

EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

Letter of Intent to the ISOLDE and Neutron Time-of-Flight Committee

Protactinium chemistry at ISOLDE from external sources

September 22, 2023

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Abstract:

Systematic studies of protactinium molecules are a promising direction to elucidate the gradual change in actinide chemistry from a transition-metal-like behavior to one dominated by $5f$ electrons. Additionally, certain Pa molecules have been proposed for precision tests of the Standard Model. However, no radiogenic atomic or molecular beams of Pa have so far been produced via the ISOL method despite successful recent efforts in production of other light actinides. We propose to determine production efficiencies of Pa beams at ISOLDE using external samples of Pa atoms. Using the ISOLTRAP MR-ToF MS for identification, we propose to study the production of atomic and molecular beams of ^{231}Pa ($T_{1/2} = 3.26 \times 10^4$ y) before and after active fluorination with CF_4 .



Requested shifts: 11 shifts without protons using an external sample (delivered in 1 run over 1 year)

1 Motivation

Actinide chemistry remains an active research field with multiple open questions [1, 2, 3]. The occupation of both the $6d$ and $5f$ orbitals by valence-shell electrons leads to an interplay in the chemical properties of the actinides, between a behavior similar to the d -orbital-based transition metals and the $4f$ -driven lanthanide series [4, 5].

Due to relativistic effects and the imperfect screening of the nuclear charge, the $5f$ orbital gradually drops in energy as a function of atomic number Z . While it lies above $6d$ in thorium, it drops under $6d$ in uranium. In protactinium, the $5f$ and $6d$ orbitals cross and are nearly degenerate. As a result, the chemistry of protactinium is an interesting case to investigate the competing influence of $5f$ and $6d$ electrons in chemical bonding and the electron correlation energy.

Experimental studies in protactinium chemistry have focused mostly on the solid and liquid phases, with few gas-phase studies available in the actinide literature, where gas-phase knowledge is generally incomplete [6, 7]. The available information highlights the interesting case of protactinium, as PaO , PaO^+ , and PaO_2 possess the lowest ionization energies across all similar actinide molecules up to curium. At the same time, PaO_2 and PaO_2^+ have the largest bond dissociation enthalpy across similar neutral and cationic actinide dioxides [6]. In addition to the thermodynamic observables, gas-phase spectroscopy can provide a precise benchmark of quantum chemistry and thus lead to a microscopic understanding of actinide bonds [8, 9], as also recently demonstrated in the study of RaF at ISOLDE [10].

Protactinium molecules have recently also gathered interest as probes for precision tests of the Standard Model of physics. The existence of permanent electric dipole moments (EDMs) in quantum systems such as the electron, the neutron, and nuclei is a signature of time-reversal (T) violation in the fundamental forces [11, 12]. A measurement of their magnitudes in the laboratory is a direct measure of the level of T violation in the Universe, which is a key ingredient of understanding the baryon asymmetry problem [13].

Of all nuclei theoretically investigated across the chart of the nuclides [14, 15, 16] so far, ^{229}Pa ($t_{1/2}$ 1.5 days) is expected to possess the largest nuclear Schiff moment, which is a property closely related to the EDM [17]. Contrary to the nuclear EDM [18], the Schiff moment is experimentally accessible, but only upper bounds have been placed so far. The most sensitive experimental pathway to measuring the nuclear Schiff moment of ^{229}Pa is through ultra-high-precision molecular spectroscopy [19]. Prior to designing a precision search for nuclear T violation, however, laser spectroscopy of the proposed

protactinium molecules needs to be performed to confirm their favorable electronic structure and suitability for precision spectroscopy. These studies can be performed on molecules that contain the long-lived isotope ^{231}Pa .

