

Nuclear Physics Tools for the Study of Molecular Ions

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ORNL is managed by UT-Battelle, LLC for the US Department of Energy



About me:





Outline

- Multidisciplinary research and challenges
- Signatures of New Physics
- Nuclear Physics Tools applied to the study of Atoms and Molecules (and back)
- Molecular ions (positive and negative)
- Simple molecules (discovery of ${}^{12}CH_2$ ++ and ${}^{13}CH$ ++ and others)
- Clusters
- Actinides



Current interests in v science

Experimentally determine the fundamental properties of ٠ neutrinos and their interactions with matter

National Laboratory

- Develop the best tools and detector technologies to support ٠ neutrino research.
- •



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LEGENDtowards 1 tonne ⁷⁶Ge experiment

ORNL/UTK Students

High efficiency laser resonance ionization of plutonium Science Reports (Nature) 2021

A Plutonium Needle in a Haystack

New results could significantly improve resonance ionization mass spectrometry ultra-trace analysis of plutonium isotopes.



Laboratories

Home **Science Features** Home | Science Features | Science Highlights

About

Science Highlights

DOE/NP

Flisa Romero

Image courtesy of Elisa Romero-Romero

Resonance ionization mass spectrometry is a highly selective and sensitive technique for analyzing extremely small amounts of elements. It uses tunable lasers to ionize atoms of the desired elements

> Final Measurement of the 235U Antineutrino Energy Spectrum with the PROSPECT-I **Detector at HFIR** PRL 2023

Highlights





Jeremy Lu



Diego Venegas



PROSPECT **Characterizes the Footprint of Neutrinos**

Experiment at Oak Ridge National Laboratory's High Flux Isotope Reactor precisely measures the antineutrino energy spectrum.

DOE/HEP



Blaine Heffron

First Detection of CEvNS



Jun 2016

Aug 2016 Oct 2016

Time

Dec 2016

Energy

Coherent Elastic neutrino-Nucleus Scattering (CEvNS)

A neutrino scatters on a nucleus via exchange of a Z, and the nucleus recoils as a whole; coherent up to $E_v \sim 50$ MeV

 Z^0

D.Z. Freedman PRD 9 (1974) Submitted Oct 15, 1973

V.B.Kopeliovich & L.L.Frankfurt JETP Lett. 19 (1974) Submitted Jan 7, 1974



CEvNS cross-section is large!

$$\frac{d\sigma}{d\Omega} = \frac{G^2}{4\pi^2} k^2 (1 + \cos\theta) \frac{(N - (1 - 4\sin^2\theta_W)Z)^2}{4} F^2(Q^2) \propto N^2$$

CEVNS cross section is well calculated in the Standard Model

Novel Method for the study of coherent scattering

- Omar Miranda
- Gonzalo Sanchez

The Weizmann Award to the best doctoral theses carried out in Mexico by young researchers

PHYSICAL REVIEW D Highlights About Editorial Team Recent Accepted Collections Authors Referees Search Press Open Access Access by Oak Ridge National Laboratory Go Mobile » Novel approach for the study of coherent elastic neutrino-nucleus

scattering

A. Galindo-Uribarri, O. G. Miranda, and G. Sanchez Garcia Phys. Rev. D **105**, 033001 – Published 3 February 2022



Gonzalo Sanchez





PHD, CINVESTAV (Mexico) 2022





COHERENT scattering – Relative measurements

- •Experiment with identical detectors
- •Different isotopic composition
- •Use enriched isotopes
- •Perform **simultaneous** measurements
- •Cancelation of some systematic errors

•Use odd	A nuc	lei (Axial)
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Mass	Natural Abundance	Decay Mode	Nuclear Spin
70	20.57%	STABLE	0+
72	27.45%	STABLE	0+
73	7.75%	STABLE	9/2+
74	36.50%	STABLE	0+
76	7.73%	STABLE	0+





Nuclear Physics Tools - Accelerators

Electrostatic Tandem Accelerator

Linear Accelerators







Cyclotrons



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Nuclear Physics Tools – Ion Filters





NP Tools - Ion Sources

A typical sputter source heated Cs reservoir, an ionizer producing a focused Cs⁺ beam at the sample, and an extraction electrode to accelerate and focus secondary negative ions from the sample into the injection beamline.



