

THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

A FRAGILE HOLD ON THE ELECTRON:
PROBING THE LIMITS OF NEGATIVE ION STUDIES

Miranda Nichols



UNIVERSITY OF GOTHENBURG

Department of Physics
University of Gothenburg
Gothenburg, Sweden 2025

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ISBN: 978-91-8115-250-0 (Print)

ISBN: 978-91-8115-251-7 (PDF)

URL: <http://hdl.handle.net/2077/86225>

Department of Physics
University of Gothenburg
SE-412 96 Gothenburg, Sweden

Printed by STEMA SPECIALTRYCK AB
Borås, Sweden 2025



To all the women who have come before me
and those who will come after

Abstract

Negative ions are unique quantum systems whose structures and dynamics are significantly influenced by electron correlation effects. Due to their weakly bound nature and the absence of long-range Coulomb potentials, these systems often lack optically allowed transitions, making high-resolution spectroscopic studies compared to those of neutral systems challenging. Therefore, negative ion research has traditionally focused on bound-continuum measurements, primarily determining electron affinity (EA) values with techniques such as laser photodetachment threshold spectroscopy (LPTS). However, accurately determining the EA for ions with electrons detached into a p -wave continuum has been limited by the slow onset of the photodetachment just above the threshold and inherently smaller photodetachment cross sections.

This thesis addresses these challenges by refining a combined method of LPTS and resonance ionization spectroscopy (RIS), enabling state-selective measurements of partial photodetachment cross sections. A novel detection scheme to differentiate signal from background was implemented, greatly improving the measurement selectivity and overall experimental resolution. The enhanced LPTS-RIS approach was demonstrated through improved EA measurements of cesium (Cs) and rubidium (Rb), significantly surpassing previous LPTS accuracies for determining p -wave detachment thresholds, thereby validating the method for future studies of more complex atomic systems.

Extending these experimental investigations to radioactive negative ions requires efficient production techniques. This thesis successfully demonstrated the feasibility of using charge exchange reactions to produce radioactive negative ions with uranium. A complementary theoretical study explored electron capture and energy loss processes in atom-ion collisions, highlighting critical factors that influence trajectory effects. By incorporating electron-nuclear coupling within the framework, the developed theo-

retical approach provides deeper insights essential for refining negative ion production models.

Most importantly, this work introduces an entirely new spectroscopic technique for probing previously inaccessible forbidden bound-bound transitions in negative ions. Leveraging the unique capabilities of a cryogenic ion storage ring, the first isotope shift (IS) measurement of an electric dipole forbidden transition was conducted using the tin anion (Sn^-). The sensitivity of IS studies to electron correlation effects, particularly through the specific mass shift component, underscores the potential of this method.

This work shows that a combined experimental and theoretical approach can overcome key limitations in negative ion spectroscopy, making it possible to probe systems and transitions that were previously out of reach. By extending high-precision methodologies to heavy ions and radioactive isotopes, developing simple yet sophisticated theoretical models, and pioneering studies of forbidden transitions, this thesis significantly expands the scope of negative ion research and opens new avenues for exploring atomic, nuclear, and quantum many-body physics.

Publications

Included in this thesis:

I. "High-resolution measurement of the electron affinity of cesium"

Navarro Navarrete, J. E., **Nichols, M.**, Ringvall-Moberg, A., Welanders, J., Lu, D., Leimbach, D., Kristiansson, M. K., Eklund, G., Raveesh, M., Chulkov, R., Zhaunerchyk, V., & Hanstorp, D. (2024). *Physical Review A* 109(2). DOI: 10.1103/physreva.109.022812

II. "The electron affinity of rubidium: A state selective measurement"

Ringvall-Moberg, A., **Nichols, M.**, Navarro Navarrete, J. E., Bērziņš, U., D'mello, V. C., Karls, J., Lu, D., Peña Rodríguez, Y., Poulou, R., Morales Rodríguez, A., Ravi, K., Ramachandran, M., Zhaunerchyk, V., Hanstorp, D., & Leimbach, D. (2024). *Journal of Physics B: Atomic, Molecular and Optical Physics* 57(15), 155002. DOI: 10.1088/1361-6455/ad5e25

III. "Investigating radioactive negative ion production via double electron capture"

Nichols, M., Athanasakis-Kaklamanakis, M., Borschevsky, A., Coccolios, T. E., Crosa-Rossa, R., de Groote, R. P., Flanagan, K. T., Garcia Ruiz, R. F., Geldhof, S., Hanstorp, D., Koszorús, L., Leimbach, D., Neyens, G., Reilly, J., Rothe, S., Wilkins, S. G., & Yang, X. F. (2023). *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 541, 264–267. DOI: 10.1016/j.nimb.2023.04.051

IV. "Trajectory effects on charge exchange and energy loss in collisions of H^+ , He^{2+} , Li^{3+} , and Be^{4+} ions with atomic hydrogen"

Nichols, M., Hanstorp, D., & Cabrera-Trujillo, R. (2024). Submitted to *Physical Review A*. DOI: 10.48550/arXiv.2411.10221

V. "Isotope shift in the stable tin anion with bound-bound electric dipole forbidden transition"

Nichols, M., Adiels, C. B., Alnis, J., Bērziņš, U., Bondarev, A., Ciniņš, A., Escobedo, B. R., Gibson, N. D., James, A., Leimbach, D., Lu, D., Martini, P., Navarro Navarrete, J. E., Pérez Guerrero, D., Poulou, R., Schmidt, H. T., Snikeris, J., Walter, C. W., Zettergren, H. T., & Hanstorp, D. *In manuscript*.

Additional publications:

VI. "Electron correlation and relativistic effects in the excited states of radium monofluoride"

Athanasakis-Kaklamanakis, M., Wilkins, S. G., Skripnikov, L. V., Koszorús, A., Breier, A. A., Ahmad, O., Au, M., Bai, S. W., Belošević, I., Berbalk, J., Berger, R., Bernerd, C., Bissell, M. L., Borschevsky, A., Brinson, A., Chrysalidis, K., Cocolios, T. E., de Groote, R. P., Dorne, A., Fajardo-Zambrano, C. M., Field, R. W., Flanagan, K. T., Franchoo, S., Garcia Ruiz, R. F., Gaul, K., Geldhof, S., Giesen, T. F., Hanstorp, D., Heinke, R., Imgram, P., Isaev, T. A., Kyuberis, A. A., Kujanpää, S., Lalanne, L., Lassègues, P., Lim, J., Liu, Y. C., Lynch, K. M., McGlone, A., Mei, W. C., Neyens, G., **Nichols, M.**, Nies, L., Pašteka, L. F., Perrett, H. A., Raggio, A., Reilly, J. R., Rothe, S., Smets, E., Udrescu, S.-M., van den Borne, B., Wang, Q., Warbinek, J., Wessolek, J., Yang, X. F., & Zülch, C. (2025). *Nature Communications* 16, 2139. DOI: 10.1038/s41467-025-55977-w

VII. "Ionization potential of radium monofluoride"

Wilkins, S. G., Perrett, H. A., Udrescu, S. M., Kyuberis, A. A., Pašteka, L. F., Au, M., Belošević, I., Berger, R., Binnersley, C. L., Bissell, M. L., Borschevsky, A., Breier, A. A., Brinson, A. J., Chrysalidis, K., Cocolios, T. E., Cooper, B. S., de Groote, R. P., Dorne, A., Eliav, E., Field, R. W., Flanagan, K. T., Franchoo, S., Garcia Ruiz, R. F., Gaul, K., Geldhof, S., Giesen, T. F., Gustafsson, F. P., Hanstorp, D., Heinke, R., Koszorús, Á., Kujanpää, S., Lalanne, L., Neyens, G., **Nichols, M.**, Reilly, J. R., Ricketts, C. M., Rothe, S., Sunaga, A., van den Borne, B., Vernon, A. R., Wang, Q., Wessolek, J., Wienholtz, F., Yang, X. F., Zhou, Y., & Zülch, C. (2024). *arXiv [Physics.Atom-Ph]*. DOI: 10.48550/arXiv.2408.14673

VIII. "Precision spectroscopy and laser-cooling scheme of a radium-containing molecule"

Udrescu, S. M., Wilkins, S. G., Breier, A. A., Athanasakis-Kaklamanakis, M., Garcia Ruiz, R. F., Au, M., Belošević, I., Berger, R., Bissell, M. L., Binnersley, C. L., Brinson, A. J., Chrysalidis, K., Cocolios, T. E., de Groote, R. P., Dorne, A., Flanagan, K. T., Franchoo, S., Gaul, K., Geldhof, S., Giesen, T. F., Hanstorp, D., Heinke, R., Koszorús, Á., Kujanpää, S., Lalanne, L., Neyens, G., **Nichols, M.**, Perrett, H. A., Reilly, J. R., Rothe, S., van den Borne, B., Vernon, A. R., Wang, Q., Wessolek, J., Yang, X. F., & Zülch, C. (2024). *Nature Physics* 20(2), 202–207. DOI: 10.1038/s41567-023-02296-w

IX. "Observation of the distribution of nuclear magnetization in a molecule"

Wilkins, S. G., Udrescu, S. M., Athanasakis-Kaklamanakis, M., Garcia Ruiz, R. F., Au, M., Belošević, I., Berger, R., Bissell, M. L., Breier, A. A., Brinson, A. J., Chrysalidis, K., Cocolios, T. E., de Groote, R. P., Dorne, A., Flanagan, K. T., Franchoo, S., Gaul, K., Geldhof, S., Giesen, T. F., Hanstorp, D., Heinke, R., Isaev, T., Koszorús, Á., Kujanpää, S., Lalanne, L., Neyens, G., **Nichols, M.**, Perrett, H. A., Reilly, J. R., Skripnikov, L. V., Rothe, S., van den Borne, B., Wang, Q., Wessolek, J., Yang, X. F., & Zülch, C. (2023). *arXiv [Nucl-Ex]*. DOI: 10.48550/arXiv.2311.04121

X. "Voltage scanning and technical upgrades at the collinear resonance ionization spectroscopy experiment"

Athanasakis-Kaklamanakis, M., Reilly, J. R., Koszorús, Á., Wilkins, S. G., Lalanne, L., Geldhof, S., **Nichols, M.**, Wang, Q., van den Borne, B., Chorlton, D., Cocolios, T. E., Flanagan, K. T., Garcia Ruiz, R. F., de Groote, R., Hanstorp, D., Neyens, G., Smith, A. J., Vernon, A. R., & Yang, X. F. (2023). *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 541, 86–89. DOI: 10.1016/j.nimb.2023.04.054

XI. "Benchmark evaluation of a single frequency continuous wave OPO seeded pulsed dye amplifier for high-resolution laser spectroscopy"

Urquiza-González, M., Au, M., Bernerd, C., Bissell, M. L., van den Borne, B., Chrysalidis, K., Cocolios, T. E., Fedosseev, V., Flanagan, K. T., Garcia Ruiz, R. F., Geldhof, S., de Groote, R. P., Koszorús, Hanstorp, D., Heines, M., Heinke, R., Hens, K., Khwairakpam, O. S., Kujanpää, S., Lalanne, L., Marsh, B. A., Neyens, G., **Nichols, M.**, Perrett, H., Pitman-Weymouth, D., Reilly, J., Sonnenschein, V., Wendt, K., Wessolek, J., Wilkins, S. G., & Yang, X. F. (2023). *Solid State Lasers XXXII: Technology and Devices* 40. DOI: 10.1117/12.2646665

Specification of contributions

I. "High-resolution measurement of the electron affinity of cesium"

This experiment marked the beginning of my PhD research and provided my first substantial exposure to experimental physics. Through this work, I acquired foundational skills essential for atomic physics experimentation including the alignment of laser systems, optimization of ion beam parameters, configuration of data acquisition and timing electronics, and detector setup. I also gained practical experience working with high-vacuum systems, frequency calibration procedures, and signal processing techniques.

Due to the limited availability of the dye laser, which was on loan, the measurements had to be completed within a strict two-week period. During this time, I worked intensively alongside José and Annie to complete the experiment. In addition to contributing to the preparation and execution of the experiment, I played a key role in the preparation of the manuscript. The drafting process was a collaborative effort shared equally among José, Annie, and myself.

II. "The electron affinity of rubidium: A state selective measurement"

Following the successful measurements on cesium, it was a natural progression to apply the same methodology to rubidium. The experiment was originally scheduled for 2021, but significant technical challenges arose with the OPO. Together with Annie and Ludi, I spent close to a year working with the technician to restore the system. Despite our efforts, the OPO could not be returned to working condition during

that period.

I was not able to be present for the measurement taking, however I was involved in the preparation of the experiment. Together with Annie, I contributed significantly to the writing of the manuscript, with the exception of the data analysis section. As Annie had completed her PhD by the time of submission, I served as the corresponding author for the publication.

III. "Investigating radioactive negative ion production via double electron capture"

This experiment was the first I led as principal investigator, submitted as a Letter of Intent to the ISOLDE and n_TOF Experiments Committee (INTC). The primary aim was to evaluate the feasibility of producing Po^- ions using a charge exchange cell as a precursor to a measurement of the electron affinity of polonium.

We could not measure the production of Po^- due to contamination of the detector from the decay of the selected Po isotope. Instead, we demonstrated the feasibility of the method using uranium-238. This result was an important outcome, as the successful detection of U^- provided critical validation of the charge exchange method for heavy ions.

I was responsible for all aspects of the experiment, including writing and submitting the Letter of Intent, coordinating the setup, and leading the experimental shifts. I also wrote the resulting publication. The experience was formative, offering valuable insights into experiment planning and logistical coordination.

IV. "Trajectory effects on charge exchange and energy loss in collisions of H^+ , He^{2+} , Li^{3+} , and Be^{4+} ions with atomic hydrogen"

Following the experimental work on charge exchange with uranium, I identified a gap in the theoretical understanding of heavy negative ion formation via this method. Motivated to explore this area further, I initiated a collaboration with Remi, who generously agreed to supervise the project despite my limited knowledge of theory at the time.

Remi proposed beginning with the simplest collision systems, bare ion projectiles interacting with atomic hydrogen, in order to benchmark

the method before applying it to more complex, many-body systems. I implemented the method *ab initio* in Python, initially constrained to one dimension due to computational limitations. Once I demonstrated a solid understanding of the approach, I was given access to a three-dimensional finite-difference classical trajectory code written in Fortran, developed by Remi. From that point, we worked in parallel, running calculations and extending the methodology.

I had the opportunity to spend a month in Mexico working to complete this project. My contributions included extending the existing Fortran code, performing simulations, co-authoring the manuscript and figures, and serving as the corresponding author.

V. "Isotope shift in the stable tin anion with bound-bound electric dipole forbidden transition"

My interest in tin began during my time at ISOLDE, where I had many discussions with my colleague and friend Michalis about the most interesting systems for probing electron correlation in negative ions. Initially, the idea was to investigate the isotope shift in the electron affinity of Sn. However, after reading the work by Scheer, Bilodeau, Brodie, and Haugen on multi-photon spectroscopy of carbon group anions, where the forbidden transitions in Sn^- were initially measured, I was compelled to test whether similar measurements could be achieved at the DESIREE facility.

The project consisted of two separate experiments, both of which I prepared and led, contributing over 200 hours of beamtime. I performed all data analysis and authored the manuscript. The theoretical calculations presented in the paper were developed by Andrey.

VI - XI. While these papers are outside the scope of this thesis, my contributions were significant as one of the five local members of the CRIS collaboration at ISOLDE-CERN for the 2021-2022 year. I participated in experiment planning, design, setup, testing, and execution, as well as maintaining the experimental beamline and laser systems and commissioning upgrades. These efforts were essential to the success of the listed publications and numerous ongoing projects.

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Chapter 1

Introduction

At the end of the 19th century, it was believed that atoms were tiny, indivisible vortices in the ether [1]. This idea persisted until J.J. Thomson's ground-breaking experiments on cathode rays proved that atoms contained smaller, negatively charged particles, which he called "corpuscles," now known as electrons [2]. Searching for the positively charged counterparts to corpuscles, Thomson began to study canal rays. By observing the nature of "positive electricity," he confirmed these rays were composed of particles, later understood to be positive ions [3]. This work demonstrated that atoms could form charged species, leading to the discovery of isotopes, the development of mass spectrometry [4], and, in turn, supporting the existence of negative ions by logical extension.

Despite this realization, negative ions remained largely unexplored among the rapid advancements in atomic and quantum physics at the turn of the 20th century. With the exception of a few studies [5, 6], it wasn't until 1939 that the interest in these systems was ignited, when Rupert Wildt proposed that hydrogen anions were responsible for absorbing and scattering radiation within a stellar atmosphere [7]. His explanation suggested that negative ions played a crucial role in the Sun's ability to support life on Earth. This marked a turning point for the study of negative ions and inspired decades of research to reveal their intricate quantum properties and fundamental roles in nature.

Negative ions are significantly different from their neutral and positively charged counterparts due to their weak binding potential. Unlike neutral atoms, which experience long-range Coulomb attraction, negative ions are bound by an induced dipole potential that scales as $1/r^4$ at large distances.

This arises from the polarization of the atomic core by the additional electron, resulting in a shallow binding potential that typically supports few or no bound excited states. In negative ions, electron-electron correlation effects are notably enhanced, which govern their structure and dynamics [8–10].

The electron affinity (EA) is the key measurable quantity when studying negative ions, which is a fundamental atomic property that refers to the energy released when an electron is added to a system to form a negative ion. It is typically determined through photodetachment spectroscopy, where a photon of sufficient energy removes the extra electron from the anion. Near the detachment threshold, the photodetachment cross section follows the Wigner threshold law, which describes the energy dependence of the cross section on the angular momentum of the ejected electron [11]. For an s -wave electron ($l=0$), the cross section exhibits a sharp onset, whereas for a p -wave ($l=1$), the threshold behavior is much more gradual.

The first EA measurements were obtained through photodetachment cross-section studies in H^- , D^- , and O^- [12, 13], confirming that negative ions exhibit unique structural and electronic properties. Since then, most stable negative ions have EA values measured with an accuracy of ~ 0.1 meV [14–18].

While the EA can be measured using multiple techniques, laser photodetachment threshold spectroscopy (LPTS) has emerged as a powerful method, particularly for high-resolution measurements of s -wave detachment thresholds [16]. However, this method has significant limitations when applied to p -wave detachment, where the cross sections are typically an order of magnitude smaller and exhibit a slower onset compared with s -wave detachment. To improve the p -wave resolution for the LPTS method, an approach integrating LPTS with resonance ionization spectroscopy (RIS) was initially proposed in [19, 20] to allow for partial photodetachment cross-section studies. This method has been applied to both EA measurements and doubly excited state investigations [20–26].

Other prominent techniques, such as laser photodetachment microscopy (LPM) [27], laser photodetachment electron spectrometry (LPES) [15], and slow-electron velocity-map imaging (SEVI) [28, 29], also have advantages in specific cases. Notably, SEVI especially excels for p -wave measurements due to event-based photoelectron detection and photodetachment channel selectivity [18]. This method has provided high-resolution studies for negative ions in the transition [30–32], lanthanide [33], and actinide [34, 35] regions, which notably have complex electronic configurations. However, a recent study found that electron-imaging methods have possibly led to systematic

overestimations of the EAs of 28 elements by around 25 μeV [36]. This highlights the importance of the direct measurement of LPTS and extending the method to be universally applied to any element on the periodic table.

Although advancements in EA measurement techniques have been fruitful, many heavy and radioactive elements have EA values that remain experimentally unknown. The first EA measurement of a radioactive isotope was performed on iodine-128 [37], but such studies remain scarce. A primary limitation is that traditional surface ionization production at radioactive ion beam facilities is ineffective for elements with low EAs [38, 39]. In these cases, charge exchange could be an alternative method for radioactive negative ion production [40]. This approach relies on a target from which the ion projectile can capture electrons and has been investigated in stable elements, ranging from helium to gold, using alkali metal vapor targets [41–44].

Atomic collisions and inelastic processes have been experimentally and theoretically studied for decades, providing key insights into fundamental atomic interactions and chemical reactions [45]. Beyond their role in negative ion production, these studies have been particularly interesting for applications in plasma and fusion research [46], astrophysics [47, 48], and medicine [49, 50]. Developing theoretical models for atomic collision studies plays an essential role in understanding highly correlated and relativistic systems [51].

Theoretical input is especially valuable for predicting cross sections, transition probabilities, isotope shifts, and hyperfine structures [52], enabling insights into areas where experimental data remain inaccessible. This is particularly crucial for understanding negative ion structure and dynamics, where nearly all bound anionic states are optically forbidden, making direct spectroscopic measurements challenging [53, 54]. This challenge has resulted in most negative ion studies focusing on bound-continuum transitions since optically allowed bound-bound transitions are rare. The only known exceptions are Os^- [55], Ce^- [56], La^- [57], Th^- [34], and U^- [35], which all have bound states of opposite parity to the ground state, rendering them optically accessible via electric dipole ($E1$) transitions.

These rare systems open the door to new applications, particularly in the search for laser cooling schemes in negative ions. Such schemes are of great interest, especially for their potential use in sympathetic cooling of antiprotons [58]. To achieve efficient laser cooling, transition frequencies must be known with high precision. Since different isotopes introduce slight variations in these frequencies, isotope shift (IS) measurements are essential for validating and optimizing cooling strategies.

Investigating IS in highly correlated systems also offers a unique oppor-

tunity to probe many-body interactions that go beyond the current insights into nuclear charge distributions and electron-nucleus interactions [59–61]. Recognizing the importance of IS studies in negative ions, an initial measurement was performed on a bound-bound transition within Os^- [62]. While some magnetic dipole ($M1$) [63, 64] and electric quadrupole ($E2$) [64, 65] anionic transitions have been observed, there has yet to be a systematic IS shift study with such a transition.

Having briefly presented the field, it's clear that significant progress has been made since the time of Thomson. However, there remain significant research gaps, which will be addressed in this thesis. Beginning with the LPTS and RIS combined method, while this has been successfully used, the accuracy remains considerably lower than ground-state measurements for EA values due to the small partial cross sections. Using a previously developed spectrometer that enables state-selective detection [66], the method will be improved and refined to achieve similar, if not better, accuracy and precision in EA values. The first tests will be conducted on the alkali metal group, with elements such as cesium and rubidium, which have well-established EAs. Ultimately, the goal is to scale this method to francium, which is the last alkali metal with an unmeasured EA, and elements in the transition, lanthanide, and actinide groups, where valence electrons commonly occupy s - and d -shells, while maintaining high resolution.

Establishing the LPTS-RIS method as a viable option for systems with strong relativistic effects is only part of the challenge. The production of heavy negative ions, which are typically radioactive and characterized by low EAs, remains an open problem. While charge exchange has proven to be a viable method, it has yet to be systematically investigated both experimentally and theoretically for heavy radioactive ions. Additionally, theoretical predictions for heavy negative ion formation cross sections are limited. In available models, the role of nuclear motion has not been well accounted for, leading to uncertainties in cross sections for electron capture and target energy loss. Understanding these trajectory effects is vital for the continued development of accurate physical models of collision-based negative ion formation, especially when moving towards systems with increasing relativistic effects.

Lastly, since it has been demonstrated that $E1$ forbidden transitions can be accessed, the next step is to extend these studies. IS measurements have never been performed on an $E1$ forbidden transition in a negative ion due to small transition rates and large background signals. The long timescale required for such transitions to occur makes them impractical for linear, single-pass experiments. However, utilizing a cryogenic storage ring

may provide the necessary conditions to render forbidden transitions more accessible.

With the overall goal of this thesis being to move towards higher precision measurements, comparable to experiments with systems bound by Coulomb potentials, this work is guided by the hypothesis that significant advancements in negative ion spectroscopy can be achieved through refined experimental and theoretical methods. The work presented here seeks to shift the standard approach to negative ion spectroscopy from photodetachment to bound-bound anion transitions. This is accomplished by refining the LPTS-RIS method for determining p -wave thresholds with improved accuracy (Papers I & II), developing a reliable production method for heavy and radioactive negative ions with charge exchange (Papers III), modeling the charge exchange process from a theoretical perspective to understand electron capture dynamics and trajectory effects in ion-atom collisions (Paper IV), and introducing a novel approach for IS studies with forbidden transitions in negative ions (Paper V). Together, these efforts validate the underlying hypothesis and aim to push the boundaries of precision spectroscopy in anionic systems and pave the way for exploring previously inaccessible negative ion species in the years to come.

Chapter 2

Fundamentals of Atomic Negative Ions

In most atomic systems, electron-electron interactions can be treated as small perturbations because they are weaker than the dominant Coulomb attraction between the electrons and nucleus. The independent particle approach, which is the cornerstone of mean-field theories, reduces a many-body problem to many effective one-body problems by approximating all interactions in a system to an average field. In atomic structure modeling, this means that each electron moves independently within an average potential created by the nucleus and the fields of all the other electrons in the atom [67, 68].

While mean-field approximations simplify computations, they fail to accurately model systems where electron-electron correlation effects are significant. Negative ions are a prime example, as their weak polarization interactions, scaling as $1/r^4$, make correlation effects essential for their stability. As a result, mean-field theories like the Hartree-Fock (HF) method generally are not sufficient for describing negative ions [69].

The HF method is a self-consistent field approach that includes exchange interactions, enforcing the Pauli Exclusion Principle, but does not fully account for the dynamics of electron correlation [70]. For this reason, the method incorrectly predicts that H^- is not bound, and it generally struggles to describe anions like O^- , which require significant correlation energy for stability [14, 71–73]. Exceptions arise for anions with half-filled or closed-subshell electronic configurations, such as C^- and F^- , which are easier to predict without additional correlation corrections due to the inherent shell

structure stability [72, 73].

This chapter will explore the importance of correlation effects in the structure and stability of negative ions and how these effects govern their dynamics, highlighting why restricted mean-field theories break down in anionic systems.

2.1 Atomic structure

This section explores the fundamental atomic structure and the unique characteristics of negative ions, which arise from their binding potential and strong electron correlation effects. These properties can be quantified through the electron affinity, which also provides insight into the overall stability of the system, as correlation and stability are closely linked. Finally, isotopic effects are discussed, highlighting their influence on spectroscopic measurements and their sensitivity to subtle nuclear effects.

2.1.1 Binding potentials

While all atomic systems share similar structural principles, the nature of the binding potential significantly influences the energy level structures. Electrostatic potentials are highly complicated but can be simplified using a multipole expansion of the atomic charge distribution. In neutral atoms and positive ions, electrons experience a long-range Coulomb potential, which originates from the monopole term in the multipole expansion. At large distances from the nucleus, this potential behaves as $1/r$, meaning that when the interaction extends over an infinite distance, it supports an infinite number of bound states.

In contrast, negative ions do not exhibit monopole interactions. Instead, the first term in the multipole expansion is a dipole term, arising from the polarization of the atomic core due to the electric field of the approaching electron $\vec{E}(r)$, whose magnitude scales as $1/r^2$. This effectively reduces the nuclear screening effects, thereby creating an electric dipole moment in the atom

$$\vec{p} = \alpha \vec{E}(r), \quad (2.1)$$

where α is the atomic polarizability. The potential energy required to induce a dipole in an atom placed in an external electric field $\vec{E}$ is given by

$$V = - \int_0^{\vec{E}} \vec{p} \cdot d\vec{E}' = - \int_0^{\vec{E}} \alpha \vec{E}' \cdot d\vec{E}' = -\frac{1}{2} \alpha E^2. \quad (2.2)$$

The resulting attractive induced dipole potential can therefore be expressed as

$$V(r) = -\frac{1}{2}\alpha \cdot E(r)^2 = -\frac{\alpha}{2r^4}, \quad (2.3)$$

which is valid for $r \gg r_{core}$. For simplicity, the potential can be approximated as scaling with the polarizability and $1/r^4$. Unlike the Coulomb potential, this shallow, short-range potential does not support many bound states. As a result, negative ions rarely possess bound excited states, and when they do exist, they are typically of the same parity as the ground state. However, many excited states of negative ions exist in the continuum rather than as true bound states of the system. Additionally, the atomic polarization enhances electron-electron interactions, leading to strongly correlated electron behavior.

2.1.2 Electron correlation

Electron correlation describes how electrons repel and adjust their positions in response to each other to reduce the probability of close-range interactions. When an additional electron is added to a system, the redistribution of charge density changes how the core electrons electrostatically repel each other. This makes correlation effects more enhanced in negative ions than in other systems [74].

Theoretically, electron correlation can be defined as the difference between the exact energy of the Hamiltonian and the HF results for that Hamiltonian [75]. Several sophisticated correlation-driven models have been developed to account for these effects, such as multiconfiguration (MC) and configuration interaction (CI) techniques [76] (e.g. MC Dirac-Hartree-Fock (MCDHF) [77]), relativistic coupled cluster approaches [78], or a combination of methods [79].

Electron correlation significantly influences the observable properties in negative ions, such as their binding energies, resonance structures, and lifetimes of excited states, often leaving discrepancies between theoretical and experimental values if not carefully treated [80, 81].

2.1.3 Electron affinity and stability

The electron affinity (EA) is defined as the energy difference between the ground states of the neutral atom and the negative ion, as seen in Fig. 2.1.