ISOLDE possesses experimental setups that are well-equipped for production and spectroscopic studies of radioactive molecules, as demonstrated in recent years with molecules of radium, actinium, uranium, and thorium at ISOLTRAP [20] and CRIS [21, 22]. These works were enabled by a series of systematic yield studies of molecular beams produced from fluorinated UC_x and ThC_x targets. However, no protactinium molecules were observed and are likely not available with conventional thick-target production methods due to the very refractory nature of Pa. Thus, a different approach has to be followed to take advantage of the ISOLDE infrastructure for protactinium chemistry investigations.

A possible pathway is the delivery of protactinium molecules from an ISOLDE source, filled with externally produced ^{231}Pa samples, without proton irradiation and radiogenic in-target production. In collaboration with FRIB under the Batch Mode Ion Source (BMIS) project [23], the method has been successfully used to provide beams of Be, Si, Al, Cr, Fe, and As from external samples. External samples have also been used to extract ^{225}Ac at MEDICIS [24]. Confirming the feasibility of this approach at ISOLDE requires an investigation of the molecular beams that can be produced using external samples before and after exposing the sample to a reacting agent, such as CF_4 , as well as an initial determination of the extraction efficiency. Using the ISOLTRAP MR-ToF MS [25], the Pa molecules that can be delivered by the ISOLDE front end for chemistry research can be identified. Moreover, the operation of ISOLDE sources with external samples can also enable a direct efficiency comparison between the ISOLDE front end and ion sources at offline laboratories, such as the RILIS-based atomic beam unit at Mainz that already performed studies of Pa [26] and the TACTICa laser ablation source [27].

2 Method

The use of a macroscopic protactinium sample deposited on a substrate foil as a source for ion production was demonstrated in Ref. [26], in which ^{231}Pa atoms dissolved in HNO_3 solution were deposited on a Zr foil, followed by heating in a tantalum oven leading to atomic vapor and laser resonance ionization of the neutral atomic beam. Despite the refractory properties of protactinium, the study demonstrated that heating in an atomic beam unit similar to an ISOLDE source was able to provide sufficient rates of resonantly laser-ionized protactinium for experimental studies.

Molecular formation has been pursued at ISOLDE to extract volatile compounds of otherwise refractory, release-limited species such as B, C [28, 29, 30, 31, 32], typically by injection of a reactive gas. This approach has also been applied in offline ISOLDE target and ion source units with external samples deposited on foils, to similar effect [23]. The operation of the BMIS using molecular extraction also enabled extraction of

refractory species (Be, Si) which are typically challenging to produce. In previous tests using laser ionization of atomic ion beams and molecular extraction by fluorination of UC_x and ThC_x targets at ISOLDE [33, 34], no protactinium atomic or molecular ions were identified with the ISOLTRAP MR-ToF MS.

With the interest in protactinium molecules in mind, we propose to perform tests for the production of molecular beams from a sample of ^{231}Pa atoms dissolved in HNO_3 and deposited on a Zr foil, delivered by the Johannes Gutenberg-Universität (JGU) Mainz. Considering a possible extraction efficiency of 0.5% given the refractory nature of protactinium, a sample of 10^{15} atoms (670 Bq, 67% of the exemption limit) could provide 100 fA as a minimum detectable amount of ions to be maintained throughout the experiment, assuming the population to be split across six molecular sidebands. By placing the sample in the target container of an ISOLDE target unit equipped with a VD5 ion source and a calibrated leak for gas injection, we propose to identify the resulting beam compositions at ISOLDE using the ISOLTRAP MR-ToF MS, with the intent to provide experimental rates of protactinium molecular ion beams. The capabilities of this technique for molecular production and identification have already been demonstrated in the case of other actinide molecules [20].

Prior to injecting CF_4 , we can produce and identify oxide compounds formed within the nitrate sample and the target unit due to oxygen-containing impurities, while using the fluorinating agent we can investigate the production of fluorides and oxyfluorides in a controlled manner.

This approach will allow quantification of the available yields and ion beam purity for future spectroscopic studies, as well as characterize a new mode of operation for the ISOLDE facility regarding beam delivery from external sources for otherwise inaccessible elements. Efficiency estimates from this experiment for the different molecular sidebands will provide further information towards the delivery of other beams using this technique.

