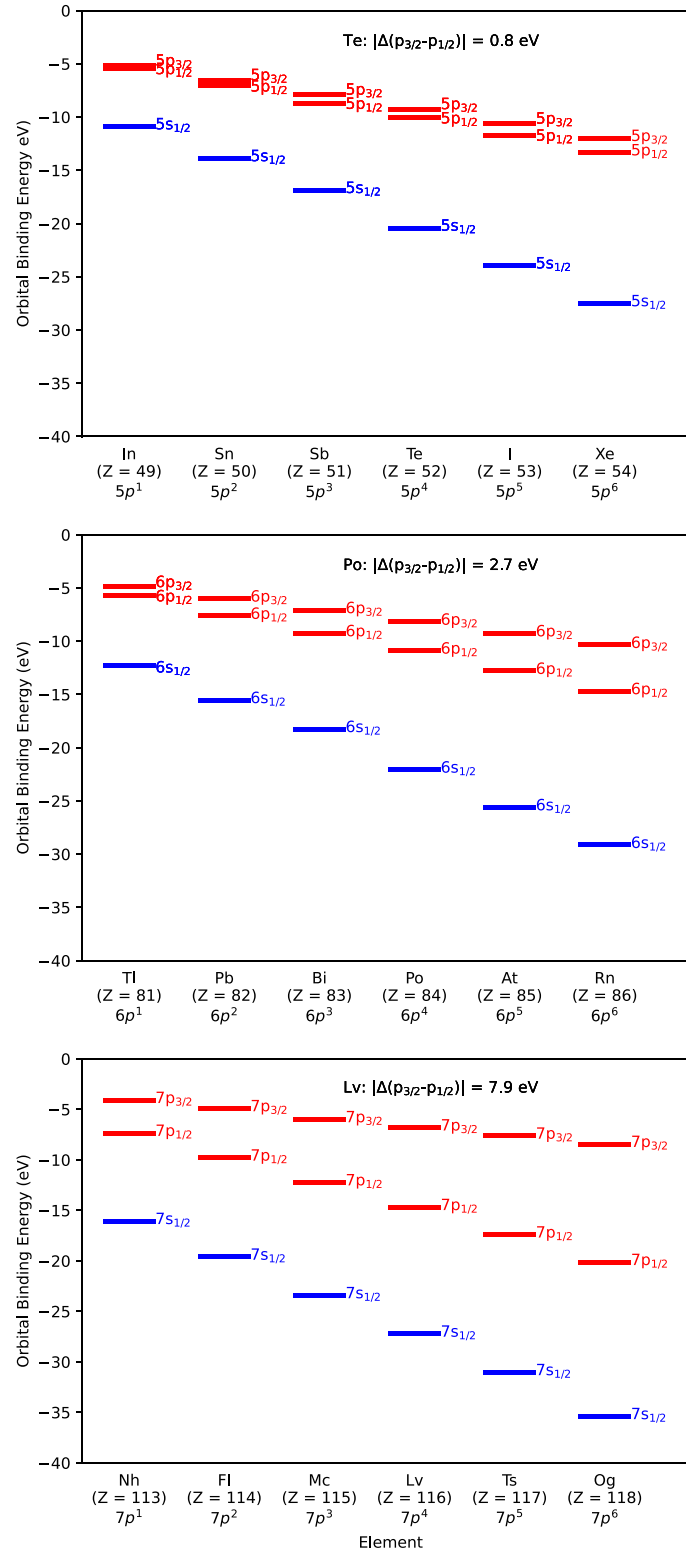


Figure 1. Calculated orbital binding energies for fifth (top), sixth (mid) and seventh (bot) row p-block elements. These results show that there is an expected enhancement in spin-orbit splitting with increasing Z . The expected energy difference between the $p_{3/2}$ and $p_{1/2}$ orbitals for elements with p^4 -electron configurations are given. These calculated data were taken from [11].

though, it is expected for polonium's chemical properties to be significantly impacted by relativistic effects, specifically from enhanced spin–orbit splitting, current experimental data are scarce to establish to what extent [20]. Notably, the inability to definitively confirm the polonium molecular species produced in experimental studies frequently leaves researchers with unanswered questions and uncertainty [6, 19, 21–23]. Polonium's electron configuration, $[\text{Xe}]6s^24f^{14}5d^{10}6p^4$, features six valence electrons, with stabilized pairs of $6s_{1/2}^2$ and $6p_{1/2}^2$ electrons and two electrons half-fill the $6p_{3/2}$ state. It would be expected that polonium could populate the -2 , $+2$, $+4$, and $+6$ oxidation states. However, to date no experimental measurement has directly identified and confirmed complexes for the -2 , $+2$, and $+6$ degrees of oxidation [20]. Also, even though the $+4$ oxidation state has been observed to be dominant in aqueous solutions [24], available data shows considerable disagreement and conflicting results [20]. Direct experimental determination of polonium species and oxidation states would significantly advance our understanding of polonium's electronic structure and oxidation state stability. Such results would then be useful in forming expectations as to the role of spin–orbit splitting for seventh and eighth row SHEs.