The EA provides direct insight into electron correlation, which strongly influences the stability of negative ions. The EA varies significantly across

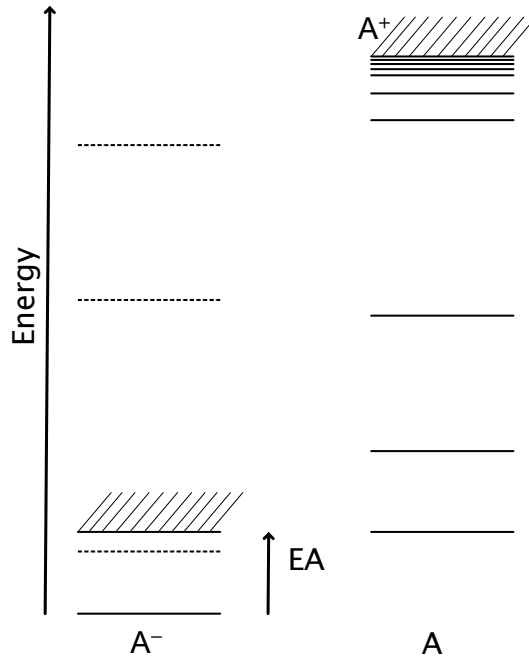


Figure 2.1: Energy level diagram of an atom (A) and a negative ion (A^-). The dashed lines represent a possible bound state, located below the detachment threshold, as well as doubly excited states situated in the continuum. The first doubly excited state forms a shape resonance, being bound just above the second excited state in A. The second doubly excited state forms a Feshbach resonance as it energetically lies below the third excited state in A.

the periodic table due to differences in electron configurations and nuclear screening effects. Elements with nearly complete valence shells, such as the halogens, possess high EAs due to the extra stability gained with the electron addition. Additionally, elements like oxygen that have high electronegativity also have high EAs. This means that these ions are considered to be the most correlated and stable systems.

On the other hand, elements such as noble gases that have closed-shell electronic configurations exhibit negative EA values. This means that the energy must be added to the system rather than released, resulting in unstable formations with no ground state configurations [82]. In some cases,

the element cannot form a stable negative ion but can exist in metastable forms such as He^- [83] and Be^- [84].

Looking closer at the alkaline earth metals, neither beryllium nor magnesium can form stable negative ions. This is due to the filled s -shell and that it is energetically unfavorable for the electron to bind to the system in the higher p -shell. Reaching calcium, it barely forms a negative ion with the smallest EA value on the periodic table of 24 meV [19].

2.1.4 Coupling schemes and term structure

In atomic systems, electrons occupy discrete energy levels characterized by the principal quantum number n , which determines the overall size of the orbital, and the orbital angular momentum quantum number l , which defines the shape of the orbital.

When multiple electrons are present, their individual angular momenta couple to form total angular momentum values that define the energy term structure of the atom. In most negative ion systems, LS coupling (also known as Russell-Saunders coupling) is the dominant scheme. Here, the total orbital angular momentum L and total spin angular momentum S are obtained by summing the individual electron contributions. These quantities define the atomic term symbol ^{2S+1}L , which characterizes the energy level within a given electronic configuration.

In heavier atoms or highly charged systems, spin-orbit interactions become more significant, favoring an alternative coupling scheme called jj coupling. Here, each electron's spin and orbital angular momenta are first combined to form an individual total angular momentum j , and these are then summed to obtain the total angular momentum J of the system. This leads to a different term structure than LS coupling and can significantly impact energy levels and transition probabilities. While some negative ion systems have been found to exhibit jj -like behavior, the majority are still well described within the LS coupling framework [81].

In LS -coupled schemes, energy terms undergo further splitting due to spin-orbit coupling, forming the fine structure (FS). The FS splitting depends on the total angular momentum of the electrons J , given by

$$\mathbf{J} = \mathbf{L} + \mathbf{S}, \quad (2.4)$$

where J takes values $|L - S|, |L - S| + 1, \dots, L + S$. In neutral atoms, FS splittings occur across the infinite range of excited states that form the Rydberg series, which converges toward the ionization threshold. However, in negative ions, the small binding energies restrict the number of bound

excited states, leading to a truncated and sparse FS spectrum. In some cases, such as in La^- [57], higher FS components may even lie in the continuum, rendering them quasibound states of the system.

If the nucleus has a nonzero spin I , the FS can further split due to the interaction between the nuclear magnetic moment and the magnetic field of the orbiting electron, called the hyperfine structure (HFS). The HFS splitting is determined by the total angular momentum of the atom F , expressed as

$$\mathbf{F} = \mathbf{I} + \mathbf{J}, \quad (2.5)$$

with F following $|I - J|, |I - J| + 1, \dots, I + J$.

2.1.5 Isotopic effects

The FS and HFS provide a sensitive framework for probing subtle changes in atomic energy levels. When comparing different isotopes of the same element, variations in nuclear mass and charge distribution lead to small shifts in these energy levels, known as isotope shifts (IS). These energetic differences offer insights into both the electronic structure and the underlying nuclear properties.

The IS is composed of mass and field shift contributions. The mass shift (MS) arises due to changes in the mass of the nucleus, which affects the motion of the orbiting electrons. This can further be broken down into a normal mass shift (NMS), which is a purely kinematic effect that results from the reduced mass effect between the electrons and nucleus, and a specific mass shift (SMS), which arises directly from electron-electron correlation effects. The field shift is caused by variations in nuclear charge distributions between isotopes, influencing the energy levels of electrons, especially near the nucleus. This shift tends to dominate in heavier elements where nuclear size and volume increase and relativistic effects become substantial [59]. The total IS is given by

$$\Delta\nu^{A,A'} = k_{\text{MS}} \frac{m_{A'} - m_A}{m_{A'} m_A} + F \delta \langle r^2 \rangle^{A,A'}. \quad (2.6)$$

Because the EA is essentially a measurement of electron correlation, the IS in EA values provides a highly sensitive tool for studying electron correlation in relation to nuclear charge distributions. These measurements are particularly sensitive to electron correlation because the SMS also directly reflects electron correlation [85, 86]. In neutral systems, IS in HFS transition energies has been an established high-resolution method for probing nuclear size and shape [60]. These studies offer two to three times higher resolution

compared with IS(EA) measurements. Up to now, such techniques have not been generally accessible for negative ions due to the lack of allowed bound-bound transitions, with the exception of the IS(Os^-) study [62].

2.2 Dynamics

In this section, we will look into the key mechanisms that govern the interactions of negative ions with external fields. While negative ions exhibit distinct behaviors under static magnetic and electric fields such as Zeeman splitting and the Stark effect [10], this work focuses on the dynamic interactions with electromagnetic fields. Photodetachment, electron-atom scattering, their resulting resonant states, and optical transitions within the anion will be highlighted.

2.2.1 Electron photodetachment

When a negative ion interacts with a photon of sufficient energy, an electron can be detached from the system if it overcomes both the attractive dipole potential of the atomic core and the centrifugal barrier. Once detached, the electron experiences an effective potential that can be approximated by

$$V_{\text{eff}}(r) \approx \frac{l(l+1)}{2r^2} - \frac{\alpha}{2r^4}. \quad (2.7)$$

This expression highlights that the orbital angular momentum l plays a significant role in the photodetachment process. In particular, at large distances from the nucleus, the centrifugal barrier dominates the effective potential. Under these conditions, the Wigner law was derived [11], which describes the photodetachment cross section near the detachment threshold as

$$\sigma \propto (E_\gamma - E_{th})^{l+1/2}, \quad (2.8)$$

where E_γ is the photon energy and E_{th} is the detachment threshold energy. The impact of angular momentum on the near-threshold behavior of the cross section is illustrated in Fig. 2.2.

In most photodetachment studies, only one channel contributes to the total cross section. However, in some cases, there can be multiple open channels, each contributing to the total cross section. If the signal from just one specific channel is measured, a partial cross section is obtained, as discussed in Papers I and II. This allows for the contribution from a particular transition to be isolated, rather than the total response of the

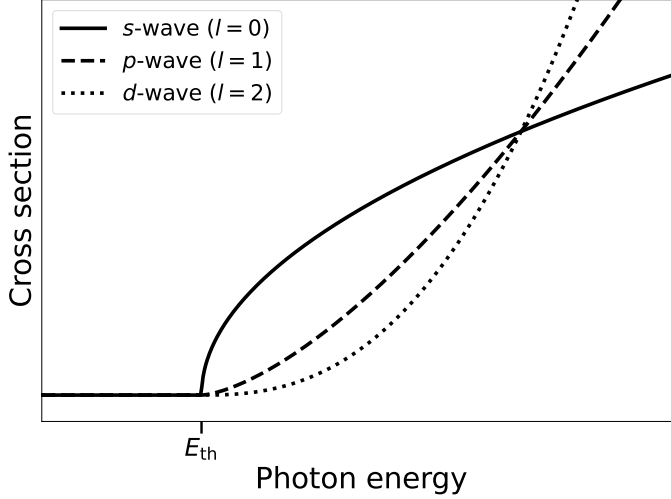


Figure 2.2: Photodetachment cross-section behavior near the energetic detachment threshold (E_{th}) for s , p , and d -waves following the Wigner law given by Eq. (2.8).

system. There are also differential cross sections, which give information about the scattering angle of the photoelectrons. This is not explored in this thesis.

2.2.2 Electron-atom scattering and resonances

Detachment and excitation processes of negative ions can be contextualized with electron-atom scattering dynamics, where emerging resonant structures are common due to electron-electron and electron-nucleus interactions. When an excited atom captures or attempts to release an electron, a doubly excited state can be formed. These are quasi-bound states that exhibit resonances upon formation and decay, classified as either shape or Feshbach resonances based on their physical origin.

Shape resonances occur when the centrifugal barrier and induced dipole potential temporarily trap an electron, exhibiting a strong angular momentum dependence. These states energetically exist above the parent state and are very short-lived, decaying via tunneling. Feshbach resonances, on the other hand, arise from multi-electron interactions where one electron is

excited to a metastable state situated below the parent state. Since the energy of this state is below the parent state, the electron cannot escape freely and must instead decay through autodetachment, resulting in a longer lifetime compared to shape resonances. However, these states are still very short-lived in the context of the overall scattering process [87, 88].

Negative ion resonances have been extensively studied in a wide range of systems, from He^- to Ca^- and heavy alkali metals [10, 89], as well as from inner-shell photodetachment [90]. That said, the studies in this thesis do not reach the energy range where these channels would significantly affect the photodetachment cross section.

2.2.3 Optical transitions and lifetimes

Electrons can be excited to higher energy levels through interactions with electromagnetic fields, where the electric interaction dominates over the magnetic interaction, as described by the Lorentz force law, $\vec{F} = q(\vec{E} + \vec{v} \times \vec{B})$. As a result, the most probable transition to occur is the electric dipole transition ($E1$), otherwise referred to as an optically allowed transition. The $E1$ transition requires a change in wavefunction parity between the initial and final states. This, along with angular momentum selection rules, determines if the transition is allowed. Higher-order transitions such as electric quadrupole ($E2$) and magnetic dipole ($M1$) and quadrupole ($M2$) are considered forbidden because they are highly improbable. However, they can still occur due to state mixing and relativistic effects [91].

The role of parity becomes particularly significant in negative ions. Since bound excited states in negative ions are often fine-structure excitations within the same electronic configuration as the ground state, they typically share the same parity. This means that $E1$ transitions cannot occur and that negative ions have to rely on forbidden transitions for radiative decay, which have longer lifetimes than $E1$ transitions, ranging from μs to hours.

The $M1$ transition is usually the main contributor and is easy to predict due to transition energy and angular momentum dependence in purely LS coupled systems [92]. For example, this is the case for ions homologous to O^- [81]. In more complex anion systems that have several bound terms within the ground configuration, such as the pnictogen group, transition probabilities are altered due to term mixing and additional $E2$ contributions [54].

Chapter 3

Experimental Methods

Having established the fundamentals of negative ions, we can now turn to how these systems are studied in a laboratory setting. Negative ions naturally exist in aqueous solutions, accompanied by counterions (e.g., Na^+ for Cl^- , K^+ for F^-), which make direct studies challenging due to solvation and electrostatic screening [93]. They are also found in plasma environments, where frequent collisions and high particle densities limit their stability, making anions difficult to preserve and extract. While photodetachment-based probe diagnostics are effective for measuring negative ion density in plasmas [94, 95], most high-precision studies rely on ion beam techniques.

Ion beams allow for precise manipulation of negative ions, enabling energy tuning, mass selection, and electrostatic steering from the source to the laser-ion interaction region. These capabilities make them especially suited for experiments that probe subtle interactions, such as electron correlation effects, which can be challenging to resolve.

Although precision atomic physics measurements are often performed using ion traps, optical lattices, and magneto-optical traps [96], these methods are less commonly applied to negative ions. While anions can be effectively trapped [97], they are often difficult to detect due to their lack of cycling transitions, so ion beams remain the standard for bound-continuum photodetachment spectroscopy.

This chapter details the experimental methods used in this thesis, giving an overview of the experimental facilities where the measurements were conducted, the different techniques for negative ion production, the spectroscopic methods developed, the specific laser systems, and the detectors used to translate the physical interactions into measurable signals that are

preserved for subsequent analysis. Finally, the application of these methods will be connected to the relevant studies, where the results are discussed in Chapter 5.

3.1 Experimental facilities

3.1.1 GUNILLA

The Gothenburg University Negative Ion and Laser Laboratory (GUNILLA) features a dedicated collinear ion beam apparatus for the study of stable negative ions using high-resolution laser spectroscopy techniques, particularly laser photodetachment threshold spectroscopy (LPTS). The collinear geometry provides high sensitivity and precision for electron affinity (EA) measurements [98, 99].

The negative ions are produced using a Middleton-type cesium sputter ion source (PS-120 Peabody Scientific) [100]. After extraction, the ions are accelerated to 6 keV and subsequently mass-separated using a 90° sector field magnet with a resolution of approximately 500 ($m/\Delta m$). This ensures the selection of a pure ion species before entering the experimental region, guided by ion beam optics.

The spectrometer used in these studies is the Rydberg Atom Detector for Anion Research (RADAR), which enables state-selective measurements by collinearly overlapping ion and laser beams while combining Laser Photodetachment Threshold Spectroscopy (LPTS) and Resonance Ionization Spectroscopy (RIS). This is shown in Fig. 3.1. A key component of RADAR is the field ionization (FI) unit, which consists of 11 parallel plates that gradually generate an electric field gradient for Rydberg atom ionization, based off the semi-empirical expression, $E \approx 3 \cdot 10^{10}/(n^*)^4$ V/m, where n^* is the effective quantum number. This setup selectively ionizes Rydberg atoms, causing a decrease in kinetic energy. In contrast, collisionally produced positive ions, which contribute to the background, remain unaffected and retain their original kinetic energy. Both sets of positive ions are deflected with an electrostatic energy analyzer. The resulting energy difference causes the two signals to follow different trajectories, allowing spatial separation and detection using a position-sensitive, microchannel plate (MCP) detector [66].

The GUNILLA facility is also equipped with many lasers which cover a broad spectral range of wavelengths from the ultraviolet to infrared regions. The relevant lasers to this work are a tunable dye laser and optical parametric oscillator (OPO), both pumped with a tunable solid-state laser.

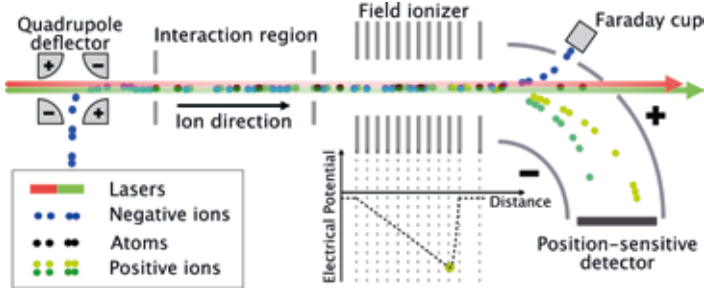


Figure 3.1: A schematic of the RADAR spectrometer. Negative ions are deflected into the interaction region by a quadrupole deflector where they interact with laser beams. Resulting Rydberg atoms can be field ionized, separated from background, and detected with a position-sensitive detector.

3.1.2 DESIREE

The Double ElectroStatic Ion-Ring ExpEriment (DESIREE) is a cryogenic ion beam storage ring facility located at Stockholm University. DESIREE enables high-precision studies of negative ions and molecular interactions by providing an ultra-cold, low-pressure environment allowing for long ion storage times. The entire apparatus, shown in Fig. 3.2, is maintained at a temperature of 13 K. This dramatically reduces background collisions, which is crucial for precision spectroscopy and fundamental studies of weakly bound systems [101].

The facility consists of two rings, one asymmetric and one symmetric. The asymmetric ring has two-fold symmetry, and the symmetric ring has four-fold symmetry, which can be used to overlap beams of different energies to study mutual neutralization. In studies for lifetimes of negative ions, only the symmetric storage ring is used, which is comprised of four 10° electrostatic deflectors, two 160° cylindrical deflectors, and four quadrupole doublets, which guide, steer, and focus the ion beam for stable long-term storage. The symmetric ring is able to store ions with energies of up to 35 keV.

Among the available ion sources at DESIREE, negative ions for our studies were produced using a National Electrostatics Corp. cesium sputter ion source (SNICS II) [102]. The lasers from DESIREE used for our studies include two OPOs with repetition rates of 10 Hz and 1 kHz. Lastly, signal detection at this facility is carried out with a resistive anode encoder coupled

to a stack of three MCPs.

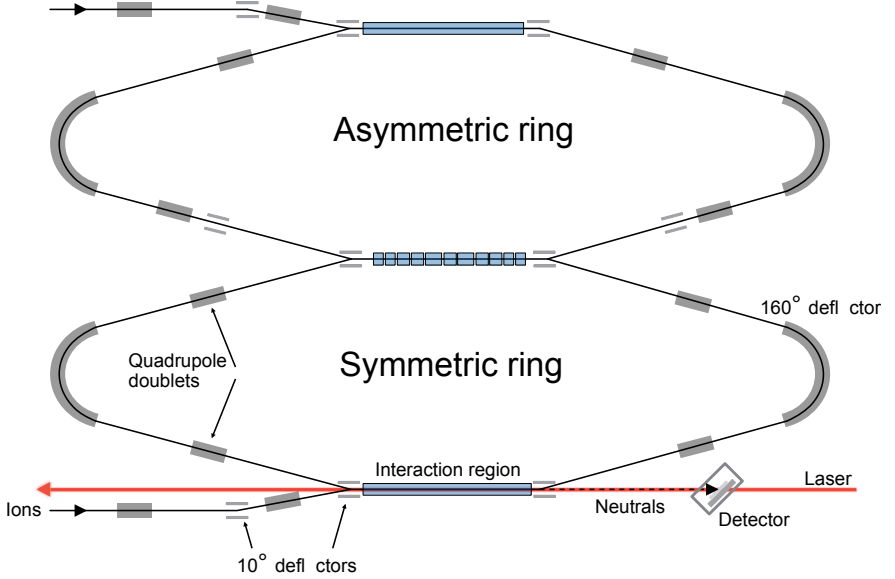


Figure 3.2: DESIREE schematic

3.1.3 ISOLDE

The Isotope mass Separator On-Line facility (ISOLDE) is a radioactive ion beam (RIB) facility, located at CERN [103]. It specializes in the production, manipulation, and study of short-lived radioactive isotopes. The facility operates by impinging high-energy proton beams from the CERN Proton Synchrotron Booster (PSB) onto targets, inducing nuclear reactions that produce a variety of isotopes [104]. These reaction products are then ionized, extracted, and mass-separated to produce high-purity radioactive ion beams.

One of the experimental setups at ISOLDE is the Collinear Resonance Ionization Spectroscopy (CRIS) experiment, designed for high-precision studies of nuclear structure and fundamental interactions [105]. The CRIS beam-line is primarily used for neutral atom spectroscopy, employing a charge exchange cell (CEC) to neutralize the positive ion beam. In the work for this thesis, the same CEC was used to produce negative ions.

3.2 Negative ion production techniques

There are several established methods for the direct production of negative ions, which can be categorized into volume production, where negative ions are produced in a plasma medium, and surface production, which includes negative surface ionization and sputter-type sources [39, 40, 106].

The efficiency of these methods scales with the EA of an element, following the general principle that elements with high EAs are more effectively produced. This is particularly relevant in surface ionization, a method commonly employed for radioactive negative ion production at RIB facilities such as ISOLDE. Surface ionization is highly effective for elements in the halogen group, where LaB₆ is often used due to its relatively low work function ($\sim 2.6\text{--}2.9$ eV) [38]. However, this method does not efficiently produce negative ions with EAs lower than the work function of the target material, resulting in yields that are too low for measurements. Efforts to develop target materials with lower work functions are ongoing [107], but alternative production techniques are still required to reliably produce negative ions with low EAs, which are often heavy and radioactive species.

Negative ions can also be produced indirectly through charge exchange, a process in which an initial positively charged ion beam collides with a neutral target and captures an electron. To form a negative ion, this process must either occur twice sequentially or involve the simultaneous capture of two electrons in a single collision. Charge exchange production has been extensively studied using alkali metal vapor targets, producing negative ions of elements from $Z=2\text{--}79$ [41–44].

In the studies presented in this thesis, the two main methods for negative ion production are sputtering, which is the technique used at GUNILLA and DESIREE, and charge exchange, which is being developed for use at RIB facilities such as ISOLDE. The following sections will discuss these two methods in detail.

3.2.1 Sputtering

Sputtering for negative ion production involves bombarding a target with ions while simultaneously forming a condensed layer on its surface, which effectively reduces the work function and increases the probability of electron attachment. Cesium (Cs) is commonly used due to its low ionization potential (IP) and high vapor pressure. The process begins with a heated reservoir of Cs, which is vaporized at temperatures between 100 and 150°C. The vaporized Cs atoms flow through a tube and are ionized upon contact

with a tantalum surface ionizer maintained at 1300°C. The resulting Cs^+ ions are accelerated to 3 keV towards a solid aluminum or copper cathode containing the target material for sputtering.

Upon impact, the Cs^+ ions sputter atoms from the cathode, while the cathode itself is water-cooled to condensate the residual, non-ionized Cs. The sputtered atoms and molecules can then capture an electron, forming negative ions. This is facilitated by the absorbed Cs, which induces a surface dipole from the electronic redistribution, resulting in a reduced work function of the cathode [108].

Interestingly enough, the exact mechanism behind negative ion formation in sputter-type sources remains unknown. It is suggested that the cathode material influences the source of electrons for capture. In metallic cathodes, a Cs plasma forms on the surface, implying that the sputtered atoms capture free electrons in the plasma. However, in carbon cathodes, electron attachment is likely attributed to the tunneling effects when the work function is reduced [109].

Studying the energy distribution of the produced negative ions provides deeper insights into the underlying sputter mechanisms. Due to the inherently stochastic nature of this technique, the system is not in thermodynamic equilibrium. As a result, the beam exhibits a broad energy distribution, which scales with the mass of the target, extraction voltage, and ion source geometry [110]. This can be approximated by the Sigmund-Thompson model,

$$f(E) \propto \frac{E}{(E + U_s)^3}, \quad (3.1)$$

where E is the energy of the sputtered product and U_s is the surface binding energy [111, 112].

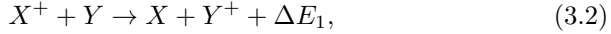
The energy spread of the beam can be reduced by accelerating ions in a homogeneous electric field, leading to a velocity compression effect which can be summarized as $\Delta v \propto 1/\sqrt{E}$. This compression mechanism leads to a more collimated and focused beam, improving its utility in high-precision applications [113].

3.2.2 Charge exchange

Charge exchange relies on an initial positive ion beam colliding with an electron donor or target medium, often an alkali metal vapor, to facilitate electron capture. The process begins with a beam of singly charged positive ions (X^+) directed into a charge exchange cell (CEC), where a target is heated to produce a vapor. Alkali metals are commonly used as the

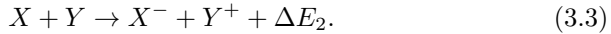
target due to their low IPs, simple electron configurations, and high vapor pressures, making them efficient electron donors. The focus will be on asymmetric charge exchange, where the projectile and target are different.

During this interaction, the positive ion first undergoes a single electron capture, represented by



where the ion captures an electron from the target and becomes neutralized. The energy defect of the reaction is given by $\Delta E_1 = IP(X) - IP(Y)$.

By increasing the vapor pressure in the CEC, the probability for a second electron capture reaction increases, leading to the formation of a negative ion through the reaction



In this case, the energy defect is given by $\Delta E_2 = EA(X) - IP(Y)$. To optimize negative ion production, the energy defects from both reactions should be as small as possible. In the first reaction, ion beam neutralization is most efficient when the projectile and target elements have similar IPs, ensuring high atomic population of the ground state. However, in the second reaction, it is almost always the case that $IP(Y)$ is larger than $EA(X)$, making this an inherent limiting factor in charge exchange negative ion production.

While increasing the target density enhances the probability of electron capture, excessive pressure can lead to an undesired third collision, where the newly formed negative ion is destroyed. As a result, target density is a critical parameter that must be optimized to achieve maximum negative ion yield.

Beyond target density, projectile beam energy also plays a significant role in optimizing negative ion production. If the collision energy is sufficiently high so that the adiabatic representation is no longer relevant, the interaction can be treated in the sudden approximation. In this regime, the collision time is approximately $\tau \simeq a/v$, where a is the effective interaction distance and v is the projectile velocity. For charge exchange to occur efficiently, the collision time must match the electron transition time, given by $\hbar/|\Delta E|$. Equating these time scales leads to an expression for the optimal projectile beam velocity

$$v \simeq \frac{a|\Delta E|}{\hbar}. \quad (3.4)$$

From this, an optimal projectile energy can be estimated [114]. Importantly, the relevant energy defect should correspond to the second (limiting) reac-

tion in the charge exchange process, which constrains the overall efficiency of negative ion production [40].

Despite the effectiveness of charge exchange for producing negative ions of essentially any element, this method results in beam quality degradation that is more prevalent than in other production techniques. The collisional nature of this process introduces unwanted charge states, requiring beam separation, as well as large angular and energy spreads in the beam. This can be addressed by optimizing the mass of the target so that it is as similar as possible to that of the projectile. Assuming kinetic energy conservation from a two-body collision, this relationship is given by the classical derivation of kinetic energy transfer,

$$E_{2,max} = \frac{4M_1M_2}{(M_1 + M_2)^2}E_1, \quad (3.5)$$

where M_1 and E_1 are the mass and energy of the projectile beam, and M_2 is the mass of the target [40]. Therefore, by selecting an appropriate target, beam divergence and energy spread can be minimized, improving transport efficiency.

Charge exchange is a versatile and highly effective method for negative ion production, especially for the heaviest elements where the aforementioned methods fall short. While the work in this thesis has taken significant steps in addressing the challenges and optimization of the charge exchange process, further advancements are necessary.

3.3 Laser spectroscopy techniques

Laser spectroscopy can be performed in both collinear and perpendicular laser-ion beam geometries. The collinear configuration is often preferred due to the longer interaction time, which enhances the signal, and higher spectral resolution, achieved through reduced Doppler broadening as the velocity spread of the ions is compressed by acceleration [98, 113]. In contrast, cross-beam geometry exhibits larger Doppler broadening effects because the transverse velocity spread is not compressed. However, it's preferred in cases requiring high-concentrated photon density and spatially isolated interaction regions, such as for efficient multi-photon absorption [65], precise photoelectron velocity mapping [29], and controlled laser modulation in animated-beam experiments for absolute cross sections measurements [115].

3.3.1 Laser photodetachment threshold spectroscopy

Laser photodetachment threshold spectroscopy (LPTS) is a method for determining EA values. In this technique, the photon energy is tuned in a narrow range around the photodetachment threshold, where the cross section follows the Wigner threshold law. Because negative ions often lack optically allowed transitions, LPTS provides one of the few experimental approaches for investigating their fundamental properties.

The LPTS measurements in this thesis utilize a collinear ion-laser beam geometry, which introduces large Doppler shifts in the observed frequencies. This can be corrected by performing experiments in both co- and counter-propagating directions and computing the geometric mean to eliminate the velocity-dependent shift.

The statistical uncertainty in this method primarily arises from the energy spread of the ion beam and the linewidth of the laser. While laser-ion beam divergence can contribute to the uncertainty by affecting spatial overlap, the impact is significantly reduced in collinear measurements compared with cross-beam setups.

3.3.2 Resonance ionization spectroscopy

Resonance ionization spectroscopy (RIS) is a highly selective technique used to excite and ionize systems through resonant transitions. When combined with LPTS, RIS enhances the precision of EA measurement, particularly for systems with slower photodetachment cross-section onsets (Papers I & II). This method enables state-selective measurements by isolating a specific electronic transition, allowing partial photodetachment cross-sections to be measured. Additionally, RIS has been instrumental in studying doubly excited states [25] and threshold behaviors [26] in alkali metal negative ions.

3.3.3 Pump-probe spectroscopy

Pump-probe spectroscopy is a time-resolved technique used to investigate electron dynamics in atomic and molecular systems. It utilizes two laser pulses, which act to excite the system and then subsequently monitor the evolution over time. A variation of this method instead uses a depletion pulse to empty excited electronic states, which has been used to measure the lifetimes of metastable states in negative ions [116] as well as for the most precise EA measurement to date [117].

Building on the deplete-probe method, this thesis introduces deplete-pump-probe spectroscopy to study negative ion dynamics with enhanced selectivity. First, a depletion laser removes electrons from excited states, ensuring high ground state population. Next, a pump laser selectively re-excites a specific state, allowing for isolated and targeted studies. Finally, a probe laser detaches the electron, enabling a direct measurement.

This method is particularly valuable for systems with multiple metastable states, as it allows for individual state separation and measurement depending on the available lasers. By controlling which states are re-excited and subsequently probed, depletion-pump-probe spectroscopy provides a powerful tool for investigating complex electron dynamics in negative ions with higher precision.

3.4 Laser systems

3.4.1 Solid-state lasers

Neodymium-doped yttrium aluminum garnet (Nd:YAG) is a crystal commonly used as a lasing medium for solid-state lasers. They can serve as pump lasers due to their high-intensity output and strong transition at 1064 nm. In our experiments, a pulsed configuration is typically preferred, which is achieved by operating in Q-switch mode. This involves blocking the cavity until the crystal reaches optimal population inversion. Q-switch mode can increase power output by up to four orders of magnitude, which is essential for higher-order harmonic generation [118].

For the experiments, the Nd:YAG lasers came integrated with the OPOs.