3 Request

We request a total of 11 shifts without protons for the production and identification of protactinium molecules using a sample of 10^{15} ^{231}Pa atoms dissolved in HNO_3 and deposited on a Zr foil, delivered by the JGU Mainz. We request the use of an ISOLDE target and ion-source unit with a VD5 ion source and a CF_4 leak. Due to the refractory nature of protactinium, prototype designs implementing heat shields for target temperature homogeneity and transfer line heating would be beneficial.

Of the 11 shifts, 1 shift is request for preparation and set up of the equipment, including beam tuning to ISOLTRAP and optimization of the MR-ToF MS, 5 are requested for the production and identification of oxygen-containing molecules prior to the injection of CF_4 . The remaining 5 shifts are requested for the production and identification of fluorine-containing molecules.

Table 1: Breakdown of shift request

	Measurement	Shifts
Preparation & optimization	Heating	1
^{231}Pa in HNO_3/Zr	Oxide identification	5
^{231}Pa in HNO_3/Zr	CF_4 injection, fluoride identification	5
Total		11

Summary of requested shifts: 11 shifts without protons using an external sample placed in an ISOLDE target unit with a VD5 ion source and a CF_4 leak.

The proposed work falls within the scope of the previously endorsed Letter of Intent CERN-INTC-2021-017 / INTC-I-227 titled *Radioactive molecules at ISOLDE*. The proposed project has received funding from the European’s Union Horizon 2020 Research and Innovation Programme under grant agreement number 861198 project ‘LISA’ (Laser Ionization and Spectroscopy of Actinides) Marie Skłodowska-Curie Innovative Training Network (ITN).

References

- [1] M. Pepper and B. Bursten. The electronic structure of actinide-containing molecules: a challenge to applied quantum chemistry. *Chemical Reviews*, 91(5):719–741, 7 1991.
- [2] N. Kaltsoyannis. Does covalency increase or decrease across the actinide series? Implications for minor actinide partitioning. *Inorganic Chemistry*, 52(7):3407–3413, 2013.
- [3] T. Vitova, I. Pidchenko, D. Fellhauer, P. S. Bagus, Y. Joly, T. Pruessmann, S. Bahl, E. Gonzalez-Robles, J. Rothe, M. Altmaier, M. A. Denecke, and H. Geckeis. The role of the 5f valence orbitals of early actinides in chemical bonding. *Nature Communications*, 8(1):16053, 2017.
- [4] M. Neidig, D. Clark, and R. Martin. Covalency in f-element complexes. *Coordination Chemistry Reviews*, 257(2):394–406, 2013.
- [5] S. Cary, M. Vasiliu, R. Baumbach, J. Stritzinger, T. Green, K. Diefenbach, J. Cross, K. Knappenberger, G. Liu, M. Silver, A. DePrince, M. Polinski, S. Van Cleve, J. House, N. Kikugawa, A. Gallagher, A. Arico, D. Dixon, and T. Albrecht-Schmitt. Emergence of californium as the second transitional element in the actinide series. *Nature Communications*, 6(1):6827, 2015.
- [6] J. Marçalo and J. K. Gibson. Gas-Phase Energetics of Actinide Oxides: An Assessment of Neutral and Cationic Monoxides and Dioxides from Thorium to Curium. *The Journal of Physical Chemistry A*, 113(45):12599–12606, 11 2009.