Important issues for AMS: Memory effects Multiple samples High currents





NP Tools- Specific Energy Loss for pairs of isobars



MeV energies

Interaction with detector

Example: Isobutane

Use of Bragg detectors digitize the "track"



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NP tools - Foil induced Coulomb explosion of molecules

Direct imaging of the molecular structure

Technique pioneered by Argonne, Lyon and Rehovot groups using small accelerators

fast molecule





PHYSICAL REVIEW A 90, 052503 (2014)

Accelerator Mass Spectrometry



NP tools - People - AMS pioneers



Study of ¹²CH₂²⁺ and other doubly charged molecules

THE ¹²CH²⁺ MOLECULE AND RADIOCARBON DATING BY ACCELERATOR MASS SPECTROMETRY

NIM B5 (1984) 208

H.W. LEE, A. GALINDO-URIBARRI *, K.H. CHANG, L.R. KILIUS and A.E. LITHERLAND

ISOTRACE Laboratory, University of Toronto, Toronto, Ontario M5S 1A7, Canada

The ${}^{12}CH_2^{2+}$ molecule has been studied and it was found that the molecule can be effectively eliminated thus allowing detection of ${}^{14}C^{2+}$ at low terminal voltages of a tandem accelerator. Some implications of this discovery for radiocarbon dating are discussed.



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Volume 83, Issue 7

1 October 1985



RESEARCH ARTICLE | OCTOBER 01 1985

Beams of doubly ionized molecules from a tandem accelerator

A. Galindo-Uribarri; H. W. Lee; K. H. Chang

Check for updates

J. Chem. Phys. 83, 3685–3693 (1985) https://doi.org/10.1063/1.449123 Article history ©

We report the observation of 3–4 MeV beams of several species of small doubly charged molecules ($^{10}B^{11}B^{++}$, $^{10}B^{++}_{2}$, $^{11}B^{12}C^{++}$, $^{9}Be^{14}N^{++}$, $^{12}C^{13}C^{++}$, $^{12}C^{13}C^{++}$, $^{12}C^{14}N^{++}$, $^{12}C_{2}H^{++}$, $^{12}CH^{++}_{2}$, $^{9}Be^{16}O^{++}$, $^{10}B^{16}O^{++}$) emerging from a tandem accelerator. These observations significantly increase the number of such molecules known. All are probably produced in metastable states with lifetimes longer than 1 µs. Substantial fluxes (>10⁸ molecules per second was shown for CN⁺⁺) of these doubly charged molecules were obtained and they were identified by observing the fragmentation of molecular ions after passing through the production of molecular ions after passing through the production of 10⁻⁴ in producing mass 25 molecules are observed to decay in flight. An efficiency of 10⁻⁴ in producing mass 25 molecules ($^{12}C^{13}C^{++} + {}^{12}C_{2}H^{++}$) has been measured. Advantage is taken of the existence of "atomic interference free" mass regions, where no atomic negative ions are formed, therefore allowing the production of pure molecular beams. Some implications of this work for accelerator mass spectrometry (AMS) are discussed. An application of doubly positive charged molecules in a search for doubly negative charged molecules was made, establishing an upper limit of 1:10¹⁰ of $^{10}B^{11}B^{-/10}B^{11}B^{-}$ and of 1:10⁹ of $^{12}C^{13}C^{-}$ $^{1/2}C^{13}C^{-}$

Only about 3 cases reported Molecular Spectra ...G. Herzberg

- Vibrationally hot (T ~ 5000 ^OK) XY⁻ molecules produced in the sputtering process on solids charge change to XY⁺⁺ after MeV collisions with argon gas.
- Intensities > 10⁸ CN⁺⁺ per second
- "Atomic interference free" mass regions where no atomic negative ions are formed



NP Tools - AMS









Holifield Radioactive Ion Beam Facility (HRIBF): AMS and RIMS at ORNL





20

AMS and Radioactive Ion Beams (RIB)