3.4.2 Optical parametric oscillators

Optical parametric oscillators (OPO) are tunable light sources that rely on optical gain from parametric amplification in a nonlinear crystal rather than stimulated emission. The OPO generates two frequency components from the pump laser, the signal and the idler, depending on phase-matching conditions in the nonlinear crystal. One of these waves, usually the signal, is selectively amplified by the optical cavity, resonating and increasing in intensity with each pass through the crystal [119].

At GUNILLA, there is one EKSPLA OPO integrated system with a repetition rate of 10 Hz (NT342C). At DESIREE, there are two EKSPLA OPO integrated systems with repetition rates of 10 Hz (NT342C) and 1 kHz (NT242). The NT342C offers a tuning range of 192 to 2600 nm, pulse

duration of 3-5 ns, and linewidth of $\leq 5 \text{ cm}^{-1}$ (150 GHz). The NT242, with a tuning range of 210 to 2600 nm, has similar specifications as the 10 Hz system but delivers pulse energies that are two orders of magnitude lower.

3.4.3 Tunable dye lasers

Dye lasers are widely used in spectroscopy due to their broad tunability and high spectral resolution. They operate using organic dye as the gain medium and require a pump laser, such as an Nd:YAG laser, to induce fluorescence [120].

The Sirah PrecisionScan dye laser used for the EA studies mentioned operates in the wavelength range of 370 to 920 nm, depending on the dye and dispersion option chosen. The linewidth is reported to be 0.075 cm^{-1} (2 GHz).

3.4.4 Continuous-wave diode lasers

Continuous-wave diode lasers are particularly useful for investigating effects that are challenging to resolve, such as isotope shifts and hyperfine structures, due to their narrow linewidth and excellent frequency stability.

A Toptica Photonics CTL 1550 continuous-wave diode laser, with an instantaneous linewidth of 0.3 kHz and an average micro motor step size of 0.5 pm, was used for investigating Sn^- .

3.5 Detectors

3.5.1 Neutral particle detectors

In experiments where an electron is photodetached from a negative ion, the residual neutral atom can be detected using a neutral particle detector (NPD). Since neutral atoms do not respond to electric or magnetic fields, detection relies on secondary electron emission. When a neutral atom collides with a conductive target, it can induce the release of secondary electrons. These emitted electrons are then collected and amplified using a channel electron multiplier (CEM), enabling indirect detection of the neutral atom and, in turn, the determination of photodetachment cross sections.

To be compatible with the collinear laser-ion geometry, the conductive target must also be optically transparent to allow laser passage. However, conductivity and transparency are opposing material properties, making the choice particularly challenging. A graphene-coated quartz plate offers a

practical compromise, with the monolayer of graphene providing sufficient conductivity and the quartz ensuring optical transparency [121].

3.5.2 Microchannel plate detectors

The microchannel plate (MCP) detector is capable of detecting individual particles, including electrons, ions, and photons. It consists of a thin plate made of an array of microscopic capillaries or channels, each functioning as an electron multiplier. When a charged particle impinges on the MCP surface, it initiates a cascade of secondary electron emissions, which are amplified as they travel through the channels.

For position-sensitive detection, the MCP is often coupled with a delay line anode, as used at GUNILLA, or a resistive anode encoder, as used at DESIREE where they are custom made to have significantly lower resistance for particle detection at cryogenic temperatures. In both systems, the signal from the MCP propagates in opposite directions along the wires. By measuring the time delay between the signals at both ends of the wire, the precise position of the detected event can be determined [122]. Alternatively, the MCP can be paired with a phosphor screen and the fluorescence can be detected using a camera, providing a visual map for the detected particles.

3.5.3 Time-of-flight detection

Time-of-flight (ToF) detection in MagneTOF detectors uses a combination of electric and magnetic fields to control the trajectories of secondary electrons emitted from the impact of a charged particle. Since the emission time and angle of these electrons vary depending on the impact location, the applied external fields are used to compensate for their trajectories. This ensures that all secondary electrons are directed to the detector with uniform transit times [123].

3.6 Application of methods

3.6.1 Alkali metal electron affinity measurements

Papers I and II detail the measurements of the EAs of Cs and Rb at the GUNILLA facility, using the RADAR spectrometer for Rydberg atom ionization and spatially resolved detection. The experiment combines LPTS with RIS, where a dye laser serves as the first step, which scans over the photodetachment threshold, and a 10 Hz OPO is used for the subsequent

resonance ionization, as shown in Fig. 3.3 for Cs. Detection is performed using an MCP detector, which provides spatially resolved signal readout.

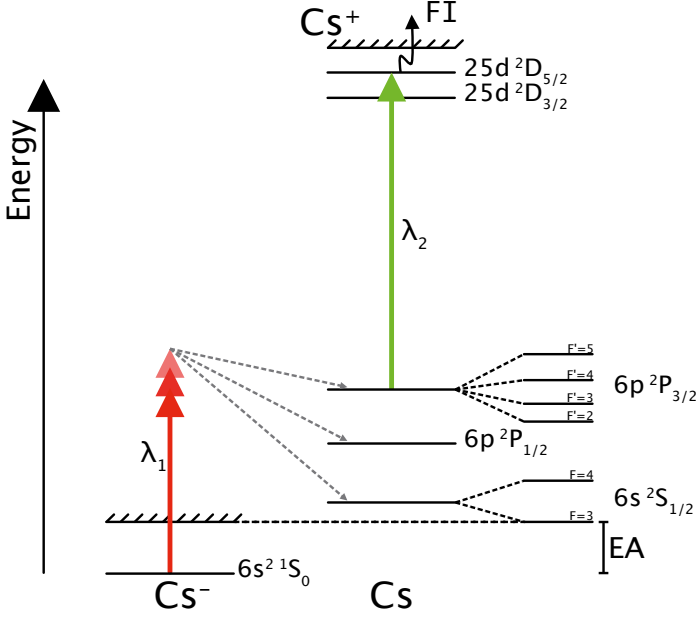


Figure 3.3: Partial energy level diagram (not to scale) for Cs^- and Cs . A photon (λ_1) from a frequency tunable laser is absorbed by a Cs^- ion (red arrows). Subsequently, the ion can decay into three different neutral states via electron emission (dashed arrows). The neutral Cs atom in the $6p^2 P_{3/2}$ excited state then absorbs another photon (λ_2) at a fixed wavelength for resonant excitation to the Rydberg state, $25d^2 D_{5/2}$ (green arrow). Finally, the Rydberg atom underwent a field ionization (FI) process (curved arrow), creating a positive ion.

3.6.2 Radioactive negative ion production

Paper III describes the production of $^{238}\text{U}^-$ at the ISOLDE facility using the charge exchange production method. Here, a beam of $^{238}\text{U}^+$ was produced using a pre-irradiated uranium carbide target in a resonant ionization laser ion source. The uranium ion beam was accelerated to an energy of 40 keV, then mass selected by the high-resolution separator and cooled and bunched in a gas-filled radio frequency quadrupole linear Paul trap (ISCOOL) [124].

After the $^{238}\text{U}^+$ beam reached the CRIS experimental setup, the ions entered the potassium-filled CEC. Potassium was chosen for the charge exchange target vapor due to its lower first IP compared to the other available option, sodium. The CEC was resistively heated with cartridge heaters and a Variac variable transformer AC power supply (200V) to a maximum relative temperature of $\sim 140^\circ\text{C}$.

After production, the negative ions were electrostatically separated from the positive and neutral charge states and detected with a MagneToF single ion detector. There was a maximum transmission efficiency for positive ions of $\sim 5\%$ to the end of the CRIS beamline from ISOLDE, meaning a few nA reached the entrance of the CEC which is more than enough to conduct experiments. This was determined by Faraday cup measurements after ISCOOL and MagneToF detector measurements in single ion counting mode placed after the bend. The experimental setup is shown in Fig. 3.4.

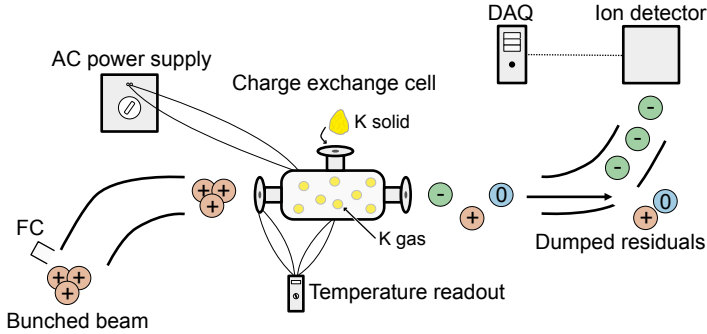


Figure 3.4: The cooled and bunched positive ion beam (red) from ISOLDE was guided to the CRIS experimental setup and into the charge exchange cell (CEC) where solid potassium (K) was inserted from the top and heated until gas phase was reached. With increasing pressure, two separate electron capture reactions between the projectile beam and the K atoms in gas phase (yellow) occurred to produce negative ions (green). The remaining positive ions that did not capture any electrons and the neutral atoms (blue) that only underwent one electron capture reaction were dumped while the negative ions were electrostatically bent towards the ion detector, which was connected to the data acquisition system (DAQ). The CEC was heated by the AC power supply and the temperature was read with thermocouples from the CEC end and center, with the center temperature values recorded for the measurement. Finally, the transmission efficiency measurements were taken between the Faraday cup (FC) and the ion detector for positive ions.

3.6.3 Isotope shift and lifetimes studies in the tin anion

Paper V reports the isotope shift (IS) measurements and lifetimes of the excited states in stable Sn^- preformed at DESIREE. For the IS measurements, a two-step laser ionization scheme in collinear geometry was employed following the depletion-pump-probe method. In the first step, an OPO at 1200 nm was used to deplete the electronic population in the $\text{Sn}^-(^2D_J)$ excited states. The second step involved using a continuous-wave diode laser in an anti-collinear geometry to drive the bound-bound $\text{Sn}^-(^4S_{3/2}) \rightarrow \text{Sn}^-(^2D_{5/2})$ transition. The same laser also acted as the probe step, which neutralized the atom. This process is shown in Fig. 3.5.

For the lifetime measurements, the same depletion-pump-probe method was used to selectively measure the lifetime of the $\text{Sn}^-(^2D_{5/2})$ state. Because there were two states with lifetimes of similar magnitude, it was advantageous to measure the longer-lived state separately to precisely determine the lifetime and use it as a fixed fitting parameter in data that measured the decay of both states.

In both cases, detection of neutral Sn resulting from photodetachment was achieved using a graphene-coated quartz plate as the secondary electron emitter, and then the signal was amplified using a stack of three MCP detectors and detected with the coupled resistive anode encoder.

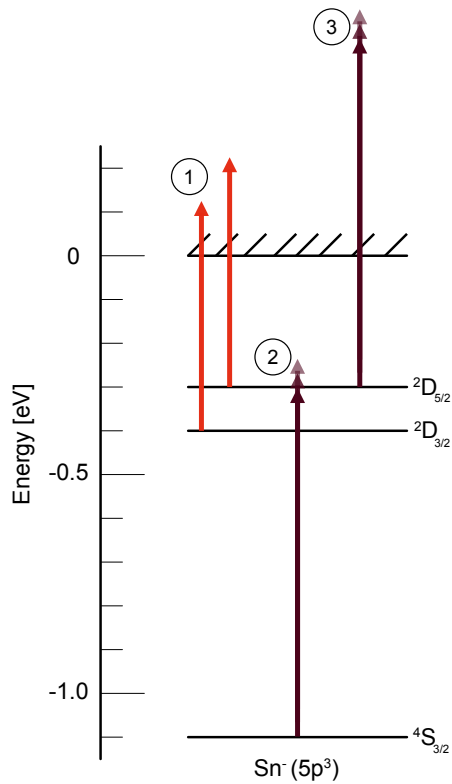


Figure 3.5: Energy level diagram of the Sn^- anion and the applied laser transitions. The circled numbers represent the step: 1 corresponds to the excited state depletion, 2 is the selective state repopulation, and 3 is the final detachment into the continuum.

Chapter 4

Theoretical Methods

Before presenting the results, the theoretical framework used to investigate trajectory effects in atomic collisions will be discussed. Traditionally, many theoretical approaches have relied on a straight-line approximation. However, recent advancements have demonstrated that accounting for electron-nuclear coupling in ion-atom collisions can significantly alter predictions of energy loss, particularly at low collision energies [125]. This highlights the necessity of reevaluating conventional trajectory approximations.

In this work, we solve the time-dependent Schrödinger equation using a lattice representation (LTDSE) to assess the impact of different trajectory models, comparing straight-line approximations with dynamically coupled electron-nuclear trajectories based off of the time-dependent electron-nuclear dynamics (END) approach [126]. The computational methodology employs a finite-difference Crank-Nicholson approach, which enables tracking of electron capture probabilities and energy deposition. Implementing this approach allows us to evaluate the limitations of classical, semi-classical, and perturbative models, particularly in systems involving bare ion projectiles such as H colliding with atomic hydrogen (Paper IV).

4.1 Numerical methods

4.1.1 Finite-difference method

The finite-difference method (FDM) is a numerical technique for approximating differential equations by discretizing a continuous problem into a system of linear equations over a finite space. This allows for differential

operators to be replaced by algebraic expressions, simplifying the computational solution.

The general form of the FD approximation can be derived from the Taylor series expansions of a function $f(x, t)$ about a point x_0 . Expanding the function to the second order in Δx gives

$$f(x_0 \pm \Delta x, t) = f(x_0) \pm \left. \frac{\partial f}{\partial x} \right|_{x_0} \Delta x + \frac{1}{2} \left. \frac{\partial^2 f}{\partial x^2} \right|_{x_0} \Delta x^2 + \mathcal{O}(\Delta x^3). \quad (4.1)$$

By retaining only the first-order term, these expressions yield the forward-difference approximation

$$\left. \frac{\partial f}{\partial x} \right|_{x_0} = \frac{f(x_0 + \Delta x) - f(x_0)}{\Delta x} + \mathcal{O}(\Delta x^2), \quad (4.2)$$

and the backward-difference approximation

$$\left. \frac{\partial f}{\partial x} \right|_{x_0} = \frac{f(x_0) - f(x_0 - \Delta x)}{\Delta x} + \mathcal{O}(\Delta x^2), \quad (4.3)$$

assuming a sufficiently small step size Δx .

To approximate the second-order derivative, the expansions in Eq. (4.1) can be added to eliminate the first-order term, given by

$$f(x_0 + \Delta x, t) + f(x_0 - \Delta x, t) = 2f(x_0, t) + \left. \frac{\partial^2 f}{\partial x^2} \right|_{x_0} \Delta x^2 + \mathcal{O}(\Delta x^3). \quad (4.4)$$

Rearranging this expression yields the centered FD approximation for the second-order derivative as

$$\left. \frac{\partial^2 f}{\partial x^2} \right|_{x_0} = \frac{f(x_0 + \Delta x) - 2f(x_0) + f(x_0 - \Delta x)}{\Delta x^2} + \mathcal{O}(\Delta x^3). \quad (4.5)$$

On a discrete numerical grid, x_k denotes the k -th grid point, with uniform spacing $\Delta x = x_{k+1} - x_k$ and $k \in \{1, \dots, N-1\}$. The second-order derivative at x_k can then be approximated using Eq. (4.5)

$$\left. \frac{\partial^2 f}{\partial x^2} \right|_{x_k} = \frac{f_{k+1}^n - 2f_k^n + f_{k-1}^n}{\Delta x^2} + \mathcal{O}(\Delta x^3). \quad (4.6)$$

This is the standard FD scheme used in numerical solutions of partial differential equations.

4.1.2 Crank-Nicolson method

The Crank-Nicolson method (CNM) is a time integration scheme used to approximate the evolution of time-dependent differential equations [127]. In the context of the time-dependent Schrödinger equation (TDSE), CNM approximates the unitary-time evolution operator $\hat{\mathbf{U}}$ propagation over a discrete time step Δt . This is an implicit method that is second-order accurate in time and is often combined with FDM for spatial discretization due to its simplicity and computational efficiency.

The TDSE in one dimension can be written as

$$i\hbar \frac{\partial}{\partial t} \psi(x, t) = \hat{\mathbf{H}} \psi(x, t), \quad (4.7)$$

where the time-independent Hamiltonian $\hat{\mathbf{H}}$ is composed of kinetic and potential energy operators:

$$\hat{\mathbf{H}} = \hat{\mathbf{T}} + \hat{\mathbf{V}}, \quad (4.8)$$

$$\hat{\mathbf{H}} = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} + V(x). \quad (4.9)$$

The exact solution to the TDSE over a time interval of length Δt is formally given by $\hat{\mathbf{U}}$, defined as

$$\hat{\mathbf{U}} = e^{-i\hat{\mathbf{H}}\Delta t/\hbar}, \quad (4.10)$$

such that

$$\psi(x, t + \Delta t) = \hat{\mathbf{U}} \psi(x, t). \quad (4.11)$$

Since $\hat{\mathbf{T}}$ and $\hat{\mathbf{V}}$ do not commute, i.e. $[\hat{\mathbf{T}}, \hat{\mathbf{V}}] \neq 0$, the exponential operator cannot be trivially factorized. To address this, $\hat{\mathbf{U}}$ can be approximated using the Strang splitting technique [128], ensuring that the overall scheme is second-order accurate in time

$$e^{-i\hat{\mathbf{H}}\Delta t/\hbar} \simeq e^{-i\hat{\mathbf{T}}\Delta t/2\hbar} e^{-i\hat{\mathbf{V}}\Delta t/\hbar} e^{-i\hat{\mathbf{T}}\Delta t/2\hbar}. \quad (4.12)$$

Because $\hat{\mathbf{V}}$ is multiplicative in position space, the exponential acts exactly on the wavefunction, resulting in

$$\tilde{\psi}^n(x) = e^{-i\hat{\mathbf{V}}\Delta t/\hbar} \psi^n(x), \quad (4.13)$$

where $\psi^n(x)$ is the wavefunction at time $t = n\Delta t$. However, because $\hat{\mathbf{T}}$ involves spatial derivatives, the exponential cannot be applied in the same

way. Instead, $\hat{\mathbf{T}}$ is discretized using the CNM over a time step Δt , yielding the implicit equation

$$\left(1 + \frac{i\Delta t}{2\hbar} \hat{\mathbf{T}}\right) \psi^{n+1}(x) = \left(1 - \frac{i\Delta t}{2\hbar} \hat{\mathbf{T}}\right) \tilde{\psi}^n(x). \quad (4.14)$$

The CN kinetic energy term $\frac{i\Delta t}{2\hbar} \hat{\mathbf{T}}$ acts on the wavefunction through the second spatial derivative, which can be discretized using the second-order centered FD approximation. Applying Eq. (4.6) at a grid point $x_k = k\Delta x$ gives

$$\frac{i\Delta t}{2\hbar} \hat{\mathbf{T}} \psi_k^n \approx -\frac{i\hbar\Delta t}{4\mu(\Delta x)^2} (\psi_{k+1}^n - 2\psi_k^n + \psi_{k-1}^n), \quad (4.15)$$

where we define the coefficient

$$\nu = \frac{i\hbar\Delta t}{4\mu(\Delta x)^2}. \quad (4.16)$$

Finally, the CN discretization for the kinetic evolution step takes the form

$$(1 + 2\nu) \psi_k^{n+1} - \nu \psi_{k+1}^{n+1} - \nu \psi_{k-1}^{n+1} = (1 - 2\nu) \psi_k^n + \nu \psi_{k+1}^n + \nu \psi_{k-1}^n, \quad (4.17)$$

and the wavefunction at the next time step ψ^{n+1} can be vectorized and written in matrix form as

$$\mathbf{A}^+ \psi^{n+1} = \mathbf{A}^- \psi^n, \quad (4.18)$$

where $\mathbf{A}^+$ and $\mathbf{A}^-$ are symmetric tridiagonal matrices

$$\mathbf{A}^\pm = \begin{bmatrix} 1 \pm 2\nu & \mp\nu & 0 & \cdots & 0 \\ \mp\nu & 1 \pm 2\nu & \mp\nu & \ddots & \vdots \\ 0 & \ddots & \ddots & \ddots & 0 \\ \vdots & \ddots & \mp\nu & 1 \pm 2\nu & \mp\nu \\ 0 & \cdots & 0 & \mp\nu & 1 \pm 2\nu \end{bmatrix}.$$

After this derivation, it can be seen that the CNM approximates the exact exponential evolution of the kinetic operator with a time-centered, implicit, and symmetric finite-difference scheme. It offers unconditional stability by preserving unitarity and avoids time step restrictions, allowing for larger time steps while maintaining accuracy.

4.2 Nuclear trajectories

4.2.1 Coupled trajectory

A time-dependent electron-nuclear dynamics (END) approach [126] is employed for coupling the electron and nuclei dynamics. The time-dependent Schrödinger equation governing the behavior of an electron in the presence of N nuclei is expressed as

$$i\frac{\partial}{\partial t}\Psi(\mathbf{r}, t) = \left[-\frac{1}{2}\nabla^2 - \sum_{i=1}^N \frac{Z_i}{|\mathbf{r} - \mathbf{R}_i(t)|} \right] \Psi(\mathbf{r}, t), \quad (4.19)$$

where $\Psi(\mathbf{r}, t)$ is the time-dependent wave function, Z_i is the charge of the i -th nuclei, and $\mathbf{R}_i$ denotes the trajectory of the heavy i -th nuclei coupled to the electron. The dynamics of the coupling are described by the equations [129]:

$$\begin{aligned} \dot{\mathbf{R}}_i &= \frac{1}{M_i} \mathbf{P}_i(t) \\ \dot{\mathbf{P}}_i &= Z_i \langle \Psi | \frac{(\mathbf{r} - \mathbf{R}_i)}{|\mathbf{r} - \mathbf{R}_i|^3} | \Psi \rangle - \\ &\quad \sum_{k \neq i}^N Z_k Z_i \frac{(\mathbf{R}_k - \mathbf{R}_i)}{|\mathbf{R}_k - \mathbf{R}_i|^3}, \end{aligned} \quad (4.20)$$

where i ranges from 1 to N number of heavy nuclei. In our specific case, we set $N = 2$.

To solve Eq. (4.20), we make use of the fourth-order Runge-Kutta method (RK4) coupled to Eq. (4.19). RK4 is a numerical method that is used for solving ordinary differential equations given the initial value problem

$$\frac{dy}{dt} = f(t, y), \quad y(t_0) = y_0. \quad (4.21)$$

The next value for y can be solved using

$$y_{n+1} = y_n + \frac{h}{6}(k_1 + 2k_2 + 2k_3 + k_4), \quad (4.22)$$

where the intermediate steps are defined as:

$$k_1 = f(t_n, y_n) \quad (4.23)$$

$$k_2 = f\left(t_n + \frac{h}{2}, y_n + \frac{h}{2}k_1\right) \quad (4.24)$$

$$k_3 = f\left(t_n + \frac{h}{2}, y_n + \frac{h}{2}k_2\right) \quad (4.25)$$

$$k_4 = f(t_n + h, y_n + hk_3), \quad (4.26)$$

and h is the step size [130, 131].

4.2.2 Straight-line trajectory

For scenarios involving straight-line trajectories, we simplify our approach by fixing the position of the target nucleus at $\mathbf{R}_1 = 0$ and defining the position of the projectile as

$$\mathbf{R}_2 = \mathbf{b} + \mathbf{v}t. \quad (4.27)$$

Here, $\mathbf{b} = b\hat{x}$ represents the impact parameter and $\mathbf{v} = v_0\hat{z}$ is the collision velocity. In this case, the projectile momentum $\mathbf{P}_2 = M_2\mathbf{v}$ remains constant throughout the collision process where $v = \sqrt{2mE}$.

4.3 Lattice definition

With the numerical methods and trajectories established, the numerical lattice framework is introduced, where the CN approach is applied [132]. Ionization is addressed by implementing a masking function that absorbs ionized electrons at each time step on the grid boundary [133]. In Fig. 4.1, the masking function acts over the box Ω at the edge of the numerical grid in the space between the blue and black boxes. It is expressed as $M(\mathbf{r}) = M(x)M(y)M(z)$, where $M(z)$ is given by

$$M(z) = \begin{cases} \cos^{1/8}\left(\frac{\pi|z-z_b+L|}{2L}\right), & |z_b - z| < L \\ 1, & \text{otherwise.} \end{cases} \quad (4.28)$$

Here, z_b indicates the boundary along the z -axis, either at z_{min} or z_{max} , and L is the absorbing width of the region Ω . The expressions are similar for the x and y cases.

The computational grid is defined as $[-18, 18]_x \times [-18, 18]_y \times [-30, 45]_z$ a.u., with a grid step of 0.4 a.u.. We select a time step of 0.01 a.u., which strikes a balance between accuracy and computational efficiency. It is also long enough to achieve a clear separation between the target and projectile at the end of our simulation. The collision time is defined as $t_0 = 2z_0/v_0$, where v_0 is the initial velocity of the projectile and z_0 is the initial projectile distance to the target. With this, Eq. (4.20) is solved with the fourth-order Runge-Kutta method coupled to Eq. (4.19). For the straight trajectories, we simply advance $\mathbf{R}_2$ according to Eq. (4.27).

To prevent numerical instabilities when nuclei $\mathbf{R}_i$ pass near a grid point $\mathbf{r}$, we arrange our impact parameter grid so that both projectile and target trajectories align with points at the center of adjacent squares in the xy -plane [132]. The impact parameter b is varied from 0.0 to 14.0 a.u. in increments of 0.4 a.u.. Initially, we position the projectile along the z -axis at a distance of $z_0 = -30$ a.u., as illustrated in Fig. 4.1.

We perform calculations for collision energies in the laboratory frame of the projectile, E_p , ranging from 0.1 keV/u up to 900 keV/u. To account for polarization effects on the hydrogen electronic cloud due to initial placement at $z_0 = -30$ a.u. and $x = b$, we compute the initial wave function using an imaginary time technique for each configuration [132], which allows for ground state convergence. Finally, we set an absorbing width $L = 4.0$ a.u., ensuring effective electron absorption without interfering with the collision region, Γ [133].

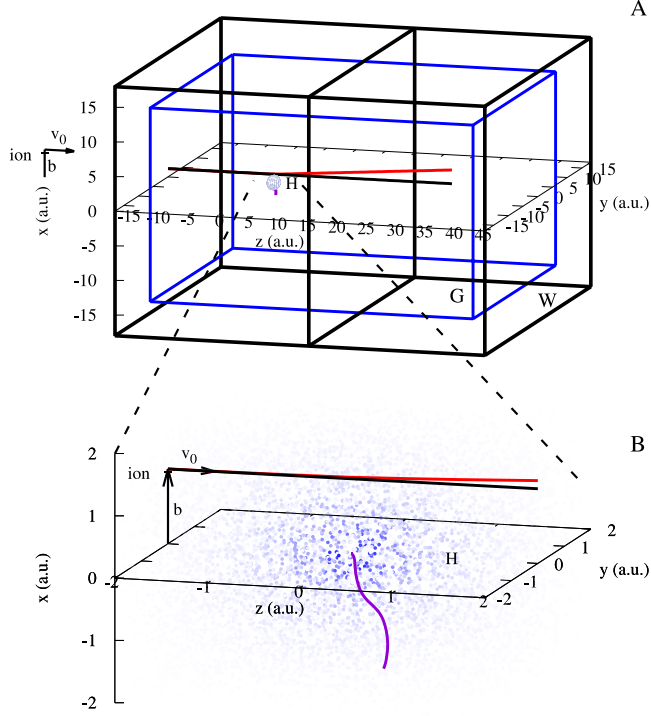


Figure 4.1: A^q+H collision rendering. In **A**, the sphere represents the 1s hydrogen electron density, b is the collision impact parameter of an ion A^q with q the initial charge, located initially at a distance z_0 , and v_0 is the initial collision velocity. The space between the inner (blue) and outer (black) boxes represents the ionization absorbing region, Ω . The box for $z > 15$ a.u. determines the electron capture by the projectile and is denoted by Γ . The black and red lines correspond to the straight-line and the electron-nuclei coupled trajectories, respectively, for $b = 1.2$ a.u. impact parameter. In **B**, an inset of the collision region around the target electronic density (dotted blue cloud) is shown. The purple line is the target recoiling trajectory in the electron-nuclei coupled scheme.

Chapter 5

Results

This chapter summarizes the results from each study conducted in this thesis, with detailed descriptions available in the appended papers. The first section focuses on high-resolution electron affinity (EA) measurements of cesium (Cs) and rubidium (Rb), performed using a combination of laser photodetachment threshold spectroscopy (LPTS) and resonance ionization spectroscopy (RIS) at GUNILLA (Papers I & II). These results push the precision limits of bound-continuum measurements in negative ions, particularly in cases where elements with photodetached *s*-shell electrons introduce challenges.

Expanding the scope of negative ion studies, this thesis also investigated an alternative negative ion production method for low-yield, heavy, and radioactive elements, focusing on uranium (U) at ISOLDE (Paper III). Developing efficient production techniques is essential for extending bound-continuum and bound-bound measurement methods to radioactive anions, which remain far less studied than their stable counterparts.

Since experimental studies on radioactive anions are inherently difficult, theoretical modeling becomes invaluable. The next section presents atomic collision theory, where the time-dependent Schrödinger equation in a numerical lattice (LTSDE) was solved to investigate trajectory effects in charge exchange and energy loss for bare ion projectiles colliding with atomic hydrogen (Paper IV). This study lays the groundwork for modeling heavy negative ion production through electron capture reactions, a necessary step toward extending high-precision negative ion spectroscopy to unexplored elements.

Further breaking into the undiscovered, the final section explores electric dipole (*E1*) forbidden bound-bound transitions in the tin (Sn) anion,

using the depletion-pump-probe method at DESIREE (Paper V). These measurements enabled high-precision isotope shift (IS) and state lifetime measurements, marking a significant milestone in negative ion spectroscopy by making forbidden transitions in negative ions experimentally accessible.