- [7] M. C. Heaven, J. K. Gibson, and J. Marçalo. Molecular Spectroscopy and Reactions of Actinides in the Gas Phase and Cryogenic Matrices. In Lester R Morss, Norman M Edelstein, and Jean Fuger, editors, *The Chemistry of the Actinide and Transactinide Elements*, pages 4079–4156. Springer Netherlands, Dordrecht, 2011.
- [8] Michael C Heaven. Probing actinide electronic structure using fluorescence and multi-photon ionization spectroscopy. *Physical Chemistry Chemical Physics*, 8(39):4497–4509, 2006.
- [9] M. C. Heaven, B. J. Barker, and I. O. Antonov. Spectroscopy and structure of the simplest actinide bonds. *Journal of Physical Chemistry A*, 118(46):10867–10881, 2014.
- [10] M Athanasakis-Kaklamanakis, S G Wilkins, L V Skripnikov, Á Koszorús, A A Breier, M Au, I Belosevic, R Berger, M L Bissell, A Borschevsky, A Brinson, K Chrysalidis, T E Cocolios, R P De Groote, A Dorne, C M Fajardo-Zambrano, R W Field, K T Flanagan, S Franchoo, R F Garcia Ruiz, K Gaul, S Geldhof, T F Giesen, D Hanstorp, R Heinke, T A Isaev, A A Kyuberis, S Kujanpää, L Lalanne, G Neyens, M Nichols, L F Pasteka, H A Perrett, J R Reilly, S Rothe, S M Udrescu, B van den Borne, Q Wang, J Wessolek, X F Yang, C Zülch, and ISOLDE. Pinning down electron correlations in RaF via spectroscopy of excited states. *Under review, arXiv:2308.14862*, 2023.
- [11] M. Pospelov and A. Ritz. Electric dipole moments as probes of new physics. *Annals of Physics*, 318(1):119–169, 2005.
- [12] T. E. Chupp, P. Fierlinger, M. J. Ramsey-Musolf, and J. T. Singh. Electric dipole moments of atoms, molecules, nuclei, and particles. *Reviews of Modern Physics*, 91(1):15001, 1 2019.
- [13] A. Sakharov. Violation of CP invariance, C asymmetry, and baryon asymmetry of the universe. *Soviet Physics Uspekhi*, 34(5):392, 1991.
- [14] V. V. Flambaum and V. A. Dzuba. Electric dipole moments of atoms and molecules produced by enhanced nuclear Schiff moments. *Physical Review A*, 101:042504, 4 2020.
- [15] V. V. Flambaum and H. Feldmeier. Enhanced nuclear Schiff moment in stable and metastable nuclei. *Physical Review C*, 101(1):1–11, 2020.
- [16] F Dalton, V V Flambaum, and A J Mansour. Enhanced Schiff and magnetic quadrupole moments in deformed nuclei and their connection to the search for axion dark matter. *Physical Review C*, 107(3):35502, 3 2023.
- [17] V. V. Flambaum and J. S.M. Ginges. Nuclear Schiff moment and time-invariance violation in atoms. *Physical Review A*, 65(3):9, 2002.
- [18] L. I. Schiff. Measurability of nuclear electric dipole moments. *Physical Review*, 132(5):2194–2200, 1963.