Gas-phase studies offer a unique advantage for investigating fundamental chemical properties by eliminating the complicating effects of condensed phases such as solvation and counterion interactions [25, 26]. Previous work has established that room-temperature reactions between metal cations (M^+) and fluorinating agents produce metal fluoride ions (MF_n^+), with the distribution of species reflecting the accessibility of specific oxidation states [27]. For example, ytterbium ($Z = 70$) preferentially forms the $+2$ state over $+3$, reflecting the stability of its closed $4f^{14}$ configuration [27], while einsteinium ($Z = 99$) exhibits a stable $+2$ state due to enhanced $5f$ stabilization from actinide contraction [28]. These studies proposed that F-abstraction proceeds via a ‘harpoon’-like mechanism, wherein electron transfer from M^+ to the F atom forms the M–F bond, and the ease of sequential F addition is correlated to the sequential ionization energies of M^+ .

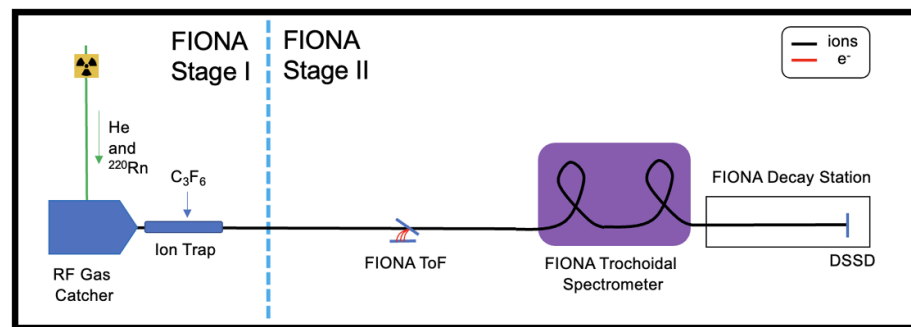
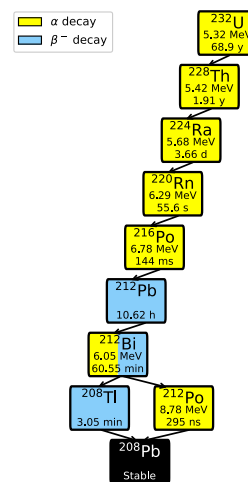
We investigated polonium's oxidation state accessibility relative to lead ($Z = 82$) in the gas phase by producing and identifying MF_n^+ ions via an atom-at-a-time technique. Our primary objectives were to determine which oxidation states are accessible to polonium and to assess the impact of spin–orbit coupling on its electronic structure and reactivity. Lead serves as a nice reference because its chemistry is well-established, both elements occupy the p-block's sixth row, and both are predicted to exhibit stable $+2$ and $+4$ oxidation states. Notably, relativistic effects, specifically the stabilization and contraction of the $6s$ orbital, make the $+4$ oxidation state significantly less accessible for lead than for its lighter group 14 homologues [29]. A comparison of the electron configurations and ionization potentials for the accessible oxidation states of these two elements is presented in table 1. Note that for polonium, only the first ionization potential has been measured, the rest are theoretical. There have been previous studies of Pb^+ reactions with other fluorinating gases, specifically CH_3F [30] and SF_6 [31], which did not observe PbF_n^+ complex formation. However, those studies identified the fluorine transfer mechanism as being insertion, in which two unpaired electrons from the metal ion insert into the F-containing molecule, followed by rearrangement and fluorine transfer to the metal. This insertion mechanism contrasts with the ‘harpoon’-type mechanism, where direct ionization of the metal ion leads to fluoride transfer. The use of hexafluoropropene (C_3F_6) in the present study may favor the harpoon mechanism over the insertion pathway.