5.1 Electron affinity measurements

This section summarizes the results from Papers I and II, which describe the most precise EA measurements to date for cesium (Cs) and rubidium (Rb), obtained using a method combining LPTS and resonance ionization spectroscopy (RIS). These refined EA measurements represent the first successes of the state-selective approach and provide benchmarks for theoretical models that account for electron correlation. Additionally, these studies establish a framework for future high-precision EA measurements, particularly at radioactive ion beam facilities. Francium is an obvious first candidate, as its EA remains experimentally unmeasured.

5.1.1 Cesium

A typical threshold measurement is shown in Fig. 5.1, where only the photodetachment cross section from the $6p\ ^2P_{3/2}$ state was measured. When fitting the data, a deconvolution technique was applied to account for the influence of the bandwidth of the laser and the velocity spread of the ions. Refer to Paper I for an in-depth explanation of this technique.

To cancel out the Doppler shift effect to all orders, measurements were alternated between co- and counter-propagation schemes and then the geometric mean was calculated. To extract the EA, the difference in energy between the ground state ($6s\ ^2S_{1/2}(F=3)$) and the excited $6p\ ^2P_{3/2}(F=2)$ state of the neutral Cs atom was subtracted from the Doppler corrected geometric mean. The EA of Cs was determined to be $0.471\,598\,3(38)$ eV.

This result is a significant improvement over previous measurements, reducing the uncertainty by an order of magnitude, as shown in Fig. 5.2. The comparison shows that the improved value is slightly lower than the widely cited $0.471\,64(6)$ eV reported by Hotop and Lineberger [15]. However, our measurement accounted for the hyperfine splitting in the residual ^{133}Cs atom, which was not explicitly considered in previous experiments. For a proper comparison, the Hotop and Lineberger value was corrected for the hyperfine splitting, which accounted for 21 μeV . Additionally, this study benefits from state-selectivity precision and mitigates systematic un-

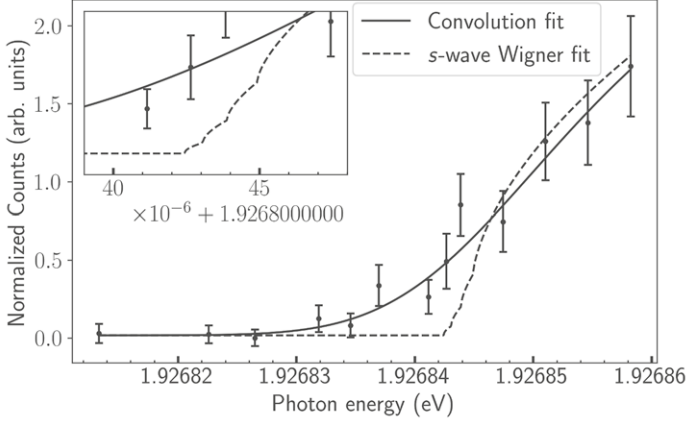


Figure 5.1: The number of registered events following the Doppler shifted partial photodetachment that leaves the neutral atom in the excited $6p\ ^2P_{3/2}, F = 2$ state, as a function of the photon energy. The ion beam and the laser used for photodetachment were merged in a co-propagating scheme. The fit was obtained with a discrete convolution between the Gaussian normalized function and the Wigner function and is shown as a solid line. The optimized parameters were then used in the Wigner function to obtain a deconvoluted s -wave Wigner function that is shown as a dashed line. The threshold for this measurement is 1.926 842 4(51) eV. The inset shows an expansion around the threshold where the hyperfine structure of the excited state are resolved.

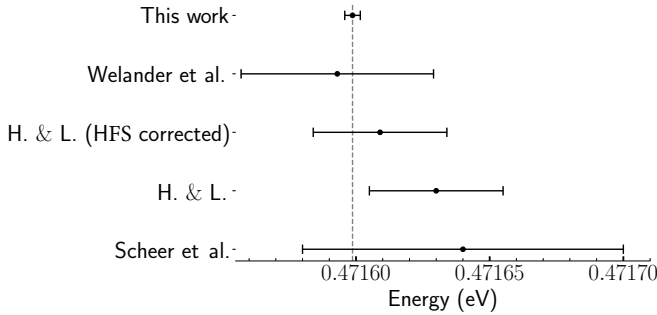


Figure 5.2: EA(Cs) experimental value from this work compared with the values from Welander *et al.* [66], Hotop and Lineberger (H. & L.) [15], the H. & L. value corrected for the hyperfine splitting (HFS corrected) of 21 μ eV, and Scheer *et al.* [134].

certainties through Doppler shift corrections, increasing confidence in the result.

5.1.2 Rubidium

Given its similar electronic structure to Cs, extending this methodology to Rb provided an opportunity to improve the EA value with comparable accuracy. Probing only the $5p\ ^2P_{3/2}$ state in the residual neutral atom, the EA of Rb was measured to be 485.887(6) meV. The co-propagating threshold can be seen in Fig. 5.3. The EA was extracted in the same way as Cs, except the use of the convolution fit function resulted in a spread of the width of the Gaussian profile by over an order of magnitude between individual threshold scans, likely caused by a lack of closely spaced data points around the onset of the threshold. Therefore, the data was fitted with a fixed value for the width of the Gaussian, determined from the Cs experiment. The same laser and ion source conditions were used in both experiments, where the laser linewidth is the dominating contributor to the broadening, so it is justified to use the same value as an approximation for the overall broadening. Details of this analysis can be found in Paper II.

Previously, the EA of Rb was reported to be 485.916(21) meV [135], meaning the present measurement reduced the uncertainty by a factor of three. Again, our measured EA value is slightly lower than the previous determinations, though the discrepancy remains within the experimental uncertainties. This difference can also be attributed to the hyperfine splitting in the residual ^{85}Rb atom, accounting for 7.32 μeV .

5.2 Radioactive negative ion production with charge exchange

Studying negative ions first requires sufficient production, which is typically achieved using surface ionization in a Cs sputter ion source. This method is highly effective for stable elements with sufficiently high EA values. However, challenges arise when dealing with elements that have low EAs or are inherently available in limited quantities; both of which are common characteristics for radioactive species. Therefore, an alternative production method for such negative ions must be developed to enable further studies.

This section explores Paper III, which details the use of electron capture reactions for $^{238}\text{U}^-$ production in a charge exchange cell. The focus is on optimizing the conditions for sequential charge exchange reactions, which

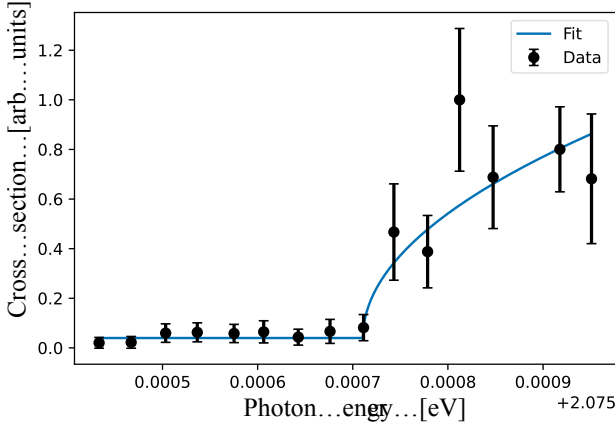


Figure 5.3: The relative photodetachment partial cross section as a function of the relative photon energy where the neutral Rb atom is left in the $5p\ ^2P_{3/2}$ state. The data was obtained in a co-propagating geometry and fitted using the Wigner law. The fit is represented by a solid line.

are required to produce negative ions from an initial beam of positive ions. Since positive ions are more easily and commonly produced at radioactive ion beam facilities, understanding this process is essential for expanding studies to radioactive negative ions, especially in heavy systems.

Figure 5.4 presents the results of $^{238}\text{U}^-$ production in a charge exchange cell, where a 40 keV beam of $^{238}\text{U}^+$ ions served as the projectile and potassium vapor as the target. The efficiency of this process was found to be highly dependent on the target vapor density, which was controlled by heating the potassium source to $\sim 140^\circ\text{C}$.

The results show that negative ion production increased with target vapor pressure until a saturation point was reached at around 134°C , after which further heating led to a decrease in ion yield. This was caused by an additional collision, which destroyed the negative ion. Hence, optimizing target density in the charge exchange cell is crucial for maximizing negative ion production.

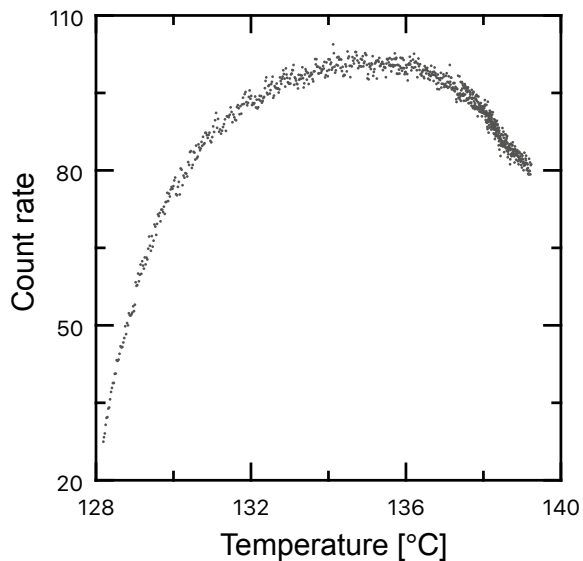


Figure 5.4: Temperature dependence of negative uranium-238 ion production in a charge exchange cell as measured with a MagneToF detector. A 40 keV projectile beam of positive uranium-238 ions collides with potassium vapor to first undergo a single electron capture reaction. As the temperature in the cell increases, so does the probability for a second electron capture reaction until the curve saturation point at $\sim 134^\circ\text{C}$. As temperature continues to increase, the cross section of a third collision also increases in which the produced negative ions are subsequently destroyed.

5.3 Modeling ion-atom collision dynamics

The previous section discussed experimental ion-atom collisions for negative ion production, highlighting the importance of understanding electron capture in such collisions. To complement this study, a theoretical framework was developed to further understand the inelastic processes in these collisions. This section reviews Paper IV, which presents a theoretical study on the role of nuclear trajectories in charge exchange and energy loss processes. This study establishes the LTDSE method with bare ion projectiles with charge $Z = 1-4$ incident on atomic hydrogen in an energy range of 0.1 to 900 keV/u.

Many previous theoretical studies have investigated these systems, but few have considered how nuclear motion affects inelastic processes. Most studies use straight-line approximations, which are inherently not energy conserving. For this reason, this study compares straight-line trajectories with an electron-nuclear coupled approach to assess the impact on charge exchange and energy loss.

In Fig. 5.5, charge exchange cross sections are found to be trajectory-independent, showing excellent agreement with available experimental and theoretical data. This suggests that electron capture is predominantly governed by electronic interactions rather than nuclear motion, which simplifies theoretical modeling in these systems.

In contrast, projectile energy loss exhibits a strong trajectory dependence, as shown in Fig. 5.6. The straight-line approximation significantly overestimates energy loss at low collision energies due to the forced linear path, which does not account for effects in the target such as nuclear recoil and polarization from the ion projectile. At very high energies, electronic stopping cross sections from electron-nuclear coupled trajectories align well with experimental measurements, confirming the validity of the model in this regime.

These results highlight the importance of considering nuclear motion in collision dynamics, particularly at low energies where polarization effects and nuclear recoil contribute significantly to stopping cross sections. Moving forward, this approach will be expanded to multi-electron targets using a Thomas-Fermi potential, allowing the study of negative ion formation and charge exchange dynamics in complex atomic systems.

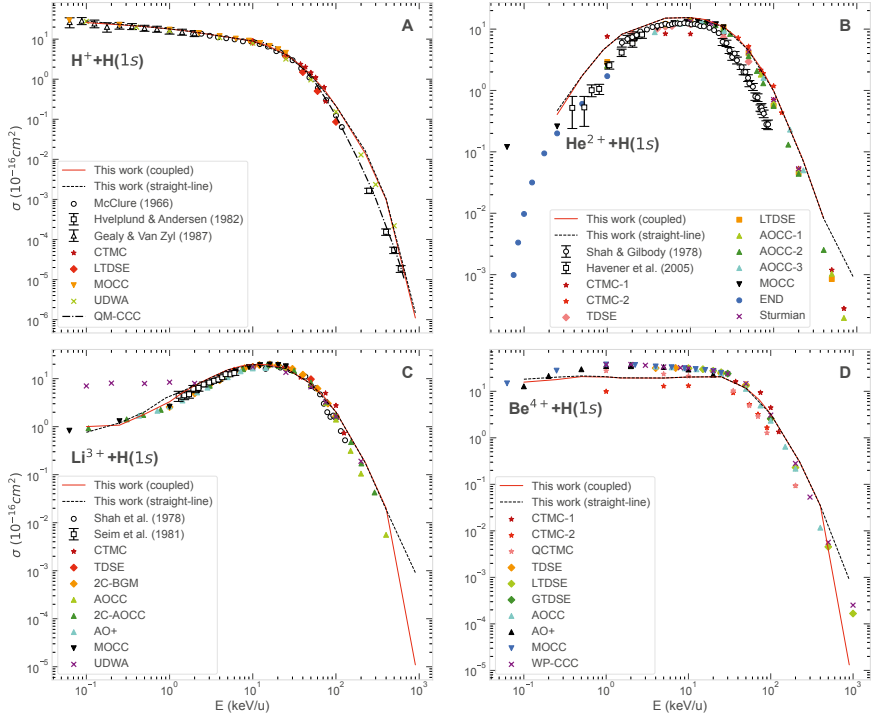


Figure 5.5: Electron capture cross sections for (A) H^+ , (B) He^{2+} , (C) Li^{3+} , and (D) Be^{4+} colliding with $\text{H}(1s)$, as a function of the ion projectile energy. Our results from the electron-nuclei coupled trajectories are shown with a solid red line and the straight-line trajectories are shown with a dashed black line. See Paper IV for references.

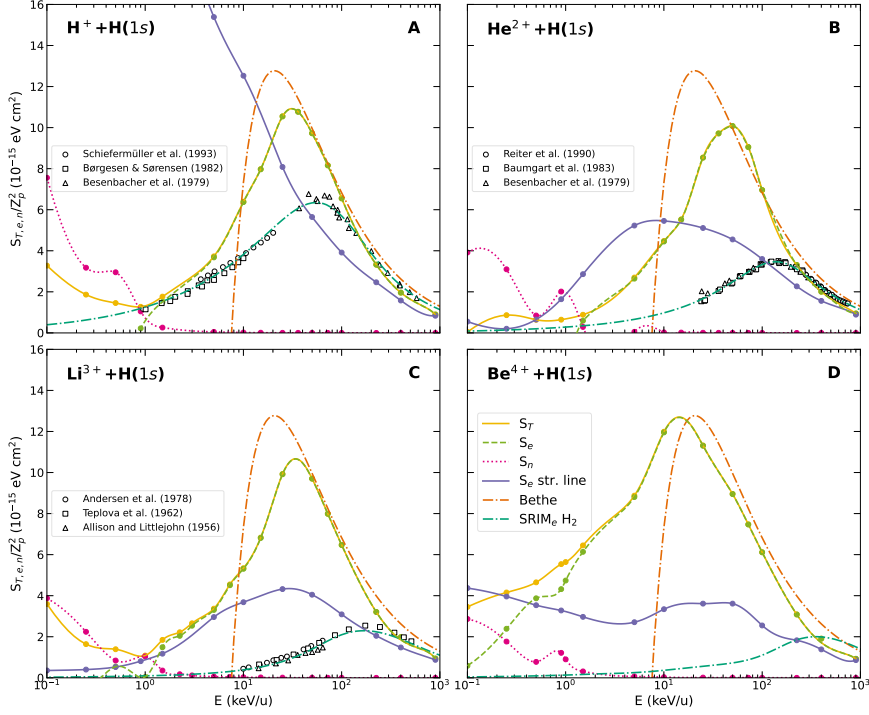


Figure 5.6: Stopping cross sections for atomic hydrogen targets by incident (A) H^+ , (B) He^{2+} , (C) Li^{3+} , and (D) Be^{4+} ions, as a function of the projectile energy.

5.4 Bound excited states in the tin anion

Isotope shifts in atomic spectra provide valuable insights into the interplay between nuclear and atomic structure, offering a means to probe nuclear charge distributions, electron-nucleus interactions, and electron-electron correlations. Sn is an excellent candidate for IS investigations due to its ten stable isotopes, the most of any element, allowing for a systematic study across a broad range of neutron-to-proton ratios. Sn^- is particularly interesting, as it possesses a bound excited state. While this is an $E1$ forbidden transition, the access to a cryogenic storage ring facility opens new avenues for high-resolution spectroscopy of negative ions.

This section summarizes the findings of Paper V, which presents the first IS measurement of an optically forbidden transition in Sn^- , along with lifetime determinations of the 2D_J states. The study represents a significant advancement in anion spectroscopy, demonstrating the feasibility of measurements of optically forbidden transitions in negative ions using a newly developed method. Although the analysis is still in progress and the reported values are preliminary, these results already set new benchmarks for theoretical models and establish a foundation for future studies of nuclear and atomic structure using anionic systems. With the increasing development of cryogenic ion storage techniques and high-resolution spectroscopy, this work paves the way for a new era of negative ion studies.

5.4.1 Isotope shift in the $\text{Sn}^-(^4S_{3/2}) \rightarrow \text{Sn}^-(^2D_{5/2})$ transition

The excitation energy from the ground state to the $^2D_{5/2}$ state in $^{120}\text{Sn}^-$ was measured to be $6512.4183(2) \text{ cm}^{-1}$. This was determined from the centroids of 40 independent measurements, each obtained from the Voigt fit of the resonance profile. A weighted average was calculated using the inverse square of the individual fitting uncertainties as weights. The given uncertainty is purely statistical, obtained by combining the weighted fit error and the standard deviation of the mean in quadrature. Fig. 5.7 shows a typical spectral resonance and Voigt profile fit for $^{120}\text{Sn}^-$.

When comparing with the work of Scheer *et al.* [64], we find that our measured resonance is approximately 50 times narrower. This improvement in spectral resolution is due to significantly reduced Doppler and pressure broadening, enabled by the cryogenic environment of DESIREE, extended interaction times, and a reduced laser linewidth by three orders of magnitude.

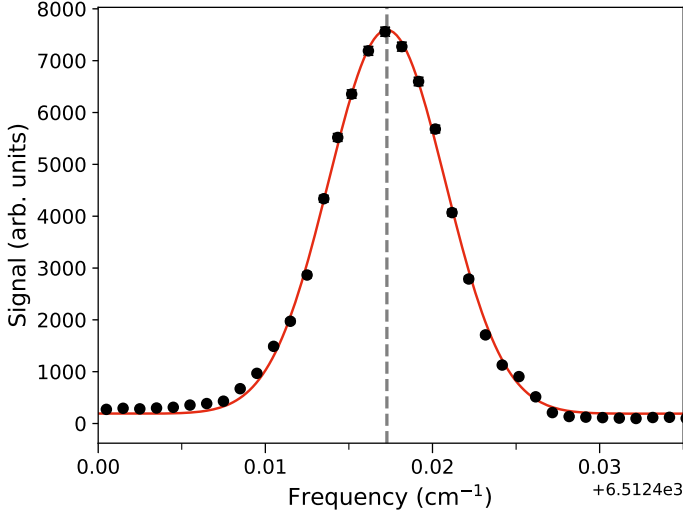


Figure 5.7: Example spectral resonance of the bound-bound $^4S_{3/2} \rightarrow ^2D_{5/2}$ transition in $^{120}\text{Sn}^-$. The data is fit with a Voigt profile (solid red line), yielding a center frequency of $6512.41727(1) \text{ cm}^{-1}$, indicated by the dashed gray line. Error bars, which are barely visible, represent square root of the signal.

The absolute frequency of the $\text{Sn}^-(^4S_{3/2}) \rightarrow \text{Sn}^-(^2D_{5/2})$ transition was measured for all stable even-mass isotopes. The most abundant isotope, ^{120}Sn ($\sim 33\%$ natural abundance), was used as the reference in determining the IS. The IS frequencies were calculated relative to ^{120}Sn , following $\delta\nu^{A,A'} = \nu^A - \nu^{A'}$. A total of ten sets of data were collected, with each set containing an average of one resonant transition frequency per isotope for $^{116-124}\text{Sn}$. Due to their low natural abundances, ^{112}Sn and ^{114}Sn (0.97% and 0.66%, respectively) were each measured twice over many hours, as more time was required to accumulate sufficient statistics. The reference isotope, ^{120}Sn , was measured an average of three times per set to reduce statistical uncertainty. The shift $\delta\nu^{A,120} = \nu^A - \nu^{120}$ was extracted individually for each isotope, where ν^{120} was typically taken as the average of the two reference frequencies if measurements were made both before and after. The IS values were then averaged across all data sets, and the associated uncertainties were calculated as the standard error of the mean. These results are summarized in Fig. 5.8.

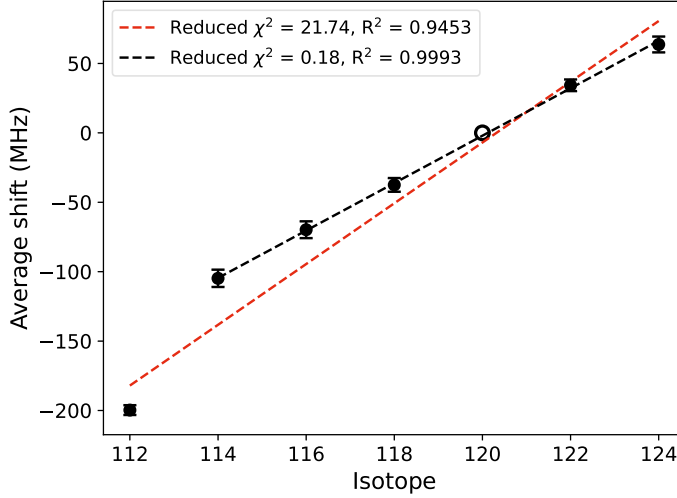


Figure 5.8: Measured isotope shifts $\delta\nu^{A,120} = \nu^A - \nu^{120}$ for the $4S_{3/2} \rightarrow 2D_{5/2}$ transition in Sn^- . Error bars represent the standard error of the mean. The reference isotope ^{120}Sn is shown as a hollow circle for context. Linear fits are shown including (dashed red line) and excluding (dashed blue line) ^{112}Sn data point, with the goodness of fit evaluated using reduced χ^2 and R^2 statistics.

The data exhibit a linear trend with increasing mass number. However, the ^{112}Sn data point deviates noticeably from this trend. To quantify this, linear fits were performed with and without mass 112, and the goodness of fit was assessed using reduced χ^2 and R^2 statistics. When all isotopes were included in the fit, the reduced χ^2 and R^2 were 21.74 and 0.9453, respectively, indicating poor agreement with the linear model given the uncertainties. Excluding mass 112 in the fit yields 0.18 and 0.9993 for the reduced χ^2 and R^2 , respectively. This suggests that the results of ^{112}Sn significantly deviate from the linear trend seen in the rest of the data and motivate its exclusion from further analysis to extract the mass and field shift factors.

These results enable a detailed analysis of the sensitivity of anions to changes in nuclear charge radii and specific mass shifts. To investigate the feasibility of such a procedure, we perform a King plot analysis based on the linear dependence of the IS on nuclear mass and charge radius, given by

$$\Delta\nu^{A,A'} = \nu^A - \nu^{A'} = k_{\text{MS}} \frac{m_A - m_{A'}}{m_A m_{A'}} + F\delta\langle r^2 \rangle^{A,A'}, \quad (5.1)$$

where k_{MS} can be further split into specific and normal mass shift components, $k_{\text{SMS}} + k_{\text{NMS}}$. By normalizing both sides of the equation by the reduced mass coefficient $\mu^{A,A'} = \frac{m_A - m_{A'}}{m_A m_{A'}}$, we obtain

$$\delta\nu^{A,A'}(\mu^{A,A'})^{-1} = k + F\delta\langle r^2 \rangle^{A,A'}(\mu^{A,A'})^{-1}. \quad (5.2)$$

This transformation removes the dominant mass dependence and allows for a more direct extraction of the constants. To compare the anionic transition measured in this work with well-known electronic transitions in neutral Sn, as reported in Ref. [136], we construct King plots to relate the isotope shifts of two different transitions across the isotope chain. Since the transitions share the same nuclear configurations for a given isotope, this eliminates the dependence on the nuclear charge radii. The resulting linear relationship between the two transitions can be described as

$$\delta\nu_i^{A,A'}(\mu^{A,A'})^{-1} = a \cdot \delta\nu_j^{A,A'}(\mu^{A,A'})^{-1} + b, \quad (5.3)$$

where

$$a = \frac{F_i}{F_j}, \quad (5.4)$$

$$b = k_i - a \cdot k_j. \quad (5.5)$$

An example King plot is shown in Fig. 5.9, where our transition in the anion is plotted against the $5s^2 5p^2 \ ^3P_2 \rightarrow 5s^2 5p 6s^3 \ ^3P_2$ transition in neutral Sn. We are encouraged to find that, despite some scatter in the data, an orthogonal distance regression fit can be drawn through all points within their error bars. This shows that the quality of the data supports a reliable preliminary analysis of the system using the initial King plot results.

The extracted field shift factor F and mass shift factor k_{MS} from Fig. 5.9 are -0.03 GHz/fm^2 and 272.3 GHz u , respectively. The normal mass shift is approximated by $k_{\text{NMS}} \approx m_e \nu$, where m_e is the electron mass and ν is the transition frequency, yielding 107.5 GHz u . Subtracting this from the total k_{MS} gives a specific mass shift of 164.8 GHz u . A detailed comparison with theoretical calculations is presented in Paper V.

5.4.2 Lifetimes of the $\text{Sn}^-(^2D_J)$ states

For determining the lifetimes of the 2D_J states, we leveraged the fact that the longer-lived $^2D_{5/2}$ state can be selectively isolated by laser-driven repopulation or by waiting 55 seconds for the population in the shorter-lived

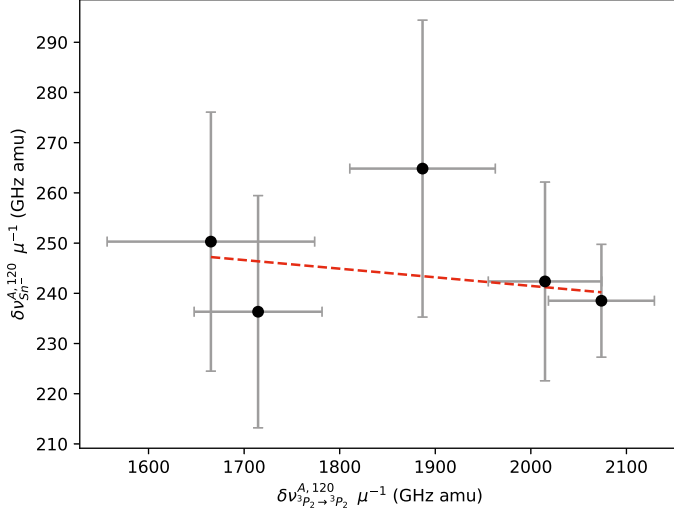


Figure 5.9: Example King plot comparing the measured anionic transition with the $^3P_2 \rightarrow ^3P_2$ transition in neutral Sn from Ref. [136]

$^2D_{3/2}$ state to be sufficiently small. This approach is advantageous, as fitting a single exponential decay function is significantly more robust than fitting a two-component combined signal. Once the lifetime of one state is known, the parameters can be fixed in subsequent fitting procedures to extract the lifetime of the other state more precisely. Measurements of both the isolated $^2D_{5/2}$ state and contributions from both states were performed with different laser powers, and the resulting lifetimes were linearly extrapolated to zero power to account for power-dependent effects and obtain the true lifetimes of the states.

The lifetimes of the $^2D_{3/2,5/2}$ states were determined to be 12(4) and 64(4) seconds, respectively. An example measurement and exponential decay fit is given in Fig 5.10, which measures only the lifetime of the longer-lived $^2D_{5/2}$ state in Sn^- . Analysis of the full dataset is still ongoing, and we expect the uncertainties on the extracted lifetimes to decrease significantly upon completion. Calculations of both $E2$ and $M1$ transition rates can be found in Paper V.

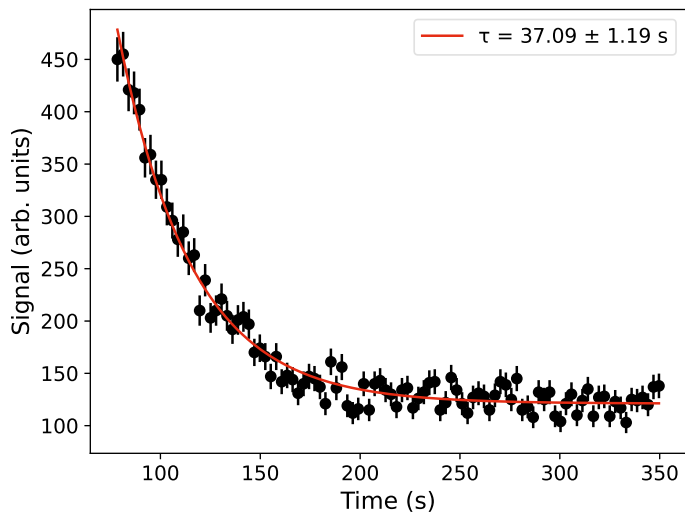


Figure 5.10: Lifetime measurement and exponential decay fit of the longer-lived $D_{5/2}$ state in Sn^- .

Chapter 6

Discussion and Outlook

Negative ions offer a unique opportunity to probe sensitive electron-electron correlation effects, which significantly influence their structure and dynamics. These features arise from the polarization of the atomic core, leading to both enhanced correlation effects and shallow binding potentials that rarely support bound excited states. As a result, negative ions are ideal systems to test theoretical approaches beyond mean-field approximations. Despite the valuable insights they offer, high-resolution spectroscopic studies of negative ions remain essentially limited to bound-continuum transition studies. Thus, it is important to establish robust experimental methods capable of universally studying these transitions across the periodic table.