- [19] G. Arrowsmith-Kron, M. Athanasakis-Kaklamanakis, M. Au, J. Ballof, R. Berger, A. Borschevsky, A. A. Breier, F. Buchinger, D. Budker, L. Caldwell, C. Charles, N. Dattani, R. P. de Groote, D. DeMille, T. Dickel, J. Dobaczewski, Ch. E. Düllmann, E. Eliav, J. Engel, M. Fan, V. Flambaum, K. T. Flanagan, A. Gaiser, R.F. Garcia Ruiz, K. Gaul, T. F. Giesen, J. Ginges, A. Gottberg, G. Gwinner, R. Heinke, S. Hoekstra, J. D. Holt, N. R. Hutzler, A. Jayich, J. Karthein, K. G. Leach, K. Madison, S. Malbrunot-Ettenauer, T. Miyagi, I. D. Moore, S. Moroch, P. Navrátil, W. Nazarewicz, G. Neyens, E. Norrgard, N. Nusgart, L. F. Pašteka, A. N. Petrov, W. Plass, R. A. Ready, M. P. Reiter, M. Reponen, S. Rothe, M. Safronova, C. Scheidenberger, A. Shindler, J. T. Singh, L. V. Skripnikov, A. V. Titov, S.M. Udrescu, S. G. Wilkins, and X. Yang. Opportunities for Fundamental Physics Research with Radioactive Molecules. *arXiv*, 2302.02165, 2023.
- [20] M. Au, M. Athanasakis-Kaklamanakis, L. Nies, J. Ballof, R. Berger, K. Chrysalidis, P. Fischer, R. Heinke, J. Johnson, U. Köster, D. Leimbach, B. Marsh, M. Mougeot, B. Reich, J. Reilly, E. Reis, M. Schlaich, Ch. Schweiger, L. Schweikhard, S. Stegemann, J. Wessolek, F. Wienholtz, S. G. Wilkins, W. Wojtaczka, Ch. E. Düllmann, and S. Rothe. In-source and in-trap formation of molecular ions in the actinide mass range at CERN-ISOLDE. *Nucl. Instrum. Methods B*, 541:375–379, 2023.
- [21] R. F. Garcia Ruiz, R. Berger, J. Billowes, C. L. Binnersley, M. L. Bissell, A. A. Breier, A. J. Brinson, K. Chrysalidis, T. E. Cocolios, B. S. Cooper, K. T. Flanagan, T. F. Giesen, R. P. de Groote, S. Franchoo, F. P. Gustafsson, T. A. Isaev, A. Koszorus, G. Neyens, H. A. Perrett, C. M. Ricketts, S. Rothe, L. Schweikhard, A. R. Vernon, K. D. A. Wendt, F. Wienholtz, S. G. Wilkins, and X. F. Yang. Spectroscopy of short-lived radioactive molecules. *Nature*, 581(May):396–400, 2020.
- [22] M. Athanasakis-Kaklamanakis, S. G. Wilkins, M. Au, R. Berger, A. Borschevsky, K. Chrysalidis, T. E. Cocolios, R. P. de Groote, Ch. E. Duellmann, K. T. Flanagan, R. F. Garcia Ruiz, S. Geldhof, R. Heinke, T. A. Isaev, J. Johnson, A. Kiuberis, A. Koszorus, L. Lalanne, M. Mougeot, G. Neyens, L. Nies, J. Reilly, S. Rothe, L. Schweikhard, A. R. Vernon, and X. F. Yang. Laser ionization spectroscopy of AcF, CERN-INTC-2021-053, INTC-P-615. Technical report, CERN, 2021.
- [23] C. Sumithrarachchi, Y. Liu, S. N. Rogers, S. Schwarz, G. Bollen, and N. Gamage. The new Batch Mode Ion Source for stand-alone operation at the Facility for Rare Isotope Beams (FRIB). *Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms*, 541(March):301–304, 2023.
- [24] J. D. Johnson, M. Heines, F. Bruchertseifer, E. Chevallay, T. E. Cocolios, K. Dockx, C. Duchemin, S. Heinitz, R. Heinke, S. Hurier, L. Lambert, B. Leenders, H. Skliarova, T. Stora, and W. Wojtaczka. Resonant laser ionization and mass separation of ^{225}Ac . *Scientific Reports*, 13(1), 12 2023.
- [25] R. N. Wolf, F. Wienholtz, D. Atanasov, D. Beck, K. Blaum, Ch. Borgmann, F. Herfurth, M. Kowalska, S. Kreim, Yu. A. Litvinov, D. Lunney, V. Manea, D. Neidherr, M. Rosenbusch, L. Schweikhard, J. Stanja, and K. Zuber. ISOLTRAP’s multi-