2. Experimental

These studies utilized the FIONA spectrometer (as seen in figure 2), located at LBNL's 88-Inch Cyclotron Facility [38]. It has previously been demonstrated that FIONA is a powerful tool for investigating the fundamental chemical properties of rare elements produced one-atom-at-a-time, as it can directly determine the identity of a produced chemical species from its mass-to-charge ratio (A/q) [39–41]. The use of FIONA is advantageous as in the past, unclear speciation in atom-at-a-time experimental studies has been a large hurdle to overcome in drawing clear conclusions [22, 42, 43]. Here, ions of ^{216}Po ($t_{1/2} = 144$ ms [44]) and ^{212}Pb ($t_{1/2} = 10.6$ h [44]) were generated as daughter decays from a radioactive source of ^{232}U . The decay scheme of ^{232}U is presented in figure 3. The ^{232}U source emanates the noble gas ^{220}Rn ($t_{1/2} = 55.6$ s [45]), which then subsequently decays to ^{216}Po and then ^{212}Pb . To introduce ^{216}Po and ^{212}Pb into FIONA, helium gas was flowed over the source, sweeping up the radioactive ^{220}Rn , and then directly injecting it into Stage I of FIONA.

Table 1. Experimental (where available) and theoretical Ionization energies (IE) and electron configurations for lead and polonium at various oxidation states.

Oxidation State	Lead			Polonium		
	Exp. IE (eV)	Theo. IE (eV)	E. Config.	Exp. IE (eV)	Theo. IE (eV)	E. Config.
0	7.4 [32]	6.9 [33]	[Hg]6p ²	8.4 [34]	8.0 [33]	[Hg]6p ⁴
I	15.0 [35]	15.6 [33]	[Hg]6p ¹	—	17.2 [33]	[Hg]6p ³
II	31.9 [36]	32.3 [33]	[Xe]4f ¹⁴ 5d ¹⁰ 6s ²	—	29.0 [33]	[Hg]6p ²
III	42.3 [35]	43.6 [33]	[Xe]4f ¹⁴ 5d ¹⁰ 6s ¹	—	39.6 [33]	[Hg]6p ¹
IV	68.8 [37]	67.2 [33]	[Xe]4f ¹⁴ 5d ¹⁰	—	61.3 [33]	[Xe]4f ¹⁴ 5d ¹⁰ 6s ²
V	—	—	—	—	74.1 [33]	[Xe]4f ¹⁴ 5d ¹⁰ 6s ¹
VI	—	—	—	—	105.7 [33]	[Xe]4f ¹⁴ 5d ¹⁰

**Figure 2.** A schematic diagram shows Stage I and II of FIONA. Ions of ²¹⁶Po are produced from ²²⁰Rn decay, thermalized, in the RF gas catcher and reduced to 1+ charge state. While contained in the ion trap, ²¹⁶Po and ²¹²Pb ions were exposed to C₃F₆ to form ²¹⁶PoF_n⁺ and ²¹²PbF_n⁺ molecular ions. These ions were identified by *A/q* measurements using FIONA ToF and/or FIONA Decay Station detectors. The FIONA ToF detector was used to survey ²¹⁶PoF_n⁺ and ²¹²PbF_n⁺ species produced with different flow rates of C₃F₆ gas. Final ²¹⁶PoF_n⁺ identifications and distributions were determined from *A/q* measurements at the decay station following their separation in the trochoidal spectrometer.**Figure 3.** The decay chain of ²³²U leads to the production of ²¹⁶Po and ²¹²Pb. To introduce these isotopes into FIONA, helium gas is swept over the source capturing emanated ²²⁰Rn. The helium and ²²⁰Rn are then directly injected into FIONA's RF gas catcher, where the ²²⁰Rn undergoes radioactive decay to produce ²¹⁶Po, which further decays eventually leading to ²¹²Pb.

The first component of FIONA is a radio-frequency (RF) gas catcher maintained at 150 Torr of high-purity helium gas. The high-pressure environment of the gas catcher quickly thermalizes the ²¹⁶Po and ²¹²Pb ions and they are stabilized as a mixture of 1⁺ and 2⁺ charge states from charge-exchange reactions with the helium gas. The ions were then guided through the gas catcher to a RF quadrupole (RFQ) cooler-buncher ion trap using a combination of RF and DC electric fields paired with the flow of the helium gas. Here, the ions were contained within a region of a few cubic millimeters for select trapping

Table 2. Experimental parameters for the production and identification of $^{216}\text{PoF}_n^+$ species.

Measurement	$^{216}\text{Po}^+$	$^{216}\text{PoF}^+$	$^{216}\text{PoF}_2^+$	$^{216}\text{PoF}_3^+$	$^{216}\text{PoF}_4^+$
A/q Setting	216/1	235/1	254/1	273/1	292/1
Duration (hr)	6	7	8	6	2

times. Note that ions are continuously loading the ion trap during this trapping time, so ions entering the trap at the beginning or end of a trapping cycle will have different exposure to the reactive gas. To form MF_n^+ ions, the reactive gas hexafluoropropene (C_3F_6) was flowed into the trap while the ^{216}Po and ^{212}Pb ions and were contained. A residual gas analyzer was connected to the ion trap to monitor the partial pressure of C_3F_6 within the trap, as well as pressures of any contaminant gases, such as H_2O and O_2 . Note, that for these measurements, it was not possible to calibrate the partial pressures given by the gas analyzer to absolute partial pressures. Following the chemical reaction any leftover metal ions and produced MF_n^+ species were ejected from the ion trap and re-accelerated to energies of several keV with a pulsed drift tube to stage II of FIONA, where A/q determination of species could be performed.