The journey of this thesis began with addressing this need, guided by the hypothesis that significant advancements in negative ion spectroscopy can be achieved through refined experimental and theoretical methods. This hypothesis was confirmed through the work presented here, starting with laser photodetachment threshold spectroscopy (LPTS), a well-established method for measuring the electron affinity (EA). The experimental resolution of LPTS varies significantly based on the electron configuration of the system, with electrons detached into an s -wave continuum yielding the highest precision. Due to the inherently smaller cross sections and more gradual threshold behavior of p -wave detachment, achieving the same precision is challenging. To overcome this limitation, significant improvements can be made by selectively detecting only the s -wave contribution to the photodetachment cross section. An approach which combines LPTS with resonance ionization spectroscopy (RIS) was developed to address this issue by measuring partial cross sections from a single photodetachment chan-

nel [19, 20]. However, the signal-to-noise ratio in early studies remained lower compared to photoelectron detection methods. Therefore, the first goal of this thesis was to refine the LPTS-RIS method to achieve resolutions comparable to, or surpassing, the alternative methods. Additionally, recent findings highlighted the systematic discrepancies in EA values obtained using photoelectron detection methods such as velocity map imaging techniques [36]. This further emphasizes the importance of neutral-yield based measurements, such as LPTS, which are direct by nature and do not introduce such systematic discrepancies.

A key challenge for improving the LPTS-RIS method was the ability to effectively differentiate and detect the individual Rydberg atoms produced by the RIS scheme from the experimental background. Previous implementations of this method, used to study Na and K anions [26, 137], relied on velocity tagging to achieve final-state selectivity. However, these studies lacked optimization flexibility as the same electric field was used for both ionization and charge-state separation. To overcome this limitation, we incorporated a specialized field ionization unit developed by Welander *et al.* [66], in which the ionization and separation steps are divided. This enabled us to selectively excite a single photodetachment channel to a Rydberg state and subsequently ionize the Rydberg atoms. The resulting kinetic energy differences between the ionized atoms and collisional background ions enabled spatial separation of the two signals with electrostatic beam deflection. This improvement significantly enhanced the resolution, precision, and accuracy of LPTS EA measurements involving p -wave detachment. This approach has been successfully demonstrated in cesium (Cs) (Paper I) and rubidium (Rb) (Paper II), improving the previously measured EA values. Consequently, the first body of work in this thesis has validated the potential for extending measurement with the LPTS-RIS method to more complex systems, including francium and elements from the transition, lanthanide, and actinide groups, whose valence electrons often occupy s - and d -shells.

With a refined, high-precision method now available for use, this can be extended to radioactive species, especially those with EAs that remain experimentally unknown. However, the next critical step for this is to develop a reliable production method of the radioactive negative ions themselves. To address this, charge exchange by electron capture reactions was investigated. In this approach, a positively charged ion beam collides with a vapor target, typically an alkali metal, under controlled pressure conditions. Through sequential collisions and electron capture reactions, the positive ions become neutralized and then negatively charged. This method was successfully demonstrated with uranium-238 (Paper III), confirming the fea-

sibility of producing radioactive negative ions via charge exchange reactions. While this method is particularly beneficial for radioactive ions, it also offers significant advantages for stable isotopes that present the same challenges in conventional sputtering and surface ionization sources, such as low EAs or limited sample sizes. For this reason, the charge exchange method offers a relatively efficient alternative for negative ion production, greatly expanding the possibilities for negative ion spectroscopy.

However, theoretical predictions for the formation cross sections of heavy negative ions remain limited. In particular, we found that in current models, ion trajectories are not adequately accounted for, leading to uncertainties in cross sections for electron capture and target energy loss during the charge exchange process. A clear understanding of these effects is vital for continuing to develop accurate physical models of collision-based negative ion formation. In our study (Paper IV), we directly address these issues by investigating trajectory effects, providing insights that are critical for refining theoretical descriptions of electron capture dynamics in negative ion production.

Following the bound-continuum measurements characteristic of EA studies, a natural progression is to investigate bound-bound transitions in negative ions. In atomic and nuclear spectroscopy, such transitions have long enabled high-resolution studies (e.g., [138]). In contrast, the resolution of bound-continuum studies in negative ions still lags behind. From a fundamental perspective, the Heisenberg uncertainty principle implies that transitions between stable states should offer the highest precision due to negligible lifetime broadening. However, in experimental settings, this precision is often limited by practical factors such as interaction times and velocity spreads in the ion beam.

Bound-bound transitions in negative ions are typically optically forbidden and thus exhibit relatively long lifetimes, making them difficult to detect in conventional experimental setups due to their weak transition probabilities. Nevertheless, they offer the potential for unprecedented resolution and precision, especially when using lasers with narrow linewidths and low-background environments such as cryogenic storage rings. These advantages make such transitions a promising yet demanding frontier in negative ion research.

Only five elements are currently known to possess negative ions with optically allowed bound-bound transitions [34, 35, 55–57], making them attractive for applications such as laser cooling. In contrast, many more negative ions exhibit bound excited states with the same parity as the ground state, rendering electric dipole ($E1$) transitions optically forbidden. However, in

quantum mechanics, *forbidden* refers to events that are highly improbable rather than strictly impossible. These can still occur via higher-order electric quadrupole ($E2$) and magnetic dipole ($M1$) processes.

Within this context, the tin anion (Sn^-) offers a particularly compelling case as it possesses a bound excited state of the same parity as its ground state. With its isotopes spanning across two neutron shell closures, Sn has long served as a siren for many in the nuclear physics community. As the element with the longest chain of stable isotopes, Sn also provides an exceptional opportunity to probe electron correlation through isotope shift (IS) measurements in the negative ion. While studies have been conducted in the IS of EAs [85, 86], the IS of an $E1$ transition within a negative ion [62], as well as $E2$ and $M1$ transitions in atomic systems [63–65], the IS of forbidden bound-bound transitions in negative ions remains unexplored.

The long timescale required for forbidden bound-bound transitions makes them impractical for conventional linear, single-pass experiments. However, in the final paper (Paper V), it was demonstrated that such transitions within negative ions can indeed be accessed and investigated using a cryogenic storage ring, enabling the first ever IS measurement of a forbidden bound-bound transition within the Sn^- system. This unprecedented experimental access to anionic forbidden transitions opens new opportunities for the negative ion field, allowing deeper insights into electron correlations as well as atomic and nuclear structures. Investigating negative ions is inherently connected to probing electron correlation effects. Moreover, isotope shift measurements, where the specific mass shift component directly depends on electron correlations, offer exceptional sensitivity to these effects. Therefore, performing IS measurements on forbidden transitions within negative ions provides a uniquely powerful approach which is doubly sensitive to electron correlation. This makes these studies a game changer for advancing our understanding of highly correlated quantum systems.

In summary, this thesis has successfully advanced the field of negative ion spectroscopy by refining and expanding experimental methodologies, enabling precise measurements across bound-continuum and previously inaccessible forbidden bound-bound transitions. By improving the resolution of LPTS through state-selective resonance ionization detection (Papers I & II), this work sets a new standard for EA measurements, particularly for systems involving p -wave detachment channels. The successful demonstration of charge exchange for producing heavy and radioactive negative ions (Paper III) and the theoretical investigation of trajectory effects in atomic collision processes (Paper IV) open pathways toward comprehensive spectroscopic studies of low-EA systems. Most significantly, the groundbreaking

measurement of an IS in a forbidden bound-bound transition in Sn^- using a cryogenic storage ring (Paper V) introduces a powerful new method with unprecedented sensitivity to electron correlation effects. This study further enhances the potential of IS studies, opening the door for virtually any negative ion transition to be studied. Collectively, these advancements position research in negative ions to explore previously unreachable regimes, making it possible to rigorously test atomic structure theories and deepen our fundamental understanding of electron correlation, atomic physics, and nuclear structure.

Looking forward, there is always more to accomplish. After all, the more you learn, the clearer it becomes how much remains unknown. Following the work of this thesis, a next step should be to extend the LPTS and refined LPTS-RIS approaches to elements whose EAs remain experimentally unknown, such as polonium and francium. With scheduled beamtime for Po^- at ISOLDE, based off an accepted experiment proposal I authored, this represents a promising step toward expanding EA measurements further into the heavy element region. Charge exchange production should be leveraged to explore isotopes far from stability, including the near-actinide and actinide species. In parallel, further progress can be made by developing and refining theoretical models to better understand these collisional dynamics, such as incorporating Thomas-Fermi potentials, to accurately predict electron capture cross sections in complex, many-body systems. Finally, the successful utilization of a cryogenic storage ring to study forbidden bound-bound transitions opens the door to novel spectroscopic studies, such as investigating electronic state population manipulation for mutual neutralization studies. Taken together, these experimental and theoretical developments are promising for the future of negative ion studies, potentially unlocking a deeper understanding of fundamental atomic interactions.

Acknowledgments

I'd first like to start
By thanking the person¹
That gave me a chance
And who thought that I was smart
From swearing on video by happenstance

Next, I'd like to thank
The person who agreed
To teach me theory²
And pulled me through
Despite frequent desire to concede

¹ My supervisor **Dag Hanstorp**, who took a chance on me and changed my life in many ways. Thank you for instantly recognizing the person that I am and wanting to work with me because of it. For being flexible, patient, understanding, kind, tolerant of profanity and tears, and always finding the humor in things. For always giving me advice but the freedom to make my own choices. And ultimately, for shaping me into the researcher I've become. I couldn't have asked for a better supervisor. If it had been anyone else, I would have not made it to the end.

² My supervisor **Remi Cabrera-Trujillo** who, again, I need to emphasize, agreed to teach me theory. I hadn't taken a quantum mechanics class since undergrad. Thank you for your unwavering patients and for bring a sense of vital force to both our work and my life. For reassuring me that everything is going to be okay, that I will find what I love to do, and to cheer up. From the first time I met you, I knew I wanted to work with you and learn from you. I am forever grateful that you took me on as a student.

My PhD wouldn't be complete
 Without acknowledging the colleagues³
 And people who made my life so sweet⁴
 To my sisters and chosen family⁵
 You are the reason I stand on my feet

³ From Gothenburg, DESIREE, and ISOLDE. I'd especially like to thank: **Lu Di**, for always being helpful no matter what it is and being the glue for the group. **Annie**, for sharing an office, coffee, words, music, laughs, and friendship with me over the years and many times giving me a reason to show up to work. **José**, for laughing unproportionately hard with me, usually for no reason, and being one of the best people to work with. **Paul**, for being so involved in the Sn runs. Their success is largely owed to you. If I could build my own team, you'd be one of my first choices. I love getting to work with you. **Jordan**, for getting me through a really tough year. Working and hanging out with you was a highlight of my time at CERN. **Michali**, for just being you. For also getting me through a really tough year. For the countless conversations, ideas, and suggestions, especially for the Sn. I'm grateful to have you in my life. **The administrative staff** in Gothenburg who continue to work everyday for the functionality and success of the department. Especially to **Elizabeth** and **Anna**, who, on top of everything else, have worked so hard to make sure I can legally be in Sweden, and to **Lukas** for always being so helpful and making it possible for me to actually receive my degree. Also to **Caroline**, who took on the responsibility for our PhD education. Thank you for your support and dedication to making sure we are all doing well. Last but not least, **the technical staff** at all three facilities. An often thankless and absolutely essential job. Without all of you, there would be no experiments.

⁴ Thank you to **all of my friends in Gothenburg**, who never once complained about sitting on my floor and have had so much understanding when I disappear for months on end. To my communities at **A Nice Place**, often the only movement and moments of stillness in my day, and at **Alkemisten**, where I would often work. Usually, the only time that I smiled or even spoke in the day, especially when I was writing this thesis, was with my friends there. And to **Asar** for reminding me of the importance of celebration and humor, giving me love and days to look forward to, and ultimately showing me what matters in this life.

⁵ **Alice, Katie, Grace, Rali, and Yaz**, who have shown me what sisterhood is like by unconditionally showing up for me, supporting me in every way possible over the years, and letting me do the same for you. **Jake**, who understands me like no one else and has shown up approximately once per quarter to confirm my existence and travel together.

And to my partner⁶
For being the reason that I eat
Last but not least
I want to thank the ones
Who made it possible for my heart to beat⁷

When I said I wanted to be a writer
This is what I meant
So here is the paper
And these words are my pen
All I had to do
Was complete a PhD
To publish poem
That will still go unread

So thanks for not reading
Because there's nothing left unsaid
More words on more paper
Like my ever growing debt
And with that-

Here lies my PhD
And everything she's meant to me
She is old and tired now
With nothing left to give
She deserves nothing more
Than simply to be let live

Not sure what she'll do next
But there's a chance that she will flee
Dreaming of a world where paper
Is only the fruit of the giving tree

⁶ **Charlie**, who moved to Sweden to care for me while I did my PhD, even though I was frequently away. Thank you for the love, support, and patience throughout the years. Part of this PhD is yours.

⁷ **My parents**, I cannot begin to fathom the words to express. You gave me everything you had, and then some more. The other part of this PhD belongs to you. Also to **my grandparents** and **brother**. I'm not sure if it's harder to watch someone go or be the one going. And I'm not sure who is who.

You'll probably find her in the forest
Starting a fire with her degree
At least she's spellbound and she's honest
And she is done with her PhD

She is, she is, she is.
I am, I am, I am.⁸

Miranda Nichols
Gothenburg, 10 April 2025, 23:59.59

⁸ A reference to **Sylvia Plath**, who never made it to the end she wrote for herself. This last year was partly for her. A last thank you to my psychiatrist, **Ruth**, my previous therapist, **Isabella**, and my new therapist **Lisabeth**. Thank you to **Vyvanse**. And thank you to **ChatGPT**. This writing style is an homage to **Carmen Maria Machado**.

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Appended Papers

Paper I

High-resolution measurement of the electron affinity of cesium

José E. Navarro Navarrete^{1,*}, Miranda Nichols,² Annie Ringvall-Moberg², Jakob Welander², Di Lu²,
David Leimbach², Moa K. Kristiansson,¹ Gustav Eklund¹, Meena Raveesh,³ Ruslan Chulkov,⁴
Vitali Zhaunerchyk,² and Dag Hanstorp²

¹Department of Physics, Stockholm University, SE-106 91 Stockholm, Sweden

²Department of Physics, University of Gothenburg, SE-412 96 Gothenburg, Sweden

³International School of Photonics, Cochin University of Science and Technology, Kochi, Kerala 682022, India

⁴Department of Physics and Astronomy, Uppsala University, SE-751 20, Box 516, Uppsala, Sweden



(Received 15 December 2023; accepted 30 January 2024; published 21 February 2024)

Negative ions are unique quantum systems where electron correlation plays a decisive role in determining their properties. The lack of optically allowed transitions prevents traditional optical spectroscopy and the electron affinity is, therefore, for most elements, the only atomic quantity that can be determined with high accuracy. In this work, we present a high-precision experimental determination of the electron affinity of cesium. A collinear laser-ion beam apparatus was used to investigate the partial photodetachment cross section for the cesium anion, leaving the neutral atom in the $6p\ ^2P_{3/2}$ excited state. A resonance ionization scheme was used to obtain final-state selectivity, which enabled the investigation of a sharp onset of the cross section associated with a Wigner s -wave threshold behavior. The electron affinity was determined to be 0.471 598 3(38) eV.

DOI: 10.1103/PhysRevA.109.022812

I. INTRODUCTION

Negative ions have a unique structure that differs from their neutral and positive counterparts due to the nature of their creation. The Coulomb potential experienced by the valence electron in neutral atoms and positive ions is proportional to $1/r$, a long-range attraction that allows an infinite series of bound so-called Rydberg states. In negative ions, on the contrary, the bond is governed by an induced dipole potential which arises from the polarization of the atomic core by the additional electron. This potential, scaling as $1/r^4$, is normally too shallow to support any electronically excited states. The lack of a long-range Coulomb interaction between the extra electron and the neutral atom leads to an enhanced importance of electron-electron correlation, which hence plays a crucial role in determining the structure and dynamics of negative ions. Therefore, studies of negative ions can be used as a probe to test theories beyond the independent-particle model which assumes the electrons to move independently in an average potential. Comprehensive overviews of negative ions can be found in reviews such as Pegg *et al.* [1], Andersen *et al.* [2], and Fano [3]. As a consequence of the shallow binding potential and lack of optically allowed transitions, the electron affinity (EA), which is the energy gained by attaching an electron to a neutral atom, is the only quantity that can be experimentally determined with high precision. Typically, this

is done utilizing the photodetachment process, where a photon with sufficient energy is used to detach an electron from a negative ion. By tuning the photon energy in a small range around the onset of the process, where the cross section of photodetachment is following the Wigner law [4], the EA can then be extracted [5] by either detecting the resulting neutral atom, as in the case of laser photodetachment threshold spectroscopy (LPTS) (e.g., [6]), or the detached photoelectron, as in the case of laser photodetachment electron spectroscopy (LPES) [7] and laser photodetachment microscopy (LPM) (e.g., [8,9]). The most precise experimental determination of any EA value to date is the recent LPTS study of ^{16}O performed at the DESIREE storage ring [10]. If the energy of the absorbed photon is sufficiently large, the atom produced in the photodetachment process can be left in an excited state. The probability for this to occur is given by the partial photodetachment cross section. By measuring the partial cross section instead of the total cross section, one can obtain detailed information about doubly excited states [11–13] as well as threshold behaviors [14]. Such measurements require a highly sensitive detection method due to the relatively small branching into a single excited state [15], but have shown to be feasible by combining laser photodetachment with resonance ionization spectroscopy (RIS) [16–19]. This method has been applied in several studies of the alkali metal negative ions, including many observations of doubly excited states (e.g., [18,20]).

Cesium (Cs) is the heaviest naturally occurring alkali metal and possesses a single stable isotope, ^{133}Cs . Neutral Cs atoms are among the most studied in atomic physics where they have been of interest for laser cooling [21], studies of Bose-Einstein condensation [22] and atomic clocks [23]. Cesium is also used for the production of negative ion beams by charge exchange processes [24] and as a mean to enhance the production of H^-/D^- , in particular for highly intense

*jose.navarrete@fysik.su.se

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beams used for heating in fusion reactors [25]. The negative ion of cesium has been studied far less than the neutral cesium atom. The first theoretical value of the EA of Cs was published in 1973 by Norcross [26]. They obtained an EA of 0.470 eV by using coupled equations of scattering theory based on semi-empirical effective potentials for the neutral atom. One year later, the first accurate EA measurements of Cs via LPTS and LPES were made by Patterson *et al.* [27], where strong resonances below the $6p^2P_{1,2,3/2}$ states were discovered, which strongly affected the photodetachment cross section. Nevertheless, they obtained an EA of 0.470(3) eV and 0.472(3) eV by LPES and LPTS, respectively [27]. In 1978, Slater *et al.* determined the 2P partial photodetachment cross section of Cs yielding an EA of 0.4715(3) eV [28]. Later on, Cs⁻ was proposed as a candidate for a stable negative ion with opposite parity bound states, but this was disproven by Scheer *et al.* [29] with the observation of the Cs⁻($6s6p\ ^3P$) states situated just above the ground state of the atom. This represented the first study to observe low-lying resonances in negative ions using photodetachment spectroscopy. Lindahl *et al.* then further investigated these resonances by extending the photodetachment energy range to higher-lying final states with partial photodetachment cross-section measurements [30]. These experiments also gave rise to a series of theoretical work investigating resonances in the photodetachment spectrum of cesium [31–39]. To date, the most accurate value for the EA of Cs was determined to be 0.471630(25) eV by Hotop and Lineberger using LPTS. However, this value was only reported in their 1985 review [40] with the detailed article about the experiment remaining unpublished. Therefore, the most accurate published value for the EA of Cs is 0.47164(6) eV [29]. Apart from a fundamental interest to facilitate theoretical studies of electron correlation in the negative cesium ion, a precise value of the EA is of utmost importance when studying doubly excited states to distinguish between Feshbach and shape resonances, which are situated below and above the parent state, respectively [41,42]. Hence, it is of great interest to update the current experimental value using modern techniques.

In this paper, we present a sensitive, high-resolution measurement of the EA of Cs by investigating the s -wave partial photodetachment cross section using LPTS in combination with RIS at the Gothenburg University Negative Ion and Laser Laboratory (GUNILLA) [43]. Here, a new field ionizer for Rydberg atom detection developed by Welander *et al.* [44] was utilized. The collinear geometry, compared to a crossed beam geometry, allowed an increased sensitivity due to the larger interaction volume as well as mitigation of the Doppler effect. At the same time, the final-state detection provided high selectivity, enabling a more accurate determination of the EA for Cs. Further, by measuring the partial photodetachment threshold, leaving the atom in the excited $6p\ ^2P_{3/2}$ state, we completely circumvented the possible influence of the shape resonance present just above the ground state of the cesium atom.

II. EXPERIMENTAL METHOD

A stable beam of Cs⁻ was produced in a Middleton type sputter ion source [45] (PS-120 Peabody Scientific) using an aluminium cathode. The ions were accelerated to a

kinetic energy of 6 keV and selected by a 90° mass separating magnet with a resolution ($M/\Delta M$) of approximately 500. The Cs⁻ ions were then deflected with a quadrupole deflector into the Rydberg Atom Detector for Anion Research (RADAR) spectrometer [44], as shown in Fig. 1. Here, the ion beam entered a 70 cm long interaction region where it was overlapped with two different laser beams at wavelengths of λ_1 and λ_2 (as indicated in Fig. 2) which were utilized for photodetachment and subsequent resonance ionization, respectively.

To populate the excited state in the neutral cesium atom, the laser pulse for photodetachment (λ_1) was set to arrive a few ns before the laser pulse for resonance excitation (λ_2), as discussed in detail below. Both photodetached and unaffected products then continued into the field ionization region where an electric field gradient was created by 11 parallel circular electrodes. The electric potentials on the first ten electrodes were set to form a slowly decreasing potential, whereas the 11th electrode was grounded. While the weak electric field in the region of the first ten electrodes did not affect Rydberg atoms, the field between the tenth and 11th electrodes was sufficiently strong to effectively ionize them. The positive ions thus created were then decelerated and exited the field ionizer with a decreased kinetic energy with respect to their initial energy. The electric potential applied to these electrodes, as a function of distance along the ion beam axis inside the field ionizer, is shown in Fig. 1. More detailed information about the field ionizer can be found in [44]. Positive ions created in the interaction region by either collisions with the residual gas or in two-photon ionization processes were, on the contrary, first accelerated and then decelerated in the field ionizer, therefore, departing the field ionizer with the same kinetic energy as they entered with. This energy difference was then used to spatially separate these background events from the signal on the position-sensitive detector, consisting of a stack of two microchannel plates (MCP) and a delay line detector by employing an electrostatic energy analyzer, deflecting the positive ions by about 90°. In addition, the field of the energy analyzer removed the remaining negative ions by deflecting them in the opposite direction, while fast neutral atoms continued on a straight forward trajectory, unaffected by the electric field.

The laser excitation scheme of this experiment is shown in Fig. 2. Negative Cs ions were photodetached by absorbing a photon from a tunable laser operating at λ_1 . A second laser was set to a fixed wavelength of λ_2 for the resonant excitation of the neutral atoms from the $6p\ ^2P_{3/2}$ excited state to the $25d\ ^2D_{J=5/2,3/2}$ Rydberg state.

For the photodetachment process a Sirah PrecisionScan dye laser was used with a solution of DCM dye in dimethyl sulfoxide (DMSO) to generate photons in the 636 nm to 680 nm range, monitored with a HighFinesse WS6-600 wavelength meter with an accuracy of 600 MHz (2.5 μ eV). The linewidth of the dye laser was specified by the manufacturer to be 0.075 cm⁻¹ (9.3 μ eV) with a pulse energy of about 1.7 mJ. An optical parametric oscillator (OPO) with a bandwidth smaller than 0.2 cm⁻¹, with a pulse energy of 100 μ J, provided photons of 514 nm for the resonant excitation. The dye laser and the OPO were pumped by two different pulsed Nd:YAG lasers with a repetition rate of 10 Hz, respectively. The

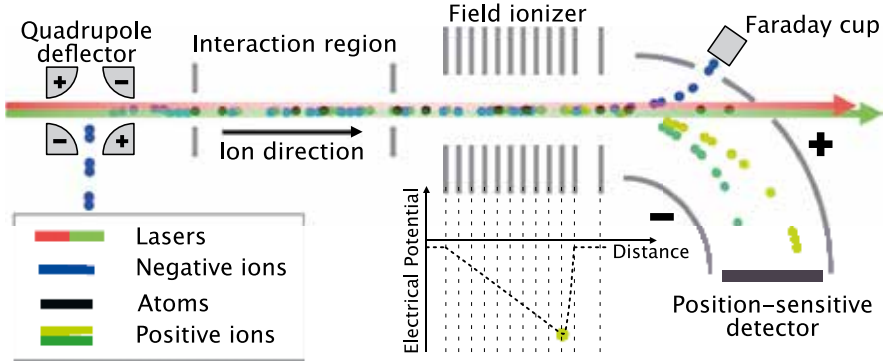


FIG. 1. A schematic figure of the RADAR spectrometer. Negative ions were deflected into the interaction region by a quadrupole deflector where they were overlapped with two laser beams. Downstream of the interaction region is a field ionizer where Rydberg atoms were field ionized. The ions and atoms were then separated by their charge and energy. Neutral atoms continued in a straight path, whereas charged particles were deflected by an energy analyzer. While negative ions were deflected into a Faraday cup, positive ions were guided onto a position-sensitive detector, where the impact position was dependent on their kinetic energy.

duration of the laser pulses was about 8 ns and 5 ns for λ_1 and λ_2 , respectively.

The time difference between the pulses was set to maximize the atomic population in the intermediate $6p\ ^2P_{3/2}$ state, which was slightly different depending on the propagation scheme (co or counterpropagating ion and laser beams). The data acquisition was triggered 4.3 μ s after the OPO pulse (λ_2) to match the ion time of flight from the end of the interaction region of the RADAR spectrometer to the position-sensitive detector. The time window for data acquisition was set to

correspond to the time of flight within the interaction region. A schematic of this time delay process is shown in Fig. 3.

Finally, we investigate the calibration of our wavelength meter by performing saturated absorption spectroscopy of rubidium gas in a low-pressure quartz cell. The light used in the calibration was of a CW external cavity diode laser centered at 780.24 nm. The hyperfine transitions in the D1 line of both ^{85}Rb and ^{87}Rb were measured and compared with tabulated values [46]. The average difference between our measured and the reported values was of 260 MHz. We could therefore with confidence use the specified accuracy of the wavemeter of 600 MHz as the uncertainty in our wavelength reading (2.5 μ eV).

III. RESULTS AND DISCUSSION

As a first step, a two-dimensional (2D) histogram of the signal's spatial distribution was recorded on the position-

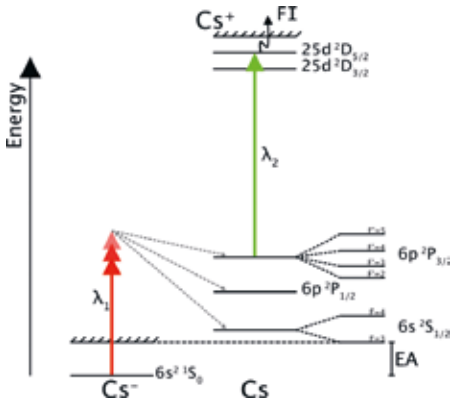


FIG. 2. Partial energy level diagram (not to scale) for Cs^- and Cs. A photon (λ_1) from a frequency tunable laser is absorbed by a Cs^- ion (red arrows). Subsequently, the ion can decay into three different neutral states via electron emission (dashed arrows). The neutral Cs atom in the $6p\ ^2P_{3/2}$ excited state then absorbed another photon (λ_2) at a fixed wavelength for resonant excitation to the Rydberg state, $25d\ ^2D_{5/2}$ (green arrow). Finally, the Rydberg atom underwent a field ionization (F.I.) process (curved arrow), creating a positive ion.

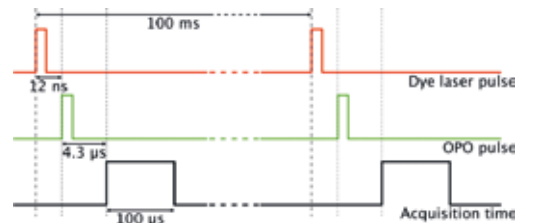


FIG. 3. Time delay and data acquisition scheme (not to scale). The signal from the dye laser pulse initialized the cycle. The delay between the dye laser and the OPO pulses was optimized to be a few ns with slightly different values for co and counterpropagating laser and ion beams, respectively. The acquisition time was triggered 4.3 μ s after the OPO laser pulse, corresponding to the time of flight from the interaction region to the detector. The entire measurement cycle was 100 ms.

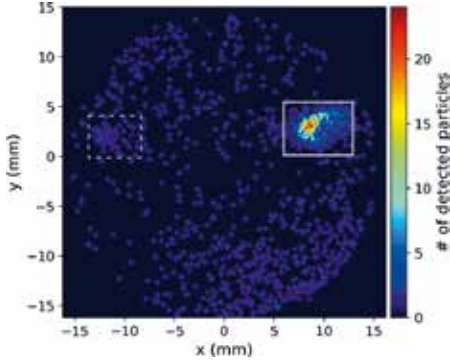


FIG. 4. Two-dimensional histogram of the events measured with the position-sensitive detector. The detector surface is shown from the perspective of the impinging ions. The signal surrounded by the solid rectangle corresponds to events associated with positive ions created by field ionization. The small signal to the left, surrounded by a dashed rectangle, corresponds to the background which consist of the positive ions produced by double photoionization and collisions with the residual gas.

sensitive detector, as shown in Fig. 4. Here, λ_1 was set to a photon energy well above the photodetachment threshold, while (λ_2) was set to be in resonance with the $25d\ ^2D_{j=5/2,3/2}$ Rydberg state. The orientation of the MCP is shown from the ion's reference frame. The signal, delimited by the solid rectangle to the right, corresponds to the positive ions created inside the field ionizer. The number of signal counts inside the solid rectangle is proportional to the partial photodetachment cross section, leaving the neutral atom in the $6p\ ^2P_{3/2}$ state. Background events such as positive ions created by two-photon ionization by absorbing two λ_2 photons or by collisions with the residual gas impinged on the left side of the MCP, within the dashed rectangle. Particles detected outside these two regions correspond to scattered particles or light or result from dark counts of the detector.