- reflection time-of-flight mass separator/spectrometer. *International Journal of Mass Spectrometry*, 349-350:123–133, 2013.
- [26] Pascal Naubereit, Tina Gottwald, Dominik Studer, and Klaus Wendt. Excited atomic energy levels in protactinium by resonance ionization spectroscopy. *Physical Review A*, 98(2):1–6, 2018.
- [27] K. Groot-Berning, F. Stopp, G. Jacob, D. Budker, R. Haas, D. Renisch, J. Runke, P. Thörle-Pospiech, Ch. E. Düllmann, and F. Schmidt-Kaler. Trapping and sympathetic cooling of single thorium ions for spectroscopy. *Phys. Rev. A*, 99:023420, Feb 2019.
- [28] Jochen Ballof. *Radioactive Molecular Beams at CERN-ISOLDE*. PhD thesis, JGU Mainz, 2021.
- [29] J. Ballof, C. Seiffert, B. Crepieux, Ch. E. Düllmann, M. Delonca, M. Gai, A. Gottberg, T. Kröll, R. Lica, M. Madurga Flores, Y. Martinez Palenzuela, T. M. Mendonca, M. Owen, J. P. Ramos, S. Rothe, T. Stora, O. Tengblad, and F. Wienholtz. Radioactive boron beams produced by isotope online mass separation at CERN-ISOLDE. *The European Physical Journal A*, 55(5):65, 2019.
- [30] U. Köster, P. Carbonez, A. Dorsival, J. Dvorak, R. Eichler, S. Fernandes, H. Frånberg, J. Neuhausen, Z. Novackova, R. Wilfinger, and A. Yakushev. (Im-) possible ISOL beams. *European Physical Journal: Special Topics*, 150(1):285–291, 2007.
- [31] R. Kirchner. Release studies of elementary and metal-fluoride ions at the GSI on-line mass separator. *Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms*, 126(1-4):135–140, 1997.
- [32] R. Eder, H. Grawe, E. Hagebø, P. Hoff, E. Kugler, H. L. Ravn, and K. Steffensen. The production yields of radioactive ion-beams from fluorinated targets at the ISOLDE on-line mass separator. *Nuclear Inst. and Methods in Physics Research, B*, 62(4):535–540, jan 1992.
- [33] M. Au, B. Reich, S. Rothe, and V. Fedosseev. Pre-irradiated target investigations under the LISA ITN project at ISOLDE. Technical report, CERN, March 2021.
- [34] M. Au, M. Athanasakis-Kaklamanakis, J. Ballof, R. Heinke, B. Marsh, M. Mougeot, L. Nies, B. Reich, S. Rothe, and S. Stegemann. Target and ion source development for laser ionization and spectroscopy of the actinides. Technical report, CERN, Dec 2021.
- [35] C. Duchemin, L. Lambert, and R. Martins. Steps to load an external source boat inside a MEDICIS target container. Technical report, CERN, August 2020.
- [36] C. Duchemin. 2023 operation with external sources - safety forms . Technical report, CERN, July 2023.

DESCRIPTION OF THE PROPOSED EXPERIMENT

Please describe here below the main parts of your experimental set-up:

Part of the experiment	Design and manufacturing
ISOLTRAP offline ion source, ISOLTRAP MR-ToF MS	<input checked="" type="checkbox"/> To be used without any modification <input type="checkbox"/> To be modified
offline tests: 1 x ^{231}Pa sample (8×10^{13} atoms, 53 Bq, < 1 LA)	<input type="checkbox"/> Standard equipment supplied by a manufacturer <input checked="" type="checkbox"/> CERN/collaboration responsible for the design and/or manufacturing
online tests: 1 x ^{231}Pa sample (10^{15} atoms 670 Bq at 67 % of exemption limit)	<input type="checkbox"/> Standard equipment supplied by a manufacturer <input checked="" type="checkbox"/> CERN/collaboration responsible for the design and/or manufacturing

HAZARDS GENERATED BY THE EXPERIMENT

Additional hazard from flexible or transported equipment to the CERN site:

Domain	Hazards/Hazardous Activities		Description
Radiation protection	Shipping and handling radioactive sources	<input checked="" type="checkbox"/>	according to [35, 36]