Most interesting RIBs are short-lived ${}^{17}F(t_{1/2} = 65 s)$

- Common problems/needs:
 - Production
 - Isobar removal
 - Stable machine operation
 - Low intensity beam diagnostics

In AMS: long-lived species ${}^{36}CI (t_{1/2} = 3.01 \times 10^{6} a)$

- Good detection tools
 - Bragg Detector
 - Projectile X-ray
 - TOF
 - 2D channel Plates
 - Gas filled magnet
 - Beam monitors

We have concentrated in:

Development of AMS methods. Pilot experiments. Proof-of-principle tests

Methodology Transmission Ion Optics Detection Systems



21

NP Tools – AMS and Radioactive Ion Beams



P. A. Hausladen et al., NIM B 223 (2004) 176 and IJMS 251, 2-3 (2006)119

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AMS Mass Measurements





Electron affinities across the periodic table.



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Experimental Setup - Photodetachment



Photodetachment





Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms Volume 268, Issues 7–8, April 2010, Pages 834-838



Selective isobar suppression for accelerator mass spectrometry and radioactive ion-beam science

A. Galindo-Uribarri ^{a, b} 옷 쩓, C.C. Havener ^a, T.L. Lewis ^b, Y. Liu ^a

detection limit: 2 pA

- No significant reduction of Cl observed.
- S suppression is about 1% when cooler is not used.



AMS measurement ³⁶CI- Pushing the limits of AMS by an order of magnitude



³⁶Cl in seawater samples from around the world: comparison



Measurement of ³⁶Cl in seawater samples

A. G-U, et al. NIM B 259 (2007)123



Sputtered molecular fluoride ions XF_n⁻

Super-halogens.

Have electron affinities much higher than those of the halogens themselves and so are of great interest to AMS

Their great electron binding energies make it possible to produce large currents with Cs⁺ sputter sources

A systematic study of anions of the type XFn (n being the number of F atoms) was therefore undertaken monitoring the secondary-ion flux in a mass spectrometer.



***SmFn⁻ mass scans**

The sputtered flux is composed of atoms as well as molecules,

the production of an abundant flux of anions by sputtering the target with Cs+ ions is a prerequisite for the ultrahigh sensitivity of AMS

Some molecular ions were found to be emitted in sputtering with (much) higher intensity

Their possible formation and ionization processes and relative abundances are still not known in detail.



The correctness of the isotopic patterns was checked



Use of Molecules (AIN) for ²⁶Al detection

- Develop a new and improved technique for the ultrasensitive AMS measurements of ²⁶Al for geological samples
- Demonstrating other source materials can outperform Al_2O_3



Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms Volume 361, 15 October 2015, Pages 281-287

The use of aluminum nitride to improve Aluminum-26 Accelerator Mass Spectrometry measurements and production of Radioactive Ion Beams

<u>Meghan S. Janzen ^{a b c}, Alfredo Galindo-Uribarri ^{a b c} A, Yuan Liu ^a,</u> <u>Gerald D. Mills ^a, Elisa Romero-Romero ^{a c}, Daniel W. Stracener ^a</u>





Al2O3





Clusters

- How big?
- Can we form cluster beams of negative ions?
- How intense?
- At what energy?
- How fragile?

31

- Can we form clusters of same isotope?
- Do the intensities reflect some structure?
- How fast the current drops as a function of n?
- How do the atoms organize?

• Samples of Cu, ultra-pure Cu, ⁶³Cu, ⁶⁵Cu, Au, C



Ultrapure Cu Mass Scan



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32

Mass Spectra of Negative Clusters



Binomial Distributions

intensities of the ⁶³Cux⁶⁵Cun-x relative The compositions follows a binomial distribution

$$F(n,x) = p^{x}(1-p)^{n-x} \frac{n!}{x!(n-x)!}$$

p= 0.6917, the natural abundance of Cu-63





Power Law Dependence

The intensity of sputtered Cu clusters decreases with size n and follows a power law dependence



 $Y(n) \propto n^{-\alpha}$

We learned how to operate the Cs source to optimize the production of clusters relative to atomic ions



Clusters Search

• We continued with clusters in Au and C





Applications e.g. Biological samples, semiconductors, etc.