A representative plot of the measured *s*-wave Doppler-shifted photodetachment cross section of the Cs negative ions is presented in Fig. 5. In this measurements, (λ_2) was fixed to the frequency of the $6p\ ^2P_{3/2} \rightarrow 25d\ ^2D_{5/2}$ transition and (λ_1) was scanned over the threshold region. In this case, both laser beams were merged copropagating as shown in Fig. 1. Each data point corresponds to the integrated number of positive ions inside the region delimited by the solid rectangle in Fig. 4. These values were then normalized to both the ion current and the laser pulse energy. The uncertainty of the signal was determined as the square root of the total number of counts, as each detected event is a process that follows a Poisson distribution. The final uncertainty of each data point was obtained by Gaussian error propagation.

A deconvolution technique was applied to account for the influence of the bandwidth of the laser and the velocity spread of the ions. Furthermore, there are four photodetachment thresholds with slightly different energies corresponding to the four hyperfine levels in $6p\ ^2P_{3/2}$ state of the neutral Cs

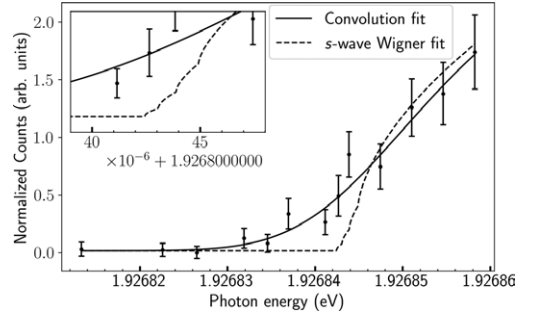


FIG. 5. The number of registered events following the Doppler-shifted partial photodetachment that leaves the neutral atom in the excited state $6p\ ^2P_{3/2}$, $F = 2$ state, as a function of the photon energy. Both the ion beam and the laser (λ_1) were merged in a copropagating scheme. The fit was obtained with Eq. (1) and is shown as a solid line. The optimized parameters were then used in Eq. (3) to obtain a deconvoluted *s*-wave Wigner function that is shown as a dashed line. The threshold for this measurement is 1.926 842 4(51) eV. The inset shows an expansion around the threshold where the hyperfine structure of the excited state is resolved.

atom. Therefore, the experimental data was fitted with the mathematical expression

$$(\sigma \circledast g)(E_n) = \sum_{E_m} \sigma(E_m)g(E_n - E_m), \quad (1)$$

which is a discrete convolution between the Gaussian normalized function

$$g(E_n - E_m) = \left(\frac{1}{\sigma_g \sqrt{2\pi}} \right) e^{-\frac{(E_n - E_m)^2}{2\sigma_g^2}} \quad (2)$$

and the Wigner function

$$\sigma(E_m) = A + B \sum_{F=2}^5 (2F + 1) \times (E_m - E_{\text{Th}F})^{l+1/2} \Theta(E_m - E_{\text{Th}F}). \quad (3)$$

Here, E_m is the photon energy, $E_{\text{Th}F} = E_{\text{Th}} + E_F$ is the sum of the photodetachment threshold energy E_{Th} and the energy of the hyperfine level F relative to the $6p\ ^2P_{3/2}$ ($F = 2$) state. This means that E_{Th} is the Doppler-shifted threshold energy where the atom is left in the lowest hyperfine level ($F = 2$) of the excited $6p\ ^2P_{3/2}$ state. All four hyperfine levels are shown schematically in Fig. 2 and the energetic differences were taken from Tanner and Wieman [47]. The corresponding terms were added and the multiplicity of every level was taken into account, following the angular coupling derivation of Peláez *et al.* [48], where the amplitude of the different channels are shown to be proportional to $(2F + 1)$. Here l is the angular momentum of the detached electron, which in this case is $l = 0$. Moreover, the Heaviside function Θ accounts for the zero cross section of photodetachment below the threshold. E_{Th} , A , B , and σ_g are the parameters that were optimized using a least square fitting algorithm. The number of terms in the sum of Eq. (1) was chosen to make the numerical bias negligible. In

this particular case, as shown in Fig. 5, the fit of the experimental data yields a value of $E_{\text{Th}} = 1.926\,842\,4(51)$ eV, where the uncertainty is the statistical error of the fit. The parameter σ_g describes the contribution of the linewidth of the laser (λ_1) and the energy spread of the ions in the convolution. An average σ_g from 15 threshold scans was determined from the statistical fit to be $6.2(7)$ μeV , which translates to a FWHM of $14.6(16)$ μeV . This sets the limit of the experimental resolution determined by a convolution of the effect of the laser linewidth and the energy spread of the negative ion beam.

To cancel out the Doppler shift effect to all orders, measurements were alternated between co and counterpropagation schemes and then calculate the geometrical mean

$$E_{\text{Th}}^{\text{Corr}} = (E_{\text{Th}} \uparrow E_{\text{Th}} \downarrow)^{1/2}. \quad (4)$$

The analytical treatment of our data is exemplified as follows: The data presented in Fig. 5 was measured in a copropagating scheme. The corresponding counterpropagating threshold was determined to be $1.925\,644\,4(44)$ eV. By applying Eq. (4), a value corrected for the Doppler shift of $1.926\,243\,3(34)$ eV was obtained. From a series of 15 measurements, switching back and forth between the co and counterpropagating schemes, a weighted average of the geometrical mean yields a value of $1.926\,239\,0(10)$ eV. To extract the EA, the difference in energy between the ground state $6s^2S_{1/2}(F=3)$ and the excited state $6p^2P_{3/2}(F=2)$ of the neutral Cs atom was subtracted from the corrected $E_{\text{Th}}^{\text{Corr}}$ mean values. Udem *et al.* [49] determined this energy difference in an absolute optical frequency measurement using a frequency comb. Their experimental value and uncertainty was given as the transition frequency expressed in Hz. By using the 2018 CODATA [50] this value can be converted to an energy of $1.454\,640\,672\,0(5)$ eV. A preliminary electron affinity of Cs of $0.471\,598\,3(9)$ eV is obtained, with an error bar which is only statistical. This statistical uncertainty include the effects of the energy spread of the ions, the linewidth of the laser and the divergence of both the laser and ion beams.

Next we consider systematic errors in the experiment. First, we estimated the size of the Ponderomotive shift caused by a strong electromagnetic laser field. For this we measured an average pulse energy of 1.7 mJ and a pulse length of 8 ns for λ_1 . The beam waist was estimated to be ~ 3 mm at full width at half maximum (FWHM). This gives a ponderomotive energy shift of 0.02 μeV in the threshold measurement. Another possible source of error, is a difference in the interception angle between the co and counterpropagating geometries (which was estimated to be 0.01 μeV , as limited by the apertures in the interaction region, following the procedure of Hanstorp [51]). Moreover, we also considered a possible drift in the kinetic energy of the ions due to fluctuations in the power supplies. According to the specifications, their stability translates into a 0.1% peak to peak ripple. This means that the drift accounts to 6 V. This is equivalent to a Doppler shift variation of 300 neV. We therefore conclude that the greatest source of uncertainty stems from the accuracy and calibration of our wavelength meter (2.5 μeV). By adding up this later error, the shift from the Ponderomotive effect (0.02 μeV), the uncertainty due to the interceptions of the ion and laser beams (0.01 μeV), a kinetic ion beam drift (0.3 μeV), and the statistical error (1 μeV), a final value of $0.471\,598\,3(38)$ eV

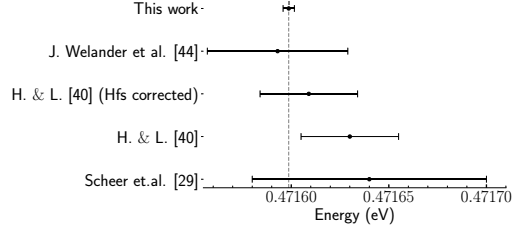


FIG. 6. The experimental value for the EA of this work is shown with a diamond marker. The error bar of this measurement is, within the resolution in this figure, almost imperceptible. The values from Hotop and Lineberger (H. and L.) and its hyperfine splitting correction of 21 μeV [40], Scheer *et al.* [29] and J. Welander *et al.* [44] are shown for comparison.

was obtained. This reduces the uncertainty of the electron affinity of Cesium by an order of magnitude in comparison to the value of $0.471\,630(25)$ eV reported in [40] by Hotop and Lineberger. This is largely due to the state-selective method which resulted in a sharp *s*-wave behavior in combination with a high signal-to-background ratio. As shown in Fig. 6, this EA value coincides with our value within their error bars. When comparing with the value of $0.471\,630(25)$ eV as presented by Hotop and Lineberger [40], we find that our value lies slightly outside their uncertainty. However, this can be explained by the fact that they did not take into account the hyperfine structure of the ground state of the Cs atom. This leads to an overestimation in their EA of 21 μeV , which is the difference between the “center of gravity” of the $6s^2S_{1/2}$ hyperfine doublet and the lowest hyperfine state ($F=2$). With this difference taken into account, their value agrees with ours within their error bars (Fig. 6). Finally, the EA of Cesium of $0.471\,593(36)$ eV from our previous work [44] is in agreement with our present value.

IV. CONCLUSION AND OUTLOOK

We determined the electron affinity of cesium to be $0.471\,598\,3(38)$ eV, obtaining an improvement of one order of magnitude in the uncertainty from the value reported in [40]. This was accomplished by combining laser photodetachment threshold spectroscopy with resonance ionization to investigate the partial photodetachment cross section between the ground state of Cs^- and the $6p^2P_{3/2}$ excited state of the neutral Cs atom. A collinear laser-ion beam geometry allowed us to achieve high sensitivity due to the large area of interaction as well as high resolution due to Doppler shift mitigation by making use of both co and counterpropagating laser-ion beam configurations. Our experimental method made use of a field ionizer developed by Welander *et al.* [44], specifically designed for partial photodetachment cross-section studies. The apparatus allowed for a highly selective detection method which facilitated the detection of a single photodetachment channel. This made it possible for us to detect the $6p^2P_{3/2}$ photodetachment channel, which yields a sharp onset of the cross section associated with a Wigner *s*-wave threshold behavior, on the contrary to previous experiments where the

slow onset of a p -wave threshold obtained when leaving the neutral atom in the ground state was investigated. Further, detection of the $6p\ ^2P_{3/2}$ channel circumvented the possible problem with the resonance situated just above the ground state of the neutral atom. It is our hope that this precise measurement will trigger new theoretical calculations of the EA of Cs. This should be tractable since it has a closed $6s^2$ valence shell.

The presented experimental method can also be applied to study other alkali metals, such as rubidium and francium. Francium, the heaviest homologue to Cs, possesses no stable isotope and has an EA which is experimentally unknown, but is predicted to be between 0.475 eV [52] and 0.491(5) eV [35]. Determining this would complete the EA measurements for the alkali metal group and could help us understand more about electron correlations and relativistic effects of heavy elements. Francium, a near-actinide element, can be studied in a facility that can produce radioactive ion beams, such as ISOLDE at CERN [53]. At this facility it has been shown that

it is possible to measure electron affinities of radioactive isotopes, where the EA of ^{128}I [54] and ^{211}At [6] were measured. Combining the abilities of a facility such as ISOLDE with the method used in this paper will allow a determination of the EA of francium in the near future. In addition, studies of near-actinides will pave the way for future studies of negative ions of actinides, for which very little is known.

The supporting data for this article is openly available from the Zenodo data repository [55].

ACKNOWLEDGMENTS

Financial support from the Swedish Research Council (Grants No. 2016-03650 and No. 2020-03505) is acknowledged. This project has received funding from the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie Grant Agreement No. 861198.

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Paper II

The electron affinity of rubidium: a state selective measurement

Annie Ringvall-Moberg¹, Miranda Nichols^{1,*} , José E Navarro Navarrete², Uldis Bērziņš³, Viola C D'mello¹, Julia Karls¹ , Di Lu¹, Yazareth Peña Rodríguez^{1,4}, Rachel Poulouse^{1,5}, Andrea Morales Rodríguez^{1,4}, Keerthana Ravi^{1,5}, Meera Ramachandran^{1,5}, Vitali Zhaunerchyk¹, Dag Hanstorp¹ and David Leimbach^{1,*}

¹ Department of Physics, University of Gothenburg, SE-412 96 Gothenburg, Sweden

² Department of Physics, Stockholm University, SE-106 91 Stockholm, Sweden

³ Institute of Atomic Physics and Spectroscopy, University of Latvia, LV-1586 Riga, Latvia

⁴ Facultad de Ciencias, Universidad Nacional Autónoma de México, Ciudad de México 04510, Mexico

⁵ Cochin University of Science and Technology, Kochi, Kerala 682022, India

E-mail: miranda.nichols@physics.gu.se and david.leimbach@physics.gu.se

Received 19 March 2024, revised 24 June 2024

Accepted for publication 2 July 2024

Published 12 July 2024



Abstract

Negative ions, which are formed when an electron is attached to a neutral system, are unique quantum systems. The lack of a long-range Coulomb force causes the inter-electronic interactions to become relatively more important. As a consequence, the independent particle model, which adequately describes atomic structure under normal conditions, breaks down. The alkali negative ions, with a closed valence *s*-shell, are among the simplest anionic systems. Hence, they can favorably be used to benchmark atomic theory. In this work, we have determined the electron affinity of ⁸⁵Rb by measuring the relative partial photodetachment cross section of the negative ion, leaving the residual atom in the $5p\ ^2P_{3/2}$ excited state. Resonance ionization spectroscopy allows for state selectivity and the ability to measure the Wigner *s*-wave threshold onset of the photodetachment process. The electron affinity of ⁸⁵Rb was determined to be 485.887(6) meV.

Keywords: negative ion, electron affinity, rubidium, laser spectroscopy

1. Introduction

The structure of negative ions is fundamentally different from any other quantum system due to the nature of the attractive force that binds the valence electron. In these systems, the outermost electron does not experience a Coulomb attraction due to the inner electrons shielding the nucleus. Therefore, the binding of the additional electron mainly arises from electron-electron correlation. The valence electron, which polarizes the

atomic core, induces a dipole potential that is proportional to $1/r^4$. Due to this shallow binding potential, negative ions are weakly bound systems that can typically support only a single bound electronic state [1, 2]. What is most interesting about these systems is the high prevalence of electron correlation, which allows the validation of theories that address the limitations of the independent particle model. In an independent particle model, each electron is assumed to move in the average potential (mean field approach) of all the other electrons. This is the basis for the Hartree–Fock model, which can be used to describe the general structure of atomic and molecular systems [3]. The movement of one electron, when influenced by the presence of all the other electrons through direct interaction, is called electron correlation, which is very complicated to model. Its treatment requires either a multi-configuration approach or a full Configuration Interaction, which is normally

* Authors to whom any correspondence should be addressed.



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treated as a perturbation [4]. The electron correlation can be probed by measuring the energy released when an electron is attached to a neutral atom, referred to as the electron affinity (EA) [5, 6]. One of the most common methods to measure the EA is laser photodetachment threshold spectroscopy (LPTS) [7]. The photon energy is scanned through a small range around the onset of the photodetachment process and either the residual neutral atoms or the detached electrons are detected. Near the detachment threshold, the cross section is described by the Wigner threshold law [8].

To study partial photodetachment cross sections, the photon requires sufficient energy so that the residual atom can be left in an excited state. State selectivity can be obtained by applying a resonance ionization scheme for detection [9, 10]. This means that the partial cross section, fitted to the Wigner law, can be strategically chosen for precision advantages. The Wigner law depends on the angular momentum of the outgoing electron. For alkali metal anions, the electron is detached into a p -wave continuum ($l = 1$) if the detected residual atom is left in its ground state. This is not ideal as the onset of photodetachment is much less defined and cannot be measured with the same precision as with the sharp onset of an s -wave. Hence, partial cross section measurements are a viable way to study negatively charged alkali metals with higher precision.

Negative alkali metals are of strong interest because they are among the simplest of anionic systems. Due to their closed s -shells, they can be described as a two-electron model at low internal energies. This makes them ideal to use as initial benchmarks for atomic structure computations of open-shell systems [11, 12]. Partial cross section studies of alkali negative ions with resonance ionization detection have already been applied to lithium (Li) [13], sodium (Na) [10], potassium (K) [9], and cesium (Cs) [14].

An interest in alkali negative ions was ignited when, while determining the alkali EAs, Patterson *et al* discovered the presence of prominent narrow resonances near the first excited 2P states [15]. While measuring the photodetachment cross section of Rb, they observed that the resonances appeared just below the $^2P_{1/2}$ threshold. However, the same behavior was not seen for the $^2P_{3/2}$ threshold due to the $^2P_{1/2}$ open channel. The discovered resonances are highly sensitive to the spin-orbit interaction due to the forbidden transition from the $\text{Rb}-(^1S)$ state to the $\text{Rb}-(^3P^0)$ state, making input from theory vital.

In the Rb^- photodetachment cross section, Johnson and Burrow provided an upper bound for a near-threshold resonance with electron scattering but could not resolve it [16]. No alkali threshold resonance was directly confirmed until Scheer *et al* resolved a narrow resonance structure slightly above the photodetachment threshold in Cs^- [17]. These resonance channels were predicted to be similar but weaker in the Rb structure partially due to its smaller polarizability compared to Cs [18]. Bahrim *et al* [12] later theoretically confirmed that the $\text{Rb}-(^3P^0_1)$ resonance, situated near the $\text{Rb}(5s)$ threshold, has a small contribution to the total photodetachment cross section.

Until now, the most accurate experimental value for the EA of Rb was 485.916(21) meV, measured with total and partial cross sections from the $^2P_{1/2}$ state [19]. We are interested to measure an updated EA value that makes use of increased energy resolution using novel experimental techniques. The measurement presented in this paper was performed with a collinear beam apparatus, known as the Gothenburg University Negative Ion Laser Laboratory (GUNILLA) [20, 21] using a field ionization and position sensitive detection spectrometer, the Rydberg Atom Detector for Anion Research (RADAR) [22]. The relative partial photodetachment cross section was investigated from the excited $5p\ ^2P_{3/2}$ state in the neutral atom by using LPTS and then resonantly exciting the atom into the $37d\ ^2D_{5/2}$ Rydberg state. As the relative partial cross section is determined from the $^2P_{3/2}$ state, the $^3P^0_1$ resonance does not influence the measurement.

2. Experimental Method

At GUNILLA, ions are created in a cesium sputter ion source (PS-120 Peabody Scientific) based on the design of Middleton [23]. A stable beam of Rb^- was created using an aluminium cathode containing a mixture of Rb and Ag powder. Rubidium has two stable isotopes ^{85}Rb and ^{87}Rb with relative abundances of 72% and 28%, respectively. The experiment was conducted using ^{85}Rb due to the larger abundance. The extracted negative ions were accelerated to an energy of 6 keV and mass separated using a 90° separator magnet with a mass resolution ($m/\Delta m$) of approximately 500 [21]. The ion beam was then guided to the RADAR spectrometer [22], shown in figure 1, using electrostatic ion beam optics.

Upon entering the interaction region, the ions were collinearly overlapped with two laser beams. With sufficient energy, the wavelength of the first laser (λ_1) neutralized the Rb anions by photodetaching the extra electron. This left the atom in either the ground or an excited state. The wavelength of the second laser (λ_2) resonantly excited the neutral atom from the $5p\ ^2P_{3/2}$ excited state to the $37d\ ^2D_{5/2}$ Rydberg state. The experimental excitation scheme is shown in figure 2.

Downstream from the interaction region, the atoms entered the field ionization region which consists of four circular, parallel electrodes, where the middle two plates were biased with -629 V and -1224 V , and the two outer plates were at ground potential, as illustrated in the lower part of figure 1. This created an electric field gradient between the third and fourth electrodes large enough for the Rydberg atoms to be ionized at the exit of the third electrode. This is explained in further detail in an earlier publication [22]. Consequently, positive ions created in this process were decelerated due to a loss of kinetic energy corresponding to the potential difference between the third and fourth electrodes. Positive ions created via collisional detachment or double photon ionization were considered to be the background. These positive ions were first accelerated and then decelerated by the field ionizer and,

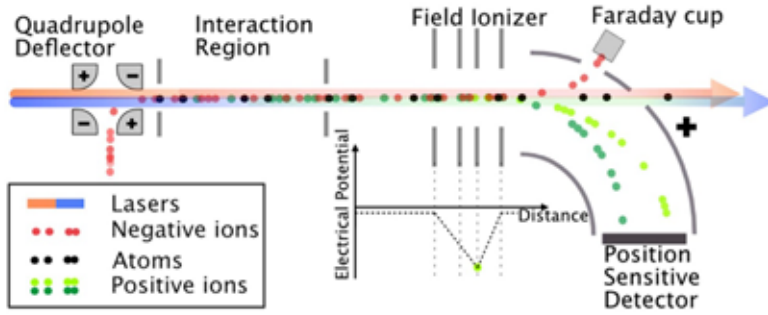


Figure 1. A schematic figure of the RADAR spectrometer. The negative ion beam was deflected by 90 degrees into the interaction region where it overlapped with the two laser beams. The first laser beam photodetached the negative ions whereas the second laser resonantly excited the atoms in the $^2P_{3/2}$ state to a Rydberg state. The excited Rydberg atoms were subsequently ionized by the electric field applied to the field ionizer plates. After the interaction region, the negative ions were deflected into a Faraday cup, while neutral atoms continued unaffected in a straight path. The positive ions were bent towards the position-sensitive detector, where the ions created via collisions had a different energy than the ions created in the field ionizer. The radius of the curvature of the positive ions is energy dependent. Hence, the impact position of the ions on the detector depended on how the ions were created.

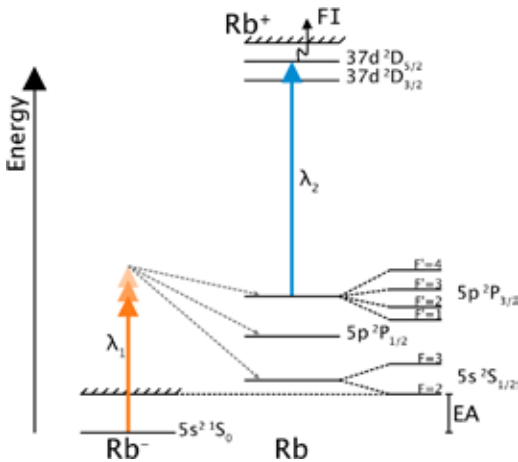


Figure 2. A partial energy level diagram (not to scale) of $^{85}\text{Rb}^-$ and ^{85}Rb . The negative Rb ion absorbed a photon, λ_1 (orange arrow), and was photodetached which left the residual atom in either the ground or an excited state. Following this, a second photon, λ_2 (blue arrow), selectively excited the atom from the $5p^2 P_{3/2}$ to the $37d^2 D_{5/2}$ Rydberg state. The Rydberg atom was then field ionized (FI) (black curved arrow).

therefore, their kinetic energy remained unchanged. All positive ions, including signal and background, were then deflected with an electrostatic energy analyzer towards a position-sensitive detector, consisting of a stack of microchannel plates

and a delay line anode. The energy difference between field ionized and background ions resulted in different trajectories when deflected by the energy analyzer, causing a spatial separation on the detector between the signal and the background. In addition, this resulted in the separation of residual negative ions and neutral atoms from the positive ions, where negative ions were directed into a Faraday cup while the neutral atoms remained unaffected. The data acquisition window was set to correspond to the time-of-flight of the ions from the interaction region to the detector.

The pulses from the two lasers were separated on the order of nanoseconds, depending on the propagation scheme, to optimize the atomic population of the $^2P_{3/2}$ excited state. A Sirah PrecisionScan dye laser (Model PRSC-D-18) and an EKSPLA NT342C-10-SH/SF-WW optical parametric oscillator (OPO), both pumped by 10 Hz Nd:YAG pulsed lasers, were used for the experiment. The dye laser, used for the photodetachment process, was circulated with Rhodamine B laser dye to generate photons in the 588–614 nm wavelength range and was attenuated to a pulse energy of around 0.5 mJ at the exit of the RADAR spectrometer. The bandwidth of this laser was specified by the manufacturer to be 0.075 cm^{-1} ($9.3 \mu\text{eV}$). The OPO, with a bandwidth of approximately 90 GHz, was then used for the resonant excitation step. To reduce power broadening effects and two-photon ionization, the corresponding pulse energy of the OPO was reduced to about $50 \mu\text{J}$. The laser frequency corresponding to λ_1 was recorded with a HighFinesse wavelength meter (WS-6) which was calibrated daily by performing saturated absorption spectroscopy of rubidium gas in a low-pressure quartz cell. The frequency corresponding to λ_2 was set by scanning the Rydberg transitions of the neutral ^{85}Rb atom. To determine the $^2P_{3/2}$ -channel

relative partial cross section, the energy of λ_1 was scanned over the photodetachment threshold region. The energy of λ_2 was set to the Doppler corrected literature value for the Rydberg transition [24]. In addition, the lifetime of the $^2P_{3/2}$ state was measured by setting the energy of λ_1 to be above the photodetachment threshold and fixing the energy of λ_2 while varying the delay in time between the two laser pulses.

3. Results and Discussion

The s -wave photodetachment relative partial cross section of $^{85}\text{Rb}^-$ was measured using a co- and counter-propagating laser-ion geometry. Each data point was normalized to both laser power and ion current. The threshold was determined by fitting the data with the Wigner law

$$\sigma(E_m) = A + B \sum_{F'=1}^4 (2F' + 1) (E_m - (E_{\text{Th}} + E_{\text{hfs}}, F'))^{l+\frac{1}{2}} \Theta(E_m - (E_{\text{Th}} + E_{\text{hfs}}, F')). \quad (1)$$

Here, E_m is the photon energy and E_{Th} is the photodetachment threshold energy. ^{85}Rb has a nuclear spin of $5/2$, which means that $^2P_{3/2}$ splits in the four hyperfine components $F' = 1, 2, 3$, and 4 . E_{hfs}, F' is then the energy corresponding to the hyperfine level, where the energies are taken from Das and Natarajan [25]. The angular momentum of the outgoing electron is denoted by l , A corresponds to the background, and B is the amplitude. The corresponding terms were added and the multiplicity of every level was taken into account, following the angular coupling derivation of Peláez *et al* [26], where the amplitude of the different channels are shown to be proportional to $(2F' + 1)$. Here F' is the hyperfine level in the residual atom. A representative graph of the data from a co-propagation scheme is presented in figure 3. The cross section below the energy threshold is almost zero. This allows for a precise Wigner law fit and does not require many points above the threshold. In cases where the integrated counts were zero, an iterative approach was used to estimate the uncertainty when fitting the data. In the initial fit to the Wigner function (equation (1)), the uncertainty of data points with a count rate of zero was approximated to a data point with one count. Subsequently, the uncertainty for data points below the photodetachment threshold was estimated using the background parameter of the fitted function. This procedure was iterated until the threshold value converged.

A series of measurements were performed in co- ($E_{\text{Th}}\uparrow\uparrow$) and counter-propagating ($E_{\text{Th}}\uparrow\downarrow$) schemes to correct for the Doppler shift. A Doppler shift can be corrected to all orders by calculating the geometrical mean value of the two respective thresholds $\nu_{\uparrow\uparrow}$ and $\nu_{\uparrow\downarrow}$ [27]

$$\sqrt{\nu_{\uparrow\uparrow}\nu_{\uparrow\downarrow}} = \sqrt{\frac{\nu_0(1+v/c)}{\sqrt{1-(v/c)^2}} \frac{\nu_0(1-v/c)}{\sqrt{1-(v/c)^2}}} = \sqrt{\nu_0\nu_0} = \nu_0, \quad (2)$$

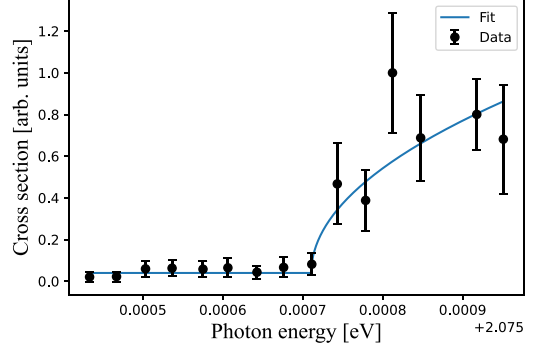


Figure 3. The relative photodetachment partial cross section as a function of the relative photon energy where the neutral Rb atom is left in the $5p\ ^2P_{3/2}$ state. The data was obtained in a co-propagating geometry and fitted using equation (1). The fit is represented by a solid line.

which includes the relativistic Doppler expression

$$\nu_{\uparrow\uparrow, \uparrow\downarrow} = \nu_0 \frac{1 \pm (v/c)}{\sqrt{1 - (v/c)^2}}. \quad (3)$$

Here ν_0 is the unshifted frequency, v is the velocity of the ions, and c denotes the speed of light. Hence, the threshold energy for the photodetachment threshold corrected to all orders can be determined by the expression

$$E_{\text{Th}}^{\text{Corr}} = \sqrt{(E_{\text{Th}}\uparrow\uparrow \cdot E_{\text{Th}}\uparrow\downarrow)}. \quad (4)$$

The resolution is determined by the combined effect of the linewidth of λ_1 and the longitudinal energy spread of the ions, which is approximated as a Gaussian profile. If the width of this profile is sufficiently large, the photodetachment threshold can be rounded off instead of appearing as the sharp threshold typical for an s -wave threshold. In a previous experiment, this effect was treated by fitting the data to a convolution of a Gaussian function and the Wigner function [14].