FIONA's trochoidal spectrometer then employs perpendicular electric and magnetic fields to filter ions by A/q . The ions enter the spectrometer with the same kinetic energy, and therefore ions with different A/q will have different velocities, leading to slightly different path lengths through the separator. The ions follow different trochoidal trajectories through the spectrometer depending on their A/q , exiting at different angles onto a double-sided silicon strip detector (DSSD) at the decay station (DS). The position of the α detection on the DSSD can be correlated to the A/q of the species. Note that as A/q is determined from the position of detected alpha decays, FIONA DS measurements for this study were sensitive just to ^{216}Po -containing species. To observe the full range of PoF_n^+ species produced, it was necessary to scale the electrical parameters of FIONA to deliver ions of specified A/q to the DSSD. The details of these measurements are given in table 2.

To determine the distribution of $^{212}\text{PbF}_n^+$ species produced relative to $^{216}\text{PoF}_n^+$, measurements were performed with a recently-installed Time of Flight (ToF) detection system, FIONA ToF [46]. FIONA ToF is positioned at the Stage II entrance downstream of the ion trap (figure 2). The FIONA ToF detector combines both a DSSD and a micro-channel plate (MCP) detector, such that when ions impact the DSSD they create a cascade of secondary electrons that are then detected by the MCP. The FIONA ToF DSSD has 32 x 32 strips, each with a 2 mm pitch such that the active area of the detector is 64 x 64 mm². The MCP detector is 40 mm in diameter and includes two Hamamatsu MCPs arranged in a Chevron configuration. The time difference between when the ions exit the ion trap and when the secondary electrons hit the MCP can then be used to determine the A/q of the ions without needing to detect the radioactive decay of the species. Here, measurements were sensitive to the observation of both alpha-emitting ^{216}Po - and beta-decaying ^{212}Pb -containing species.

For this study, the DSSD employed at the FIONA DS was contained 58 (1 mm) x 29 (2 mm) strips with an active area of 58 x 58 mm². The detector was positioned such that the 58 1 mm strips surveyed the horizontal mass-dispersion plane and the 29 2 mm strip were positioned in the vertical direction. In these measurements, signals from the DSSD detectors were passed through MPR-16 lin-log preamplifiers before being processed and digitized with CAEN VX2740 digitizers. These signals were recorded with CAEN's CoMPASS software [47] and processed with the CAEN DPP-PHA firmware. FIONA ToF's MCP signal was processed with a fast-timing amplifier before then being digitized with a CAEN VX2740 digitizer. Signals from the CAEN VX2740 digitizers were recorded with the CAEN CoMPASS software. Prior to the experiment, the energies of events recorded by the DSSDs were calibrated with a triple- α source containing isotopes of ^{239}Pu , ^{241}Am , and ^{244}Cm . Energy gates were then placed on the data to select ^{216}Po events observed in the range of 6.4–7.0 MeV.

3. Results

3.1. Distribution of $^{216}\text{PoF}_n^+$ and $^{212}\text{PbF}_n^+$ species observed with FIONA ToF

Initial survey scans were performed with FIONA ToF to observe the production of $^{216}\text{PoF}_n^+$ and $^{212}\text{PbF}_n^+$ species from different combinations of trapping times and C_3F_6 flow rates as are shown in figure 4. Survey scans were performed in two hour measurements where the trapping time was set to 50 ms and flow rates of 0, 10^{-5} , 10^{-4} , and 10^{-3} mbar L s⁻¹ of C_3F_6 into the RFQ trap were investigated. In this study, 10^{-3} mbar L s⁻¹ was the maximum flow rate allowed by FIONA's vacuum system. An additional measurement was performed tripling the trapping time for ions to be exposed to a flow rate of 10^{-3}