Winograd, N. (2005). Analytical Chemistry, 77(7), 142-A.



Injector for Radioactive Ion Species 2 (IRIS 2)

FC 3



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Electroformed Cu

- In typical materials U and Th decay-chain contaminants are found at levels of µg/g to ng/g, which produces unacceptable backgrounds.
- Electroforming copper in a carefully-controlled and clean environment allows one to produce copper with U and Th with ultra-low levels.
- Standard conventional assay techniques are far from being able to reach the required sensitivity.





²⁴⁴Pu and Accelerator Mass Spectrometry



A. Wallner^{1,2}, T. Faestermann³, J. Feige², C. Feldstein⁴, K. Knie^{3,5}, G. Korschinek³, W. Kutschera², A. Ofan⁴, M. Paul⁴, F. Quinto^{2,†}, G. Rugel^{3,†} & P. Steier²

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Signal consists of two counts! Cs-Sputtering source for actinides of the order of 0.1-1% efficiency Motivation for a more efficient method for trace analysis ²⁴⁴Pu half-life: T1/2= 80.8 million years



Ultrapure Cu with AMS at ANU





- We tuned the low energy with ${}^{63}Cu_{3}{}^{65}Cu$
- Use of charge state +5 and TOF system
- We observed events of Th and U in ultrapure Cu







²³⁸UO⁻ ²³⁸U⁶³Cu⁻

²³²ThO⁻

²³²Th⁶³Cu⁻

⁶³Cu₃⁶⁵Cu⁻

Resonant Ionization Mass Spectrometry

Three Step Resonant Ionization schemes



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43



1 mg plutonium 30 μCi













Sample wrapped in Zr foil of \sim 4 x 4 x 0.025 mm

Level schemes search Sample size: 40 µg



Efficiency Measurement

Measured Efficiency: 51% ± 4% !!

• Sample: 4 µg Pu(10¹⁶ atoms) wrapped in Zr foil







45



New Brunswick Laboratory

U.S. Department of Energy



Converging series Rydberg states - IP

The most precise method for determining IPs is the analysis of the converging series of atomic energy levels with a high principal quantum number n, known as Rydberg states. The Rydberg series of an atom can be observed in the ionization spectrum of the final transition of a step-wise resonant ionization scheme.



Observed Rydbergs



Scheme A

MMM

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48

Physical and Chemical methods and techniques in AMS

- Negative atomic ion properties:¹⁴N⁻ for ¹⁴C⁻, ²⁶Mg⁻ for ²⁶Al⁻ and ¹²⁹Xe⁻ for ¹²⁹l⁻
- Negative molecular ion properties PuF4⁻ and UF5⁻
- Fully stripped ions followed by magnetic analysis
- Selective isobar suppression for AMS and RIB science using photodetachment
- Gas-filled magnets
- Projectile HI X-ray emission
- TOF
- dE/dx, range (Bragg detectors, multianode IC, bolometers)
- Selective ion-gas reactions at eV energies in a radio-frequency quadrupole cell to selectively attenuate both atomic and molecular isobars (IsoTrace; Isobarex)
- LASIS: The laser assisted sputter ion source
 - John S. Vogel (LLNL-AMS), NIM 438 (2019)
 - o O. Tarvainen, et al., (Jyvaskyla) J. Appl. Phys. 128 (2020) 094903











HFIR and REDC enable heavy element production at ORNL

- HFIR and REDC began operation in 1965 and 1966
- Operation is expected to continue at least until 2040
- High-end aspects of isotope production (heavy actinides, specialty medical isotopes), neutron scattering, and materials irradiation
- Unique capabilities for radioisotope separations (>400 isotope shipments annually to universities, hospitals, industry, and other research institutions)

Radiochemical Engineering Development Center Unique capabilities for radiochemical processing and related R&D

- Heavily shielded hot cells for radiation control and alpha containment
- Shielded caves for radiochemical processing and R&D
- Glove box labs for final product purification and R&D
- Radiochemical labs for sample preparation and analysis
- Cold labs for chemical make up, cold testing, and target fabrication



REDC is fully utilized for research and production for industrial, medical, and research partners