The convolution function was defined as

$$(\sigma \otimes g)(E_n) = \sum_{E_m} \sigma(E_m) g(E_n - E_m), \quad (5)$$

which is a discrete convolution between the Gaussian normalized function,

$$g(E_n - E_m) = \left(\frac{1}{\sigma_g \sqrt{2\pi}} \right) e^{-(E_n - E_m)^2 / (2\sigma_g^2)}, \quad (6)$$

and the Wigner function shown in equation (1).

In this work, likely caused by a lack of closely spaced data points around the onset of the threshold, the use of the convolution resulted in a spread of the width of the Gaussian profile mentioned above by over an order of magnitude between individual threshold scans. Therefore, we fitted the data to equation (5) using a fixed value of the width of a FWHM

of $14.6(16) \mu\text{eV}$ (or σ_g of $6.2(7) \mu\text{eV}$), as determined in the investigation of the Cs anion [14]. The same laser and ion source conditions were used in both experiments, where the laser linewidth is the dominating contributor to the broadening. The energy spread caused by a 6 keV beam of rubidium (cesium) is estimated to be $1.76 \mu\text{eV}$ ($1.4 \mu\text{eV}$), the linewidth of the laser light is specified to be $9.3 \mu\text{eV}$. It is therefore justified to use the same value of $14.6(16) \mu\text{eV}$ as an approximation for the overall broadening.

The threshold was measured 27 times in both co- and counter-propagating geometries. By applying equation (4), we obtained an average value of $2.0749432(13) \text{ eV}$ for the threshold energy. The EA was then determined by the equation

$$\text{EA} = E_{\text{Th}}^{\text{Corr}} - [E(^2P_{3/2, F'=1}) - E(^2S_{1/2, F=2})], \quad (7)$$

where the energy difference between the $^2P_{3/2}$ and $^2S_{1/2}$ states is $1.589\,049\,06 \text{ eV}$ [24]. The detuning required to reach the transition between the $F' = 1$ and $F = 2$ was reported as $6.763 \mu\text{eV}$ [28]. These two values were added together for a final energy difference of $1.589\,055\,823 \text{ eV}$, which then is subtracted from the threshold value to obtain the EA.

The total uncertainty in the EA was obtained by adding in quadrature the statistical uncertainty of the threshold measurement ($1.3 \mu\text{eV}$) and the uncertainty of the linewidth of the broadening caused by the energy spread of the ions and the laser linewidth ($0.7 \mu\text{eV}$). The uncertainties of the wavelength calibration ($2.5 \mu\text{eV}$) and the ^{85}Rb D2 line ($2 \mu\text{eV}$) were linearly added as this cannot be reduced statistically. All other systematic effects, such as the ponderomotive shift and the uncertainty in the angle between the overlap of laser and ion beams, are negligible. With this, the final EA value was determined to be $485.887(6) \text{ meV}$.

Previously, the EA of Rb was measured to be $485.916(21) \text{ meV}$ [19]. While both values were measured with partial cross sections, our mean value lies $3 \mu\text{eV}$ outside of their uncertainty. We note that this discrepancy arises from how the EA value is defined. Frey *et al* [19] defined their EA value as the difference between the ground state of the neutral and the ground state of the negative ion. If hyperfine splitting had been considered in their work, their value would have been reduced by $7.32 \mu\text{eV}$. This is the energy difference between the degeneracy-weighted center of the $^2S_{1/2}$ state and the $^2S_{1/2, F=2}$ level. Accounting for this correction, our value falls within their uncertainty.

We also determined the lifetime of the excited $^2P_{3/2}$ state in the neutral ^{85}Rb atom by measuring the yield of positive ions as a function of the time delay between the pulses of the detachment and resonant ionization lasers. For time delays on the order of the lifetime, a considerable number of atoms decayed to the ground state before they interacted with λ_2 . This resulted in a decrease in the positive ion signal. This is shown in figure 4, where the recorded positive ion counts are shown as a function of the delay time between the two laser pulses. An exponential function was used to obtain the decay constant corresponding to the lifetime of the state. The weighted average of two scans resulted in a lifetime of

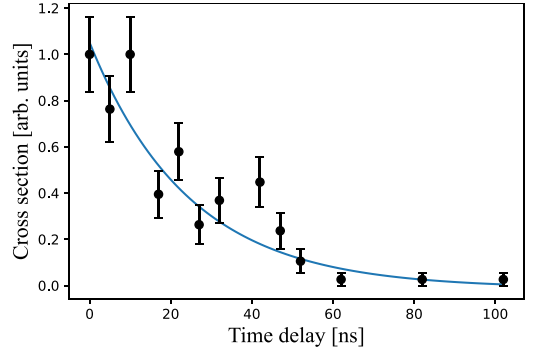


Figure 4. The number of detected positive ions as a function of the delay between the two laser pulses. The lifetime of the excited $^2P_{3/2}$ state was determined by fitting a single exponential function represented by the solid blue line.

$24.3(2.4) \text{ ns}$. This is in good agreement with the value of $26.0(1.8) \text{ ns}$, reported by Theodosiou [29].

4. Conclusion and outlook

The EA of ^{85}Rb has been determined to be $485.887(6) \text{ meV}$ by investigating the relative partial photodetachment cross section from $\text{Rb}^-(^1S_0)$ to $\text{Rb}(^2P_{3/2})$. This value is in excellent agreement with the previous measurement [19]. For the present measurement, a two-step laser scheme of LPTS followed by resonance ionization spectroscopy was used. The resonance ionization scheme made it possible to select only the $^2P_{3/2}$ detachment channel which results in a Wigner s -wave threshold behavior, i.e. a sharp onset for the cross section curve. The experiment was performed in both co- and counter-propagating laser-ion geometries to account for the Doppler shift.

In addition, the lifetime of the $^2P_{3/2}$ excited state was measured to be $24.3(2.4) \text{ ns}$, which is in agreement with the previous reported value [29]. This served as an additional confirmation that the correct state in the Rb atom was selected. Hence, this technique could also be used to determine lifetimes of excited states that are relatively short.

In the future, the method presented in this paper can be applied to study francium (Fr), the heaviest alkali metal that has no stable isotopes. The EA of Fr has not been experimentally determined, but it has been predicted to be $0.491(5) \text{ eV}$ by Ladau *et al* [11] and 0.475 eV by Hill and Peterson [30]. Francium can be studied at radioactive ion beam facilities such as CERN-ISOLDE [31] by using double electron capture reactions for anion production due to the predicted low EA. As it has been recently shown that $^{238}\text{U}^-$ can be produced with this method [32], the Fr $^-$ investigation will further aid in developing anion production and experimental techniques such as a three-step laser scheme for elements with significantly higher ionization potentials than the alkali metals.

Data availability statement

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

Acknowledgments

Financial support from the Swedish Research Council No. 2020-03505 is acknowledged. This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie Grant Agreement No. 861198. U B acknowledges the support by ERDF Project No. 1.1.1.1/19/A/144 'Technologic research for elaborating the next generation boron ion implantation apparatus with TRL level near to 4' and by Latvian Science Council's Fundamental and by Applied Research Project (No. lzp-2023/1-0199): 'The Laser Photodetachment Spectroscopy on Negative Ions'.

ORCID iDs

Miranda Nichols  <https://orcid.org/0000-0003-3693-7295>

Julia Karls  <https://orcid.org/0000-0002-1978-2642>

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Paper III



Investigating radioactive negative ion production via double electron capture

M. Nichols^{a,*}, M. Athanasakis-Kaklamanakis^{b,c}, A. Borschevsky^d, T.E. Cocolios^c,
R. Crosa-Rossa^d, R.P. de Groote^c, K.T. Flanagan^e, R.F. Garcia Ruiz^f, S. Geldhof^c, D. Hanstorp^a,
Á. Koszorús^{c,g}, L. Lalanne^c, D. Leimbach^a, G. Neyens^c, J. Reilly^e, S. Rothe^b, S.G. Wilkins^f,
X.F. Yang^h

^a University of Gothenburg, SE-41296 Gothenburg, Sweden

^b CERN, CH-1211 Geneva 23, Switzerland

^c KU Leuven, B-3001 Leuven, Belgium

^d University of Groningen, 9712 CP Groningen, The Netherlands

^e The University of Manchester, Manchester M13 9PL, United Kingdom

^f Massachusetts Institute of Technology, Cambridge, MA 02139, USA

^g Belgian Nuclear Research Centre (SCK CEN), B-2400 Mol, Belgium

^h Peking University, Beijing 100871, China

ARTICLE INFO

Keywords:

Negative ion
Radioactive
Charge exchange
Electron affinity
ISOLDE
CRIS

ABSTRACT

The relative cross sections for radioactive negative ion production via double electron capture have been measured for collisions between a 40 keV projectile beam of uranium-238 and potassium vapor. This was performed at the collinear resonance ionization spectroscopy (CRIS) experiment at CERN-ISOLDE and is a step towards measuring the electron affinities (EAs) of elements that cannot be efficiently produced in negative ion sources at radioactive ion beam (RIB) facilities. This includes short-lived radioactive isotopes that have low production quantities and heavy and superheavy elements that systematically have smaller EAs than work functions of available ion source materials. Negative ions are particularly sensitive to electron–electron correlation effects, which make such studies ideal for benchmarking atomic structure models that go beyond the independent particle model. While the EAs of most light elements have been measured, experimental investigations on heavier elements, namely the actinides, remain scarce due to their radioactive nature and production difficulty. By developing negative ion production by charge exchange, we aim to make these studies feasible at RIB facilities.

1. Introduction

Negative ions have a valence electron that is bound in a shallow induced dipole potential which arises from pronounced electron–electron correlation effects and are thus excellent systems to investigate these correlations [1]. Due to this weak potential, negative ions have binding energies that are usually an order of magnitude smaller than neutral atoms. This binding energy is called the electron affinity (EA), which is the amount of energy released when an electron binds to a neutral atom to make it negatively charged [2].

Electron affinity measurements are useful for benchmarking calculations of highly-correlated and relativistic systems [3], targeted alpha therapy using astatine-211 [4], uranium mine management [5], and future production of antiprotonic ions [6], to name a few. By measuring the isotopic shift (IS) in EAs of many-electron systems one can determine the specific mass shift (SMS). This quantity is sensitive

to electron–electron correlation unlike the normal mass shift (NMS), which is a purely kinematic effect. The SMS cannot be readily calculated and otherwise prevents the extraction of the field shift (FS) from IS measurements. Therefore, measuring the SMS is relevant for nuclear physics where the FS is necessary for determining changes in mean-square charge radii and, in turn, nuclear charge radii [7,8].

Traditionally, negative ions have been produced in sputter and plasma ion sources which require large samples, and surface ion sources which work most effectively for elements with EAs larger than the work function of the material [9]. The first EA measurements for radioisotopes were iodine-128 (¹²⁸I) [10] and astatine-211 (²¹¹At) [11] performed at CERN-ISOLDE. They were accomplished with negative ions produced from an LaB₆ surface ionization source ($\phi_{eff} \approx 2.6$ – 2.9 eV) [12–14]. However, when producing beams of radioactive negative ions that have relatively low EA values, the aforementioned

* Corresponding author.

E-mail address: miranda.nichols@physics.gu.se (M. Nichols).

<https://doi.org/10.1016/j.nimb.2023.04.051>

Received 17 February 2023; Received in revised form 23 April 2023; Accepted 26 April 2023

Available online 27 May 2023

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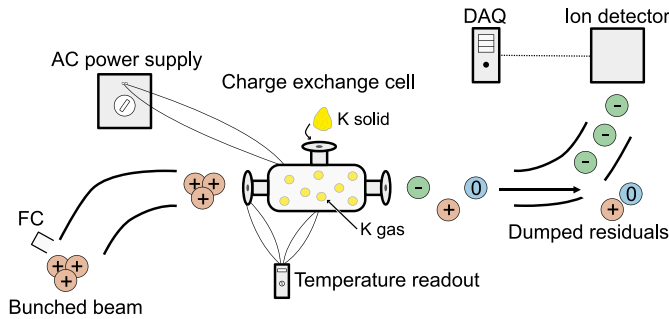


Fig. 1. The cooled and bunched positive ion beam from ISOLDE (red) was guided to the CRIS experimental setup and into the charge exchange cell (CEC) where solid potassium (K) was inserted from the top and heated until gas phase was reached. With increasing pressure, two separate electron capture reactions between the projectile beam and the K atoms in gas phase (yellow) occurred to produce negative ions (green). The remaining positive ions that did not capture any electrons and the neutral atoms (blue) that only underwent one electron capture reaction were dumped while the negative ions were electrostatically bent towards the ion detector, which was connected to the data acquisition system (DAQ). The CEC was heated by the AC power supply and the temperature was read with thermocouples from the CEC end and center, with the center temperature values recorded for the measurement. Finally, the transmission efficiency measurements were taken between the Faraday cup (FC) and the ion detector for positive ions.

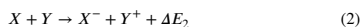
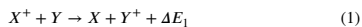
methods will not suffice. An alternative to producing such beams is with a projectile beam of positive ions that collides with a target vapor and captures two electrons, also known as double charge transfer or exchange. This has been studied with metal vapor targets such as cesium [14,15], magnesium [16], and sodium [17], but has been limited to stable projectiles. While neutralization cross sections have been studied for elements up to $Z = 89$ [18], further investigations are required to understand radioactive negative ion production with charge exchange.

As we improve and develop production and experimental techniques, studying radioactive elements, such as the actinides, can become more attainable. For these negative ion studies, we need to rely on production via double electron capture reactions. Here, we demonstrate the feasibility of negative ion production in a charge exchange cell with uranium-238 (^{238}U) at the collinear resonance ionization spectroscopy (CRIS) experiment at ISOLDE [19,20].

2. Experimental method

2.1. Negative ion production

Negative ions can be produced via two sequential electron capture reactions from a projectile beam of positive ions and an electron donor target, most commonly gas phase alkali metal atoms. This process is known as double charge exchange and depends on the projectile beam energy, the EA of the projectile, the ionization potential (IP) of the charge exchange target vapor, and the vapor density [9,14]. The double electron capture process can be described by the following reactions:



Here X is the projectile beam, Y is the target vapor, and ΔE is the energy defect for the reaction. In the first electron capture reaction (1), ΔE_1 is equal to $IP(X) - IP(Y)$, while in the second electron capture reaction (2), ΔE_2 is equal to $EA(X) - IP(Y)$. Negative ion yields are optimal when the energy defects for both reactions are as small as possible [9,14]. For ion beam neutralization, it is common to choose elements that have similar IPs to ensure a relatively large atomic ground state population. This cannot be done for the latter reaction because EAs are significantly smaller than IPs. Therefore, it is necessary to minimize the energy defect as it will always be negative.

2.2. Experimental parameters and setup

Radioactive isotopes are produced when protons from the PSBooster impinge on the ISOLDE target which are subsequently ionized and extracted as a positively charged ion beam [21]. The beam is then mass selected by the high-resolution separator and cooled and bunched in a gas-filled radio frequency quadrupole linear Paul trap (ISCOOL) [22]. For this experiment, a beam of $^{238}\text{U}^+$ with an energy of 40 keV was produced with a pre-irradiated uranium carbide target and the resonant ionization laser ion source (RILIS).

After the $^{238}\text{U}^+$ beam reached the CRIS experimental setup, the ions entered the potassium (K) filled charge exchange cell (CEC) where two electron capture reactions must occur for negative ion production, as previously explained. Potassium was chosen for the charge exchange target vapor due to its lower first IP compared to the other available option, sodium (Na) ($IP(K) = 4.34$ eV and $IP(Na) = 5.14$ eV [23]; $EA(U) = 314.97(9)$ meV [24]). The CEC was resistively heated with cartridge heaters and a Variac variable transformer AC power supply (200 V) to a maximum relative temperature of ~ 140 °C. The recorded temperature of the cell was taken from the center with thermocouples. It took about one hour of consistent heating to collect all data points.

After production, the negative ions were electrostatically separated from the residual products and detected with a MagneToF single ion detector. This required the polarity of the electrostatic benders to be flipped. Lastly, there was a maximum transmission efficiency for positive ions of $\sim 5\%$ to the end of the CRIS beamline from ISOLDE. This was determined by Faraday cup measurements after ISCOOL and MagneToF detector measurements in single ion counting mode placed after the bend. The experimental setup is shown in Fig. 1.

3. Results and discussion

We successfully produced $^{238}\text{U}^-$ in a CEC from collisions between a 40 keV projectile beam of $^{238}\text{U}^+$ and gas phase K atoms. The results are shown in Fig. 2. We recorded negative ion production rates as a function of increasing temperature to determine optimal production conditions. The first electron capture reaction dominates the onset of the curve at lower temperatures. As the pressure in the cell increases, the cross section for negative ion production also increases. The second electron capture reaction is prevalent until the saturation point at around 134 °C. We then see a decrease in negative ion production. This can be explained by a third reaction where the negative ion is destroyed due to sufficiently high pressure within the cell. A similar temperature dependence curve was observed by Alton et al. for production of negative calcium ions with a lithium vapor target [25].

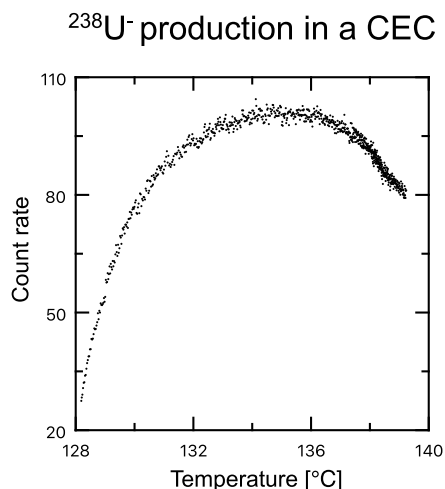


Fig. 2. Temperature dependence of negative uranium-238 ion production in a charge exchange cell as measured with a MagneToF detector. A 40 keV projectile beam of positive uranium-238 ions collides with potassium vapor to undergo a single electron capture reaction. As the temperature in the cell increases, so does the probability for a second electron capture reaction until the curve saturation point at ~ 134 °C. As temperature continues to increase, the cross section of a third collision also increases in which the negative ions are subsequently destroyed.

The cross section of negative ion production with charge exchange heavily depends on the target vapor density. However, we were unable to determine the K vapor density because the absolute temperature of the vapor was unknown due to the measurement method. From Heine-meier et al. we also know that beam energies between 10 and 30 keV typically result in higher efficiencies of negative ion production [16, 17]. From their results for similar EA elements, we could expect an efficiency for $^{238}\text{U}^-$ production at $\sim 10\%$. For technical reasons, we did not have a choice in beam energy nor were we able to determine production efficiency because we did not have a way to detect all three charge states simultaneously.

4. Conclusion

We have shown that ^{238}U negative ions can be produced in a charge exchange cell. Future studies of interest include varying the projectile beam energy, projectile element, and charge exchange target. Upgrades to the pre-existing beamline and detectors are required to facilitate these studies. The aim is to open up possibilities of studying short-lived radioactive isotopes that cannot be produced in efficient quantities from sputter, plasma, or surface ion sources. We are most interested in studying heavy, radioactive negative ions, such as the actinides, because little is known about their atomic properties. However, there are still lighter radioactive elements, such as polonium and francium, which have EA values that are experimentally unknown and will be investigated. By measuring these elements first, we will be able to better understand the production mechanisms and develop more precise experimental techniques.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

We thank the support of the ISOLDE collaboration and technical teams. This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 861198 and support from the Swedish Research Council for individual project grants with Contracts No. 2020-03505. The CRIS experiment is further supported by the ERC Consolidator Grant No. 648381 (FNPMLS); STFC, United Kingdom grants ST/L005794/1, ST/L005786/1, ST/P004423/1, ST/M006433/1, ST/P003885/1 and Ernest Rutherford Grant No. ST/L002868/1; the U.S. Department of Energy, Office of Science, Office of Nuclear Physics under grant DESC0021176 and DE-SC0021179; GOA 15/010 and C14/22/104 from KU Leuven, Belgium, EOS MANASLU No. 40007501; the FWO-Vlaanderen (Belgium); the European Union Grant Agreement 654002 (ENSAR2); National Key R&D Program of China (Contract No:2018YFA0404403); the National Natural Science Foundation of China (No:11875073).

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Paper IV

Trajectory effects on charge exchange and energy loss in collisions of H^+ , He^{2+} , Li^{3+} , and Be^{4+} ions with atomic hydrogen

Miranda Nichols,^{1,2,*} D. Hanstorp,¹ and R. Cabrera-Trujillo^{2,1,†}

¹*Department of Physics, University of Gothenburg, SE-412 96 Gothenburg, Sweden*

²*Instituto de Ciencias Físicas, Universidad Nacional Autónoma de México, Ap. Postal 43-8, Cuernavaca, Morelos, 62251, México*

The charge exchange and energy loss processes provide insights into fundamental processes across physical, chemical, and engineered systems. While this field has been thoroughly investigated, a clear study on trajectory effects is lacking, particularly in the context of inelastic processes at low energies. In this work, we address this gap by solving the time-dependent Schrödinger equation for the electron in a numerical lattice with a coupled electron-nuclear dynamics approach as well as a straight-line trajectory approximation for the nuclei to assess trajectory effects on charge exchange and energy loss. The collision dynamics are studied using bare ion projectiles with charge $Z = 1-4$ incident on atomic hydrogen in an energy range of 0.1 to 900 keV/u. We find that the charge exchange process is trajectory-independent within the energy range considered, showing excellent agreement with available experimental and theoretical data. However, projectile energy loss exhibits strong trajectory dependence, with the straight-line approximation overestimating energy loss at low collision energies due to the forced linear path. Our results for electronic stopping cross sections with electron-nuclear coupled trajectories are consistent with the available experimental data at high collision energies. At low energies, nuclear energy loss becomes prominent, driven by polarization effects induced by the ion charge on the hydrogen target. Overall, our work highlights the importance of nuclear trajectory considerations in collision dynamics and offers a foundation for further investigations of more complex systems.

I. INTRODUCTION

Ion-atom collisions have been researched for over a century due to their role in understanding fundamental atomic structure [1, 2]. Bare ions, which are completely stripped of electrons, are the simplest systems to conduct these studies with because they lack the complexity of multi-electron systems. In a collision, many inelastic processes can occur such as the transfer of an electron from the target to the projectile. This is called charge exchange or electron capture, and it plays a central role in the neutralization process [3].

The charge exchange process has been studied in many fields such as plasma and fusion research, astrophysics, and medicine. The necessity for diagnostics in plasma confinement devices such as tokamaks propelled the early interest for electron capture reactions, especially in fully stripped low- Z ions [4, 5]. Solar wind, rich in protons and alpha particles, was found to drive charge exchange processes responsible for characteristic X-ray emissions from comets [6], planetary atmospheres [7], and even in regions of the interstellar medium [8]. Additionally, charge exchange plays an important role in ion beam radiation therapy for cancer treatment [9], particularly in the context of proton impact on hydrogen for water dissociation, where understanding radiation damage at the molecular level is crucial [10].

To maximize the efficacy of these applications, it is essential to understand the physics that governs the col-

lision dynamics. For slow and low- Z ion-atom collisions, the atomic framework breaks down. In the energy region of less than 1 keV/u, a quasi-molecular representation becomes relevant, which treats the ion and atom as a single entity due to the sharing of the electron [11, 12]. If the ion-atom pair exhibits nuclear symmetry, the lower-lying stationary states become degenerate. The H_2^+ molecule is the simplest example, where the electron oscillates between the resonant molecular states [13]. This is known as resonant charge transfer, which was first observed in the $\text{H}^+ + \text{H}(1s)$ system by Lockwood and Everhart [14]. Since then, electron capture cross sections for low- Z bare ion collisions with atomic hydrogen have been extensively studied, especially for the $\text{H}^+ + \text{H}(1s)$ [15–18], $\text{He}^{2+} + \text{H}(1s)$ [19–23], and $\text{Li}^{3+} + \text{H}(1s)$ [24, 25] systems. However, the $\text{Be}^{4+} + \text{H}(1s)$ collision remains experimentally untouched due to the poisonous nature of beryllium.

In cases where experimental data is difficult or impossible to obtain, theoretical models are invaluable. These models also serve as complements to experimental results and help to contextualize findings. For instance, the resonant charge transfer process was investigated using the electron-nuclear dynamics (END) method for the $\text{H}^+ + \text{H}(1s)$ system [26] to understand the importance of non-adiabatic effects for higher collision energies [27] and for the $\text{He}^{2+} + 1-3\text{H}$ systems to study isotopic effects on charge transfer [28]. The END method has also been used to study charge exchange and energy loss of the proton-hydrogen collision [29]. In fact, the development of computational approaches to study the inelastic processes of ion-atom collisions has been significant. The main methods and

* miranda.nichols@physics.gu.se

† trujillo@icf.unam.mx

models include solving the time-dependent Schrödinger equation (TDSE) [30, 31], lattice TDSE (LTDSE) [32–35], GridTDSE (GTDSE) [36, 37], basis generator method (BGM) [37, 38], classical trajectory Monte Carlo (CTMC) [34, 37, 39–46], atomic orbital close-coupling (AOCC) [34, 37, 47–53], molecular orbital close-coupling (MOCC) [40, 45, 46, 54, 55], and other close-coupling treatments such as the Sturmian-pseudostate [56], hidden crossing (HCCC) [19, 55, 57], hyperspherical (HSCC) [58], common-reaction-coordinates (CRC) [58], wave-packet convergent (WP-CCC) [37, 59], and two-center quantum mechanical convergent (QM-CCC) [60] methods. There are also perturbative methods which have been shown to be more successful for high energy collisions than most of the classical and semi-classical methods mentioned above. These include various distorted wave approximations such as boundary-corrected continuum-intermediate-state method (BCIS) [61], unitarized-distorted-wave-approximation (UDWA) [62], and continuum-distorted wave (CDW) [21] models. Other perturbative approaches include adiabatic [13], first Born [51], and eikonal impulse approximations [43], as well as the Bohr-Lindhard model [63].

While there are extensive methods for studying ion-atom collisions, the primary theoretical works for calculating electron capture cross sections of bare ion projectiles include the (L)TDSE, AOCC, and CTMC methods. The first application of the TDSE method used a two-center-basis representation for fully stripped ions with charge $Z=1-5$, done by Lüdde and Dreizler [30, 31]. However, the method required a large number of basis states, which made initial computations expensive. Later, the LTDSE solution was developed to bridge gaps between theoretical results and offered a level of precision that compared to that of the leading models including AOCC and MOCC, despite no use of basis sets [32]. Among the AOCC approaches, methods used by Fritsch and Lin (AO expansion) (AO+) [47, 48], Lin *et al.* (two-center (2C)-AOCC) [52], and Toshima (AOCC) [50] have been successfully applied to He^{2+} , Li^{3+} , and Be^{4+} projectiles for a wide range of energies. A comparative study by Minami *et al.* [34] evaluated the LTDSE, AOCC, and CTMC methods in an energy range of ~ 1 to 1000 keV/u by comparing with experimental values for total and state-selective cross sections for electron capture in the $\text{He}^{2+}+\text{H}(1s)$ collision. They found that while both LTDSE and AOCC agree well with experiment in the entire energy range, LTDSE is ideal for low energies where the atomic orbital framework breaks down. They also note that CTMC gains reliability for high energies and capture into higher n levels, which can be classically described. Previously considered less accurate for low energy collisions, the CTMC method has seen recent developments. Work by Ziaean and Tökési on the $\text{Be}^{4+}+\text{H}(1s)$ system demonstrated that accounting for quantum behavior significantly improves the accuracy of CTMC, rivaling semi-classical models [42].

It is clear that theoretical studies within the field of

atomic collision dynamics are plentiful, yet most rely on straight-line trajectories and overlook potential trajectory effects. In this work, we address this gap by investigating energy transfer in collisions by comparing the straight-line approximation with dynamic trajectories that account for electron-nuclear coupling. Our approach utilizes LTDSE solutions to evaluate the efficacy of the method with fully stripped ions. Motivated by the recent straight-line trajectory calculations for energy deposition within a time-dependent density functional theory (TDDFT) framework [64–67], we believe that settling the question of trajectory effects is necessary.

We focus on charge transfer and energy deposition processes in collisions of H^+ , He^{2+} , Li^{3+} , and Be^{4+} ions with the ground state of atomic hydrogen over an energy range of 0.1 to 900 keV/u. By comparing trajectory calculation methods, we evaluate the role of nuclear motion and identify the limitations of the straight-line approximation in these systems. Our method enables precise convergence at each time step within the lattice structure, so that our results can serve as a benchmark not only for the current studied systems but also for more complex multi-electron systems.