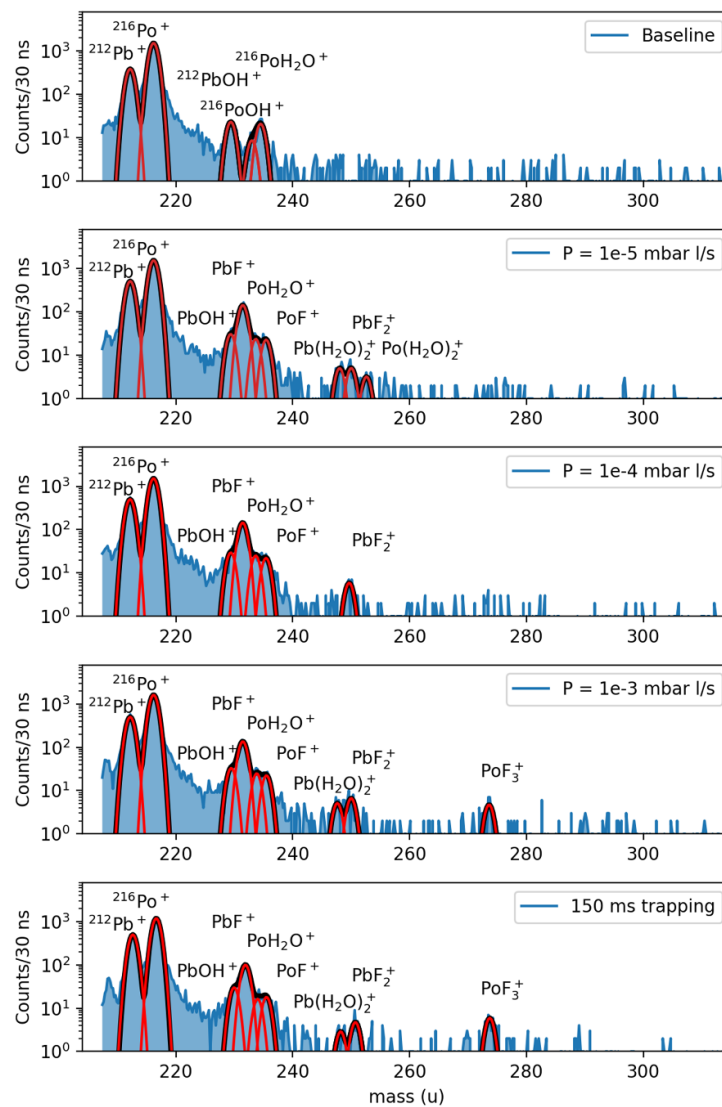


Figure 4. Survey scans of PoF_n^+ productions were performed at the FIONA ToF detector system in two hour measurements where the trapping time was set to 50 ms and flow rates of 0, 10^{-5} , 10^{-4} , and 10^{-3} mbar L s^{-1} of C_3F_6 into the RFQ trap were investigated. Additionally, a measurement was performed at a flow rate of 10^{-3} mbar L s^{-1} C_3F_6 and 150 ms trapping time.

mbar L s^{-1} C_3F_6 from 50 ms to 150 ms, effectively allowing ions three times as many interactions with the gas. Going to even longer trapping times was avoided given the 144 ms half-life of $^{216}\text{Po}^+$.

In the baseline spectrum (figure 4(a)), taken with no C_3F_6 gas within FIONA, species consistent with hydroxide and aquo assignments were observed to be formed for both polonium and lead. Such species have been observed previously in FIONA and are believed to be produced from water contaminants in the RF gas catcher [41]. Following the addition of C_3F_6 , $^{212}\text{PbF}_n^+$ and $^{216}\text{PoF}_n^+$ species were observed to be produced. The distribution of products observed for the different combinations of gas flow and trapping times investigated are given in table 3. In these FIONA ToF measurements, the highest order fluoride species clearly produced for Pb and Po were PbF_2^+ and PoF_3^+ , respectively. It is possible that higher order species also formed, but at levels indiscernible from the background at higher A/q flight times. Following the survey measurements performed at the FIONA ToF detector to look for higher-order $^{216}\text{PoF}_n^+$ species, the flow rate of 10^{-3} mbar L s^{-1} was selected as optimal for the production of PoF_n^+ species.

3.2. Distribution of $^{216}\text{PoF}_n^+$ species observed at the FIONA DS

Following the survey measurements performed at FIONA ToF, it was then retracted to allow ions to pass through the FIONA trochoidal mass spectrometer, before impinging on a DSSD at the FIONA DS. Here, the position of the α detection on the DSSD can be correlated to the A/q of the species. The bare ion rate of $^{216}\text{Po}^+$ observed at the FIONA decay station was on the order of 2 Hz. Prior to each measurement on the production of PoF_n^+ species, a 1 h baseline measurement was taken without C_3F_6 gas

Table 3. Product ion abundances for Pb/Po under different conditions.