51

Shielded cave set up for dissolution



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²²⁶Ra handling/processing at ORNL

- In 2016, ORNL started a focused effort to recover ²²⁶Ra from legacy medical devices • (waste items)
 - The recovery and purification of ²²⁶Ra is performed in hot cells located at ORNL
 - This material is used mainly for production of medical isotopes at HFIR (228 Th and 227 Ac)
- ²²⁶Ra is available from the DOE Isotope Program (isotopes.gov)
- ²²⁶Ra has also been used at ORNL for other experiments •
- The ORNL team has experience with packaging ²²⁶Ra salts (nitrate or carbonate) for transfer on-site and for off-site transportation



²²⁶ Ra and the ²³⁸U Decay Chain

- ²²⁶Ra is a decay product of ²³⁸U
- Long half life ($t_{1/2} = 1600$ years)
- Decays by alpha emission to 222 Rn ($t_{1/2}$ = 3.8 days)
- ²²²Rn subsequently decays by alpha/beta emission via shortlived daughters to ²¹⁰Pb
- Radon is a gas and contributes to emissions from this process
- The exhaust stack is monitored and emissions are reportable



Legacy Radium Medical Devices



Sources contain various amounts of ²²⁶Ra (1 mCi up to 100 mCi) Devices are mechanically opened, and radium is chemically dissolved from the fragments





²²⁶Ra purification is performed in a hot cell facility at ORNL



Cherenkov radiation from dispensed ²²⁶Ra in glass vials (1 mCi each)





Use of Electrostatic Rings ?



ELISA Aarhus

CSR



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Astrophysical interest in H₃⁺





• The triatomic hydrogen ion still poses great experimental challenges.



Polarized Targets for RIBs – ORNL/PSI



Dynamic Nuclear Polarization Technique
Thickness ~ 0.1 - 20 mg/cm² Polystyrene
Low temperatures : T = 225 mK ,
High Magnetic Fields : B = 2.5 T

Juan Pablo Urrego-Blanco Ph.D. UTK



Shell Oil Chairman's Award 2017

Target is contained in a superfluid helium leak tight cell with 500 nm thick Si_3N_4 windows. Polarization is sampled in real time with an NMR coil attached to the target.

Proof of Principle at PSI (Switzerland) using elastic scattering:

$$\overrightarrow{p}({}^{12}C,{}^{12}C)p$$
 at 38 MeV

J.P. Urrego-Blanco et al., Nucl. Instr. and Meth. B 261 (2007) 1112



CONCLUSIONS

Demonstrated a method to detect Th and U in ultrapure Cu using AMS Established the highest efficiencies on Th, U and Pu and the highest sensitivity using RIMS

Determined a new value of IP for plutonium significantly more accurate than the NIST value



Summary

- Heavy nuclei with static octupole deformations, such as Fr, Ra, Th, Pa, and others, can have hadronic CP violation sensitivity enhancements up to a thousandfold larger than spherical nuclei. Combined with relativistic enhancements from their high mass, molecular species with deformed nuclei can be up to 10⁶ times more intrinsically sensitive than the current atomic Hg, which is the most sensitive atomic or molecular hadronic CPV experiment.
- Efficient and ultra-sensitive analysis of actinides for underground physics
- Spectroscopy studies to search for efficient ionization schemes for U, Th and Pu using RILIS
- Overall efficiency of 51% for Pu, 40% for Th and 9% for U was obtained by RILIS
- We demonstrated that RIMS is a highly selective powerful method that meet the requirements for ultra-trace detection having a high efficiency and the required sensitivity
- We established a new value for the ionization potential of plutonium with two analysis methods.
- Studied formation of molecules and large clusters of atoms
- ORNL has the radiochemical expertise to handle actinides safely
- 226Ra and 225Ra could be available for research...

²²⁶Ra is important for the DOE Isotope Program

- This shows the network of isotopes produced at HFIR during irradiation of a ²²⁶Ra target

 this is a valuable feedstock for production of alpha-emitting radioisotopes, including ²²⁹Th, which decays to ²²⁵Ra
- ORNL is uniquely qualified for large scale processing and irradiation of ²²⁶Ra targets