Species	Low flow		Med flow		High flow		High flow (150 ms)		FIONA DS
	Pb	Po	Pb	Po	Pb	Po	Pb	Po	Po
M ⁺	78.3(9)	98.6(1)	77.7(9)	98.6(1)	77.6(9)	98.4(2)	83.3(8)	98.1(2)	98.6(4)
MF ⁺	20.9(8)	1.3(1)	21.5(8)	1.4(1)	19.7(8)	1.3(1)	16.0(7)	1.3(1)	1.1(3)
MF ₂ ⁺	0.7(1)	—	0.9(1)	—	0.8(2)	—	0.7(1)	—	< 0.05
MF ₃ ⁺	—	—	—	—	—	0.4(1)	—	0.4(1)	0.2(1)
MF ₄ ⁺	—	—	—	—	—	—	—	—	< 0.03
MF ₅ ⁺	—	—	—	—	—	—	—	—	< 0.02

present to check for any background species. The results, including baseline measurements and PoF_n⁺ production with C₃F₆ gas, are presented in figure 5. The observed counts of each PoF_n⁺ species were normalized to the measurement time for direct comparison. The distribution of PoF_n⁺ species observed at the FIONA DS are given alongside those observed with FIONA ToF in table 3. There is good agreement as to the distribution of PoF_n⁺ species observed with the two techniques. Following the full set of measurements, a 70 h background measurement was taken to observe the background rate of ²¹⁶Po⁺-like events on the DSSD.

4. Discussion

Previous gas-phase studies have demonstrated that the interaction of M⁺ ions with select fluorinating gases can produce MF_n⁺ ions, where successive fluoride addition depends on the ionization energy required to oxidize electrons from the metal [27, 28]. A ‘harpoon’-type mechanism that was proposed in those studies for d-block and f-block metals and may apply to the fluoride species observed here. Polonium presents an interesting case for studying sequential electron oxidation for probing the potential impact of spin–orbit splitting of the *p*_{1/2}–*p*_{3/2} orbital pair. The electron configuration of Po⁺ is [Xe]4f¹⁴5d¹⁰6s²6p³, featuring a stabilized 6p²_{1/2} pair and a single 6p_{3/2} electron. In contrast, Pb⁺ has the configuration [Xe]4f¹⁴5d¹⁰6s²6p¹. Comparing the sequential fluorination of Pb⁺ and Po⁺ provides insight into the accessibility of their respective oxidation states.

When ²¹⁶Po and ²¹²Pb ions were exposed to C₃F₆ gas, the production of ²¹⁶PoF_n⁺ and ²¹²PbF_n⁺ species was observed. As shown in table 3, these measurements reveal significantly different chemical behavior between the two elements in their product distributions. Comparing the fluoride production between these two elements provides insight into the relative stability of different oxidation states. For ²¹²Pb, the species PbF⁺ and PbF₂⁺ were consistently produced across all tested flow rates and trapping times, corresponding to the +2 and +3 oxidation states, respectively. Although the +4 oxidation state is well-established for Pb in the literature, PbF₃⁺ was not detected. This could indicate either that the +4 state is not accessible under these reaction conditions, or that PbF₃⁺ was produced below the detection sensitivity of FIONA ToF. The behavior of Po was notably different from that of Pb. At low and mid-flow rates, only PoF⁺ was observed, with PoF₃⁺ appearing exclusively at high flow rates. Very little, if any, PoF₂⁺, PoF₄⁺, or PoF₅⁺ was detected in these measurements. Upper limits are reported for these species, as the observed counts cannot be definitively distinguished from background events.

Overall, as is evident from the values listed in table 3, the fluorination of ²¹²Pb and ²¹⁶Po proceeded with notably low efficiency. Unfluorinated ions dominated the observed species, with Pb⁺ and Po⁺ comprising approximately 78% and 98% of the products, respectively. Between the two, ²¹²Pb showed higher fluorination efficiency than ²¹⁶Po. For Po in particular, the extremely low yield may be evidence that these reactions are taking place with the small subset of ions that are not thermalized with in the trap and that the reaction is not actually exothermic in room temperature conditions. This low reactivity for these p-block metals stands in sharp contrast to the behavior of early d-block transition metals [27, 30, 31], which readily access multiple oxidation states through efficient fluorination. The discrepancy suggests that fluorination is inherently hindered for these heavy p-block elements.

In considering the formation of products assuming a harpoon mechanism, the formation of PbF⁺ and PoF⁺ (corresponding to the +2 oxidation state) would require the removal of one valence electron from the metal ion. Even though the experimental data suggest that formation of these fluoride species is unfavorable overall, among the fluorinated products that did form, 21% of Pb products were PbF⁺

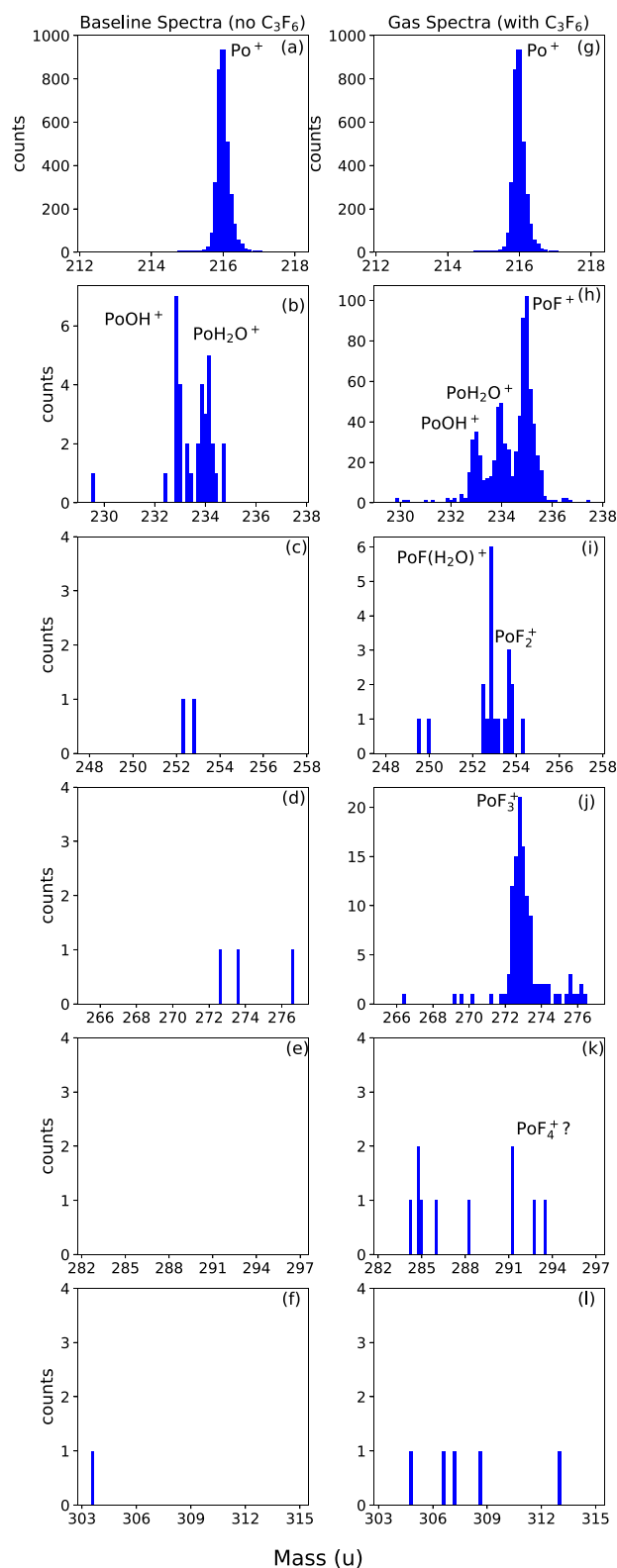


Figure 5. Spectra of PoF_n^+ species observed at the FIONA decay station. (a)–(f) One hour baseline spectra taken at each FIONA A/q setting with no C_3F_6 gas in the system (216/1 (a), 235/1 (b), 254/1 (c), 273/1 (d), 292/1 (e), and 311/1 (f)). (g)–(l) Measurements taken with C_3F_6 injected into FIONA at a flow rate of 10^{-3} mbar L s^{-1} for $A/q = 216/1$ (g), 235/1 (h), 254/1 (i), 273/1 (j), 292/1 (k), and 311/1 (l).

compared to only 1% of Po products as PoF^+ . This striking difference suggests that Pb(II) is significantly more accessible than Po(II) under these reaction conditions. The preferential formation of PbF^+ indicates that removal of the $6p_{1/2}$ electron from Pb^+ is more favorable than removal of a $6p_{3/2}$ electron

from Po^+ . This interpretation is consistent with the second ionization energies of 15 eV for Pb [35] versus the predicted ~ 17 eV for Po [33], reflecting the expected greater difficulty in oxidizing polonium.

Formation of PbF_2^+ and PoF_2^+ (corresponding to the +3 oxidation state) requires sequential removal of additional electrons. Interestingly, for Pb^+ , this requires breaking the $6s_{1/2}$ pair, and for Po^+ , this requires breaking the $6p_{1/2}$ pair, both of which are stabilized by relativistic effects. Here, both elements showed very low production of difluoride species: less than 1% for Pb and less than 0.05% for Po.

In contrast to Pb, Po exhibited more complex behavior at higher oxidation states. Pb was not observed to form species beyond PbF_2^+ , whereas PoF_3^+ was observed. The observation of PoF_3^+ and non-observation of PbF_3^+ is inline with the predicted lower fourth ionization energy of 39.6 eV for Po [33] compared to 42.3 eV for Pb [35] (see table 1). Interestingly, although PoF_2^+ formation was extremely rare, PoF_3^+ was observed at an intensity approximately 4 times higher than the upper limit for PoF_2^+ . This striking difference is suggestive that once PoF_2^+ is produced, the resulting $6p_{1/2}^1$ configuration of Po is highly unstable and reactive. Such that, the unpaired $6p_{1/2}$ electron can be readily oxidized to form PoF_3^+ (with a closed-shell $6s_{1/2}^2$ configuration), which is energetically more favorable. Notably, the potential closed-shell $6s_{1/2}^2$ of Po in PoF_3^+ would be the same as for Pb in PbF^+ , which was also found to be a preferred product for Pb. These results could be indicative of the difficulty of oxidizing the $6s_{1/2}^2$ electron pair to form higher-order fluoride species. Production of PoF_{4-5}^+ species would require sequential oxidation of the $6s_{1/2}^2$ pair, which appears to be prohibitively difficult.

The observed product distribution for Po provides preliminary evidence for the stabilization of the $6p_{1/2}$ orbital relative to the $6p_{3/2}$. This stabilization is likely driven by spin-orbit coupling effects, which are enhanced in heavy elements like polonium. To directly test this hypothesis, analogous measurements of tellurium (Te, $Z = 52$), Po's lighter homologue, would be particularly valuable. Because spin-orbit splitting is expected to be significantly weaker in Te than in Po (figure 1), a direct comparison of their TeF_n^+ and PoF_n^+ product distributions would isolate the effects of spin-orbit coupling on p-block element chemistry and provide definitive evidence for the role of relativistic effects in determining accessible oxidation states.

5. Implications for superheavy elements

For SHEs in the seventh row of the periodic table's p-block, the energy difference between the $7p_{1/2}$ and $7p_{3/2}$ orbitals is expected to be even more pronounced than for their sixth-row counterparts. (see figure 1). This enhanced spin-orbit splitting is expected to lead to a further breakdown of the periodic table's periodicity, with elements like flerovium ($Z = 114$) potentially behaving more like a noble gas than oganesson ($Z = 118$) [48, 49], as the filled $7p_{1/2}$ orbital could act as an 'inert pair'. Experimental gas-phase studies of SHEs, similar to the one reported here for polonium, could provide valuable insights into the oxidizability of the $7p_{1/2}$ orbital under room temperature conditions. For polonium's seventh-row counterpart livermorium (Lv, $Z = 116$), it is predicted that the splitting of the $p_{1/2}$ and $p_{3/2}$ orbitals is potentially three times greater than for polonium. Consequently, livermorium could exhibit a maximum oxidation state of +2, such that only LvF^+ would then be observed in a similar experiment to that reported here. Looking to other SHE, a stabilization of the $7p_{1/2}$ electron pair could limit the maximum oxidation state of moscovium ($Z = 115$), tennessine ($Z = 117$), and oganesson ($Z = 118$) to +1, +3, and +4, respectively. An experimental comparison of the distribution of fluoride species produced for SHE relative to their lighter sixth-row homologues would provide valuable insights into the evolution of spin-orbit coupling with increasing Z . Interestingly, the electron configuration of Mc^+ is analogous to that of atomic flerovium, featuring a closed $7p_{1/2}^2$ pair. It would be intriguing to investigate whether this pair is truly inert by examining the formation of McF^+ in a similar chemical reaction with C_3F_6 . However, if formed, McF^+ might be highly reactive and rapidly oxidized to McF_2^+ , similar to the facile production of PoF_3^+ from PoF_2^+ . Studies of SHE oxidation states would be highly valuable to elucidating their chemical properties and could, in turn, inform predictions regarding the chemical properties of the eighth-row elements yet to be added to the periodic table.

6. Conclusion

This study demonstrates the production and identification of polonium fluoride molecular cations and reveals how their chemistry compares to that of lead. The observed distribution of PoF_{1-5}^+ species provides insights as to the potential impact of relativistic effects, specifically, the stabilization of the $6p_{1/2}^2$

and $6s_{1/2}^2$ electron pairs, as evidenced by the limited formation of species beyond PoF_3^+ . Similar measurements with polonium's lighter homologue tellurium would be highly insightful. This experimental technique opens a pathway to investigate seventh-row spin–orbit coupling effects and their influence on superheavy element chemistry. Such studies will provide valuable insights into the chemical properties of future discovered elements, enabling predictions for those yet to be placed on the eighth row of the periodic table.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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