II. THEORY: LATTICE APPROACH

In this study, we employ a time-dependent electron-nuclear dynamics (END) approach [26] for coupling electrons and nuclei dynamics. The time-dependent Schrödinger equation governing the behavior for an electron in the presence of N nuclei is expressed as

$$i\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = \left[-\frac{1}{2}\nabla^2 + \sum_{i=1}^N \frac{Z_i}{|\mathbf{r} - \mathbf{R}_i(t)|} \right] \Psi(\mathbf{r},t), \quad (1)$$

where $\Psi(\mathbf{r},t)$ is the time-dependent wave function, Z_i is the charge of the i -th nuclei, and $\mathbf{R}_i$ denotes the trajectory of the heavy i -th nuclei coupled to the electron. The dynamics of the coupling are described by the equations [68]:

$$\begin{aligned} \dot{\mathbf{R}}_i &= \frac{1}{M_i} \mathbf{P}_i(t) \\ \dot{\mathbf{P}}_i &= Z_i \langle \Psi | \frac{(\mathbf{r} - \mathbf{R}_i)}{|\mathbf{r} - \mathbf{R}_i|^3} | \Psi \rangle - \sum_{k \neq i}^N Z_k Z_i \frac{(\mathbf{R}_k - \mathbf{R}_i)}{|\mathbf{R}_k - \mathbf{R}_i|^3}, \end{aligned} \quad (2)$$

where i ranges from 1 to N number of heavy nuclei. In our specific case, we set $N = 2$. For scenarios involving straight-line trajectories, we simplify our approach by fixing the position of the target nucleus at $\mathbf{R}_1 = 0$ and defining the position of the projectile as

$$\mathbf{R}_2 = \mathbf{b} + \mathbf{v}t. \quad (3)$$

Here, $\mathbf{b} = b\hat{x}$ represents the impact parameter and $\mathbf{v} = v_0\hat{z}$ is the collision velocity. In this case, the projectile momentum $\mathbf{P}_2 = M_2\mathbf{v}$ remains constant throughout the collision process and the projectile velocity is proportional to the collision energy.

To numerically solve Eq. (1), we utilize a lattice approach. A three-point finite-differences method within the Crank-Nicholson approach [69] is applied to a uniform grid, as shown in [70]. We address ionization by implementing a masking function that absorbs ionized electrons at each time step on the grid boundary [71]. In Fig. 1, the masking function acts over the box Ω at the edge of the numerical grid in the space between the blue and black boxes. It is expressed as $M(\mathbf{r}) = M(x)M(y)M(z)$, where $M(z)$ is given by

$$M(z) = \begin{cases} \cos^{1/8}\left(\frac{\pi|z-z_b+L|}{2L}\right), & |z_b - z| < L \\ 1, & \text{otherwise.} \end{cases} \quad (4)$$

Here, z_b indicates the boundary along the z -axis, either at $z_{\min}$ or $z_{\max}$, and L is the absorbing width of the region Ω . The expressions are similar for the x and y cases.

The computational grid is defined as $[-18, 18]_x \times [-18, 18]_y \times [-30, 45]_z$ a.u., with a grid step of 0.4 a.u., as shown in Fig. 1. Although this results in an approximate hydrogen ground state energy of $E_H = -0.490$ a.u., it is adequate for estimating charge exchange probabilities, excitation levels, and energy loss. Our focus is more on capturing the shapes and behaviors of the total wave functions, which is accomplished with this grid step size.

We select a time step of 0.01 a.u. which strikes a balance between accuracy and computational efficiency. It is also long enough to achieve a clear separation between the target and projectile at the end of our simulation, which is demonstrated in Fig. 2. The collision time is defined as $t_0 = 2z_0/v_0$, where v_0 is the initial velocity of the projectile and z_0 is the initial projectile distance to the target. With this, Eq. (2) is solved with the fourth-order Runge-Kutta method coupled to Eq. (1). For the straight trajectories, we simply advance $\mathbf{R}_2$ according to Eq. (3).

To prevent numerical instabilities when nuclei $\mathbf{R}_i$ pass near a grid point $\mathbf{r}$, we arrange our impact parameter grid so that both projectile and target trajectories align with points at the center of adjacent squares in the xy -plane [70]. The impact parameter b is varied from 0.0 to 14.0 a.u. in increments of 0.4 a.u.. Initially, we position the projectile along the z -axis at a distance of $z_0 = -30$ a.u., as illustrated in Fig. 1.

We perform calculations for collision energies in the laboratory frame of the projectile, E_p , ranging from 0.1 keV/u up to 900 keV/u. To account for polarization effects on the hydrogen electronic cloud due to initial placement at $z_0 = -30$ a.u. and $x = b$, we compute the initial wave function in Eq. (1) using an imaginary time technique for each configuration [70], which allows for ground state convergence. Finally, we set an absorbing

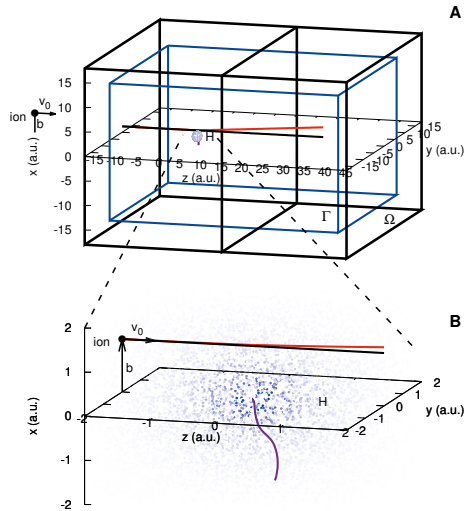


FIG. 1. A^q+H collision rendering. In **A**, the sphere represents the $1s$ hydrogen electron density, b is the collision impact parameter of an ion A^q with q the initial charge, located initially at a distance z_0 , and v_0 is the initial collision velocity. The space between the inner (blue) and outer (black) boxes represents the ionization absorbing region, Ω . The box for $z > 15$ a.u. determines the electron capture by the projectile and is denoted by Γ . The black and red lines correspond to the straight-line and the electron-nuclei coupled trajectories, respectively, for $b = 1.2$ a.u. impact parameter. In **B**, an inset of the collision region around the target electronic density (dotted blue cloud) is shown. The purple line is the target recoiling trajectory in the electron-nuclei coupled scheme.

width $L = 4.0$ a.u., ensuring effective electron absorption without interfering with the collision region, Γ [71].

III. RESULTS

A. Electron capture probability

In ion-atom collisions, the probability of electron capture by the projectile depends on both the impact parameter and collision energy. We quantify this probability using the electronic density distribution, $\rho(\mathbf{r}, t) = |\Psi(\mathbf{r}, t)|^2$. Fig. 2 illustrates this projected over the xy -plane, given as $\rho(z) = \iint \rho(\mathbf{r}, t) dx dy$, for various projectile ions (H^+ , He^{2+} , Li^{3+} , and Be^{4+}) colliding with atomic hydrogen at 5 keV/u and an impact parameter of $b = 1.2$ a.u.. The plot is divided into two regions: the left side ($-30 \leq z < 15$ a.u.) representing the region for excitation probability of the target, and the right side ($15 \leq z \leq 45$ a.u.) showing the electron capture proba-

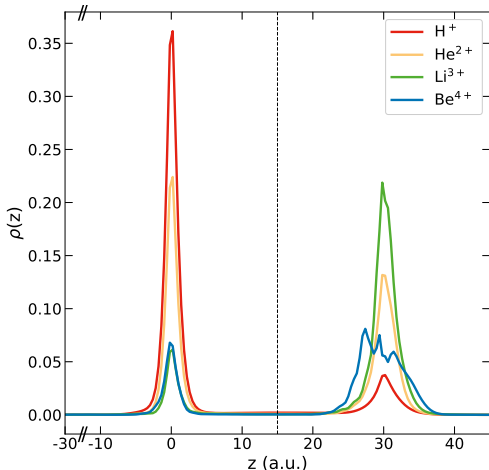


FIG. 2. Electronic density as a function of z when projected over x and y coordinates for H^+ , He^{2+} , Li^{3+} , and Be^{4+} colliding with atomic hydrogen at 5 keV/u and an impact parameter of $b = 1.2$ a.u.. There are two regions delineated by the vertical dotted line. The region on the left between $-30 \leq z < 15$ a.u. determines the excitation region of the target. The region between $15 \leq z \leq 45$ a.u. is a well-separated region after the collision where the electron capture by the projectile is determined.

bility by the projectile ions.

Referring to the left side of Fig. 2, it can be seen that the target electronic density is notably higher for H^+ compared to the other ions. On the right side of Fig. 2, we observe that the electron capture probability increases with the ionic charge, with Li^{3+} exhibiting the highest peak for the given impact parameter and projectile energy. Interestingly, Be^{4+} shows a significantly wider probability than Li^{3+} despite its higher charge. The can be explained by considering the highest probable state populated, which is determined from the energy conservation within the system. In this case, the initial hydrogen electronic energy should equal the final projectile electronic energy once the exchange occurs for $t \rightarrow \infty$, i.e. no projectile-target interaction. This can be summarized as

$$-\frac{Z_t^2}{2n_i^2} = -\frac{Z_p^2}{2n_f^2}, \quad (5)$$

with n_i and n_f being the initial and final quantum number, in the target and projectile, respectively. From here, one finds that $n_f = Z_p n_i / Z_t$, where the charge of the target, Z_t , and the initial quantum n_i -level are both equal to 1, therefore $n_f = Z_p$. This means that it is most likely for the projectile ion to capture the electron in the quantum n -level that matches its nuclear charge. In the case

of Be^{4+} , the most probable capture will occur in the level $n=4$, which has angular momentum of $l = 0, 1, 2$, and 3 corresponding to the s, p, d , and f orbitals. The introduction of higher angular momentum orbitals inherently increases the complexity of the system and can explain the broader behavior of the capture probability.

The electron capture probability is given as the integration of the electronic density in the region of the projectile well after the collision, Γ (Fig. 1), $P_{CX} = \langle \Psi(\mathbf{r}, t) | \Psi(\mathbf{r}, t) \rangle_{\Gamma}$. The analysis of weighted probabilities against impact parameter for energies ranging from 0.1 keV/u to 100 keV/u, as shown in Fig. 3, provides more insights on n -level capture. As H^+ is most likely to capture in the $n=1$ level, the $H^+ + H(1s)$ collision in Fig. 3A demonstrates a strong resonant electron capture effect for energies below 10 keV/u. This tends to be stronger at lower energies due to the dominant Coulomb interaction and ease of resonant channel coupling. At higher energies, shorter interaction times result in lower electron capture probabilities. There is also no resonant charge exchange for higher energies as interaction time determines the number of oscillations. In other words, oscillations dampen with increasing energy due to coupling to different, non-resonant channels of the system.

The other ion collisions show varying degrees of this resonant effect. The $He^{2+} + H(1s)$ collision in Fig. 3B is only slightly asymmetric and therefore exhibits resonant effects which appear the strongest at 1.5 keV/u projectile energy. As the ionic charge increases, so does the asymmetry of the collision, which causes the resonant channel coupling to become weaker. Like He^{2+} , the $Li^{3+} + H(1s)$ collision in Fig. 3C also has the highest probability for 10 keV/u but diminishing resonant effects at 1.5 keV/u. While there still appears to be a resonant channel for the $Be^{4+} + H(1s)$ collision in Fig. 3D, it deviates from the trends observed in the other collisions. Here, the maximum electron capture probability occurs at $b=6.4$ for a collision energy of 0.25 keV/u. The preference for Be^{4+} to capture in higher b values can be traced back to Eq. (5) where $n = 4$ is more extended than the other systems.

B. Electron capture cross section

The area under the electron capture probability curves of Fig. 3 is proportional to the electron capture cross sections, since

$$\sigma = 2\pi \int b P_{CX} db. \quad (6)$$

In Fig. 4, we show the electron capture cross sections as a function of the projectile collision energy for H^+ , He^{2+} , Li^{3+} , and Be^{4+} colliding with atomic hydrogen. In Fig. 4A, we compare our H^+ results with the experimental data from McClure [15], Hvelplund and Andersen [16], and Gealy and Van Zyl [17], as well as the theoretical results from CTMC [39], LTSDE [35], MOCC [54], UDWA [62], and QM-CCC [60]. Due to the resonant character of

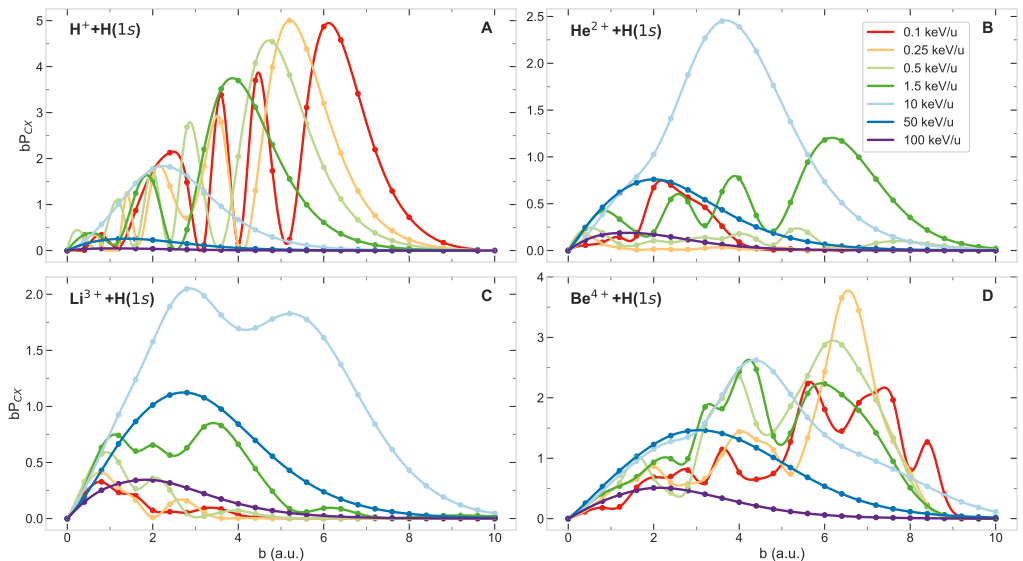


FIG. 3. Electron capture probability, weighted by the impact parameter, as a function of the impact parameter for collision energies of 0.1, 0.25, 0.5, 1.5, 10, 50, and 100 keV/u. Results for (A) $H^+ + H(1s)$, (B) $He^{2+} + H(1s)$, (C) $Li^{3+} + H(1s)$, and (D) $Be^{4+} + H(1s)$ are shown. The data points correspond to our electron-nuclei coupled results of Eq. (2), and the solid lines represent cubic spline fits and serve only as a visual guide.

the electron capture, $n_i = n_f = 1$ (s orbital) in Eq. (5), as the projectile energy is reduced, the electron capture cross section increases [13]. We observe that our numerical results agree with the experimental data within the experimental error bars for the low and intermediate energy ranges. Our results from both the straight-line and the electron-nuclei coupled trajectories agree well with each other. This implies that the electron capture process is not affected by the trajectory at these collision energies. This is due to the adiabatic molecular pseudo-potential formed by the projectile and target in this energy range, which only depends on the projectile-target distance. Thus, the formation of the pseudo-potential, and in turn the electron capture cross sections, are not significantly influenced by the kinematics of the collision [13].

In Fig. 4B, we compare our He^{2+} results with the experimental data from Shah and Gilbody [20] and Havener *et al.* [19], as well as the theoretical results from CTMC-1 [34], CTMC-2 [39], TDSE [31], LTDSE [34], AOCC-1 [34], AOCC-2 [50], AOCC-3 [53], MOCC [54], END [28], and Sturmian-pseudostate [56]. Here, the electron is most likely captured in $n_f = 2$, which involve the s and p orbitals. Consequently, the electron capture cross sections for the He^{2+} projectile exhibit a different trend compared to those for the H^+ projectile. The trend shows a peak at 10 keV/u and decreases for lower collision ener-

gies, which slightly overestimates the experimental data but still reflects the same behavior.

In Fig. 4C, we compare our Li^{3+} results with the experimental data from Seim *et al.* [24] and Shah *et al.* [25], as well as theoretical results from CTMC [39], TDSE [31], 2C-BGM [38], AOCC [50], AO+ [47], 2C-AOCC [52], MOCC [54], and UDWA [62]. In this case, the electron capture occurs mostly for states with $n_f \leq 3$ involving s , p , and d orbitals which result in a peak around 15 keV/u. There is a very good agreement of our numerical results to the experimental data and other theoretical approaches except for the UDWA model [62] for energies of 20 keV/u and less.

There is no experimental data for the $Be^{4+} + H(1s)$ collision, so in Fig. 4D, we compare our results to the theoretical results from CTMC-1 [39], CTMC-2 [42], QCTMC [42], TDSE [31], LTDSE [33], GTDSE [36], AOCC [50], AO+ [48], MOCC [54], and WP-CCC [59]. Interestingly, we find that the electron capture cross section remains almost constant for collision energies below 25 keV/u. This could be a consequence of the uniform distribution of angular momentum orbitals in the higher- n capture levels. Contrary to Eq. (5), some n -partial cross section studies observed that the electron is predominantly captured into the $n = 3$ level for low to intermediate collision energies and the $n = 2$ level for the high-energy region [36, 48, 59]. Nevertheless, the physi-

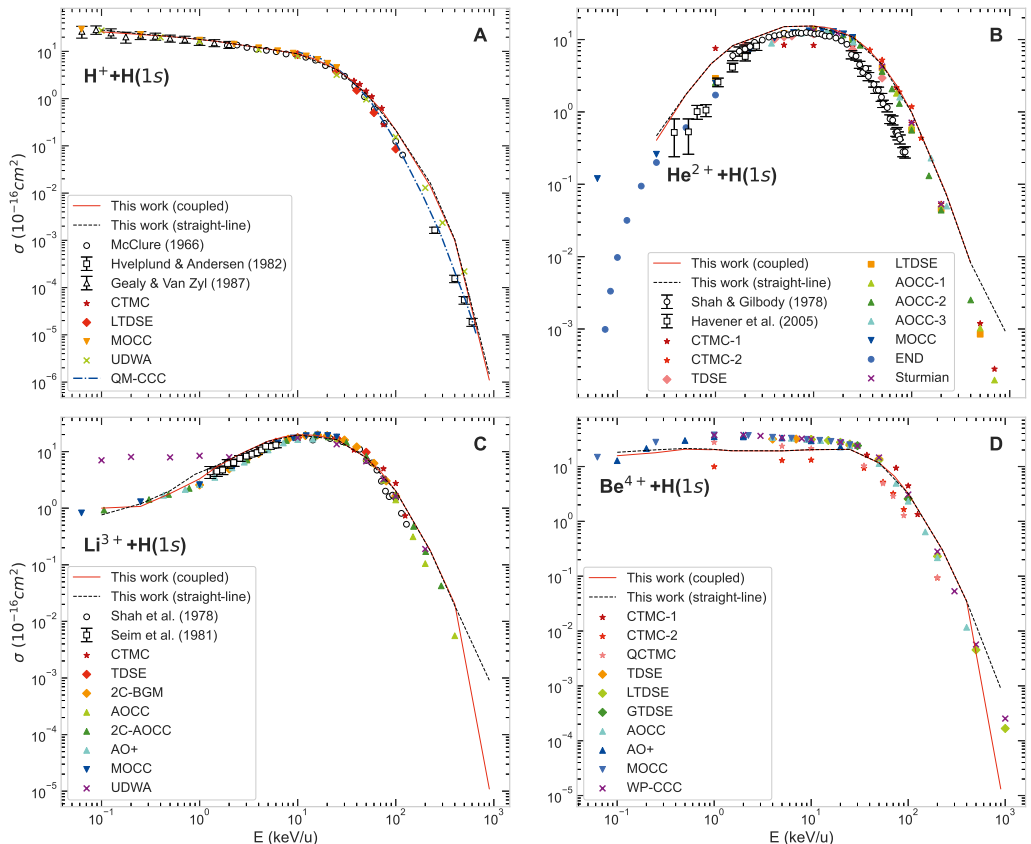


FIG. 4. Electron capture cross sections for (A) H^+ , (B) He^{2+} , (C) Li^{3+} , and (D) Be^{4+} colliding with $H(1s)$, as a function of the ion projectile energy. Our results from the electron-nuclei coupled trajectories are shown with a solid red line and the straight-line trajectories are shown with a dashed black line. In A, we compare with the experimental data from McClure [15], Hvelplund and Andersen [16], and Gealy and Van Zyl [17], as well as the theoretical results from CTMC [39], LTDSE [35], MOCC [54], UDWA [62], and QM-CCC [60]. In B, we compare with the experimental data from Shah and Gilbody [20] and Havener *et al.* [19], as well as the theoretical results from CTMC-1 [34], CTMC-2 [39], TDSE [31], LTDSE [34], AOCC-1 [34], AOCC-2 [50], AOCC-3 [53], MOCC [54], END [28], and Sturmian-pseudostate [56]. In C, we compare with the experimental data from Seim *et al.* [24] and Shah *et al.* [25], as well as the theoretical results from CTMC [39], TDSE [31], 2C-BGM [38], AOCC [50], AO+ [47], 2C-AOCC [52], MOCC [54], and UDWA [62]. In D, we compare with the theoretical results from CTMC-1 [39], CTMC-2 [42], QCTMC [42], TDSE [31], LTDSE [33], GTDSE [36], AOCC [50], AO+ [48], MOCC [54], and WP-CCC [59].

cal behavior in the energy region is consistent with the compared theoretical models.

C. Projectile energy loss

The energy required to induce the excitation and charge transfer processes comes from the kinetic energy

loss of the projectile. This is given by $\Delta E_T = K_f - K_i$, where K_f and K_i are the final and initial kinetic energy of the projectile. The kinetic energy is represented by $K = \mathbf{P}_2^2/2M_p$, where the final projectile momentum, $\mathbf{P}_2$, is given by Eq. (2). The projectile energy loss is divided into two components: the energy loss within the relative system when the target at rest, and the energy loss from the displacement of the target. Thus, the relative energy

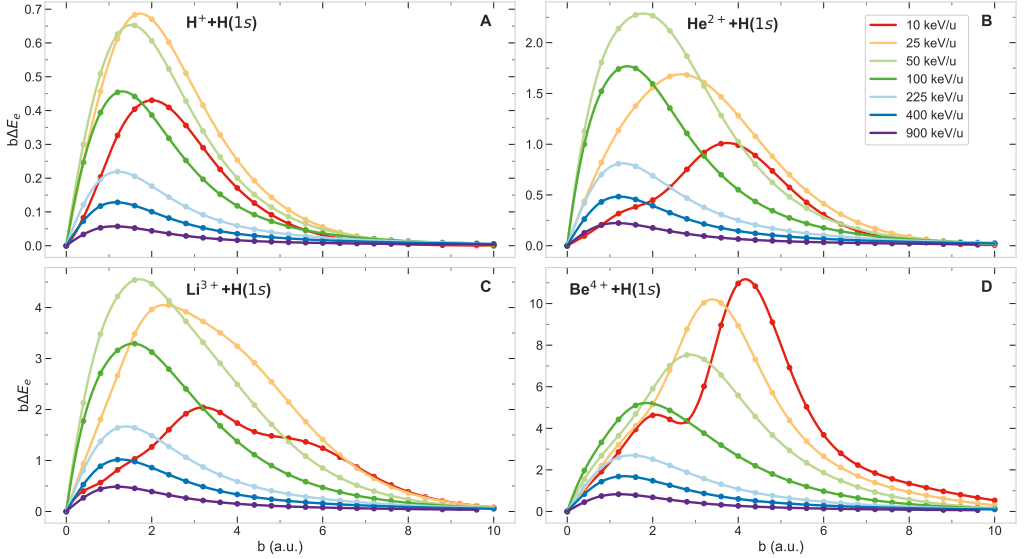


FIG. 5. Projectile electronic energy loss, weighted by the impact parameter, as a function of the impact parameter for collision energies of 10, 25, 50, 100, 225, 400, and 900 keV/u.. Results for (A) $H^+ + H(1s)$, (B) $He^{2+} + H(1s)$, (C) $Li^{3+} + H(1s)$, and (D) $Be^{4+} + H(1s)$ are shown. The data points correspond to our electron-nuclei coupled results of Eq. (2), and the solid lines represent cubic spline fits and serve only as a visual guide.

loss is $\Delta E_e = K_f^r - K_i^r$ with $K^r = p_r^2/2\mu_p$, where p_r is the relative momentum of a projectile with reduced mass $\mu = M_p M_t / (M_p + M_t)$. The energy loss in the relative system results in excitations or ionization of the target, which is referred to as the electronic energy loss.

In Fig. 5, we show the projectile electronic energy loss, weighted by the impact parameter, as a function of the initial projectile energy and impact parameter. By comparing with the results of Fig. 3, we observe a correlation between the charge exchange process and the projectile electronic energy loss. Specifically, the transfer of kinetic energy from the projectile to the target results in electronic loss within the target, which can be absorbed by the projectile.

However, the energy loss of the projectile also contributes to displacing the hydrogen atom, causing the nucleus of the target to recoil as a result of the momentum transferred by the projectile. As the hydrogen atom momentum is initially at rest, given by Eq. (2), the energy gained by the target as nuclear recoil is $\Delta E_n = K_t^f = \mathbf{P}_t^2/2M_t$. Therefore, the total energy loss is the sum of these two contributions, $\Delta E_T = \Delta E_e + \Delta E_n$. At high collision energies or large impact parameters, the target recoil is negligible. However, at low collision energies or small impact parameters, the target kinetic energy increases due to polarization effects induced by the projectile on the hydrogen target.

Once the electronic energy loss is determined, the electronic stopping cross section is given by

$$S_e(E_p) = 2\pi \int b \Delta E_e db, \quad (7)$$

where the nuclear stopping cross section, S_n , is given by replacing ΔE_e with ΔE_n . For the electronic energy loss in the straight-line trajectories, the constant projectile velocity results in $\Delta E_T = 0$. However, it is customary to subtract the electronic energy loss of the projectile from the electronic energy gain of the target. This approach is commonly used in TDDFT methods [64–67]. By calculating the final electronic energy of the target from the final wave function in the interval $-30 < z < 15$ a.u. and subtracting the initial ground state energy of the target, we isolate the straight-line contribution to the electronic energy loss.

In Fig. 6, we show the total (solid goldenrod line), electronic (dashed green line), and nuclear (dotted pink line) stopping cross sections, S_T , S_n , and S_e , respectively, for atomic hydrogen targets by incident projectile ions. Since the target is the same and only the projectile varies, the stopping cross sections are normalized by the square of the projectile charge.

We compare our electronic stopping cross sections with experimental data for H_2 targets by incident H [78–80], He [80–82], and Li [83–85] ions, compiled by Helmut Paul

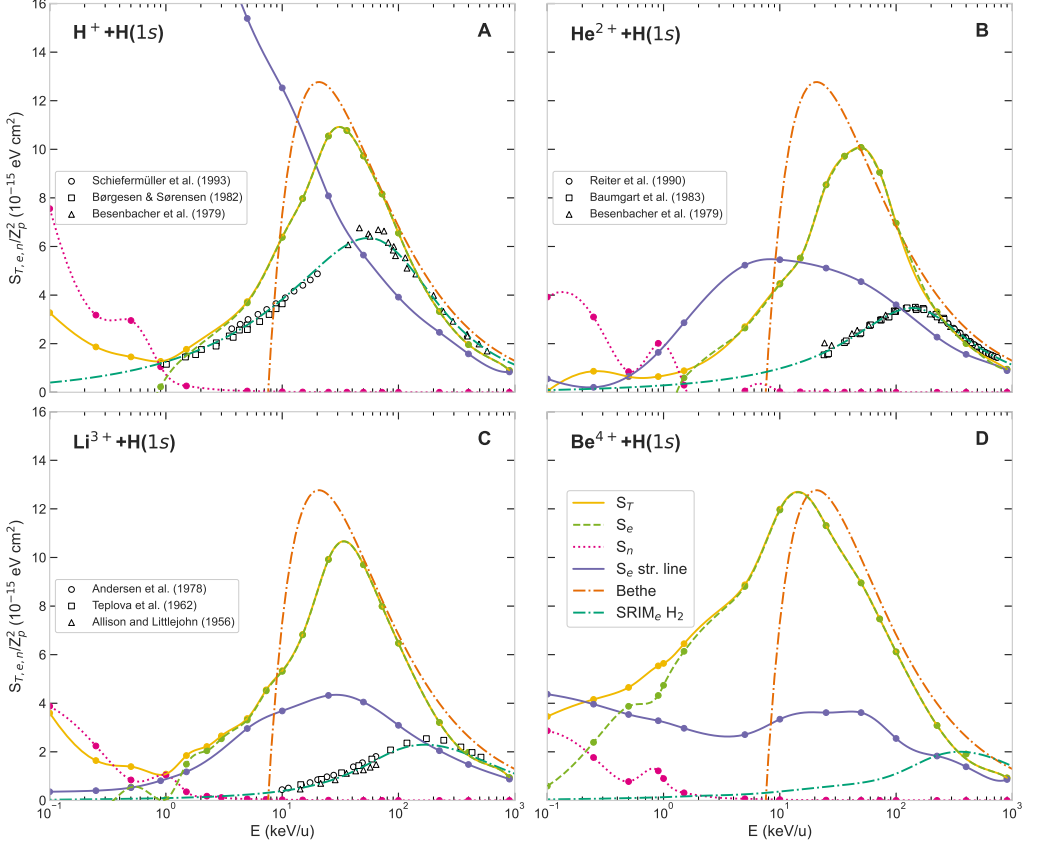


FIG. 6. Stopping cross sections for atomic hydrogen targets by incident (A) H^+ , (B) He^{2+} , (C) Li^{3+} , and (D) Be^{4+} ions, as a function of the projectile energy. The solid goldenrod line corresponds to the total stopping cross section, S_T , determined from the coupled trajectories of Eq. (2). The dashed green line is the electronic contribution, S_e , which is obtained by subtracting the nuclear energy loss from the total energy loss. The dotted pink line represents the nuclear stopping cross section, S_n . The solid purple line shows the electronic stopping cross section from the straight-line trajectories of Eq. (7), determined by the electronic energy gain from the target. The data points correspond to our results, fitted with a cubic spline as a guide. For the S_e line in B, the data is fitted with a piecewise cubic Hermite interpolation to preserve the curve shape. For comparison, we plot the Bethe analytical solution (Eq. (8)) [72–74], with a dash-dot dark-orange line. The dash-dot dark-green line represents the electronic stopping cross sections for H_2 targets by incident (A) H, (B) He, (C) Li, and (D) Be ions from SRIM [75]. Select experimental data, compiled in Helmut Paul’s database [76, 77], are also shown for H_2 targets by incident (A) H [78–80], (B) He [80–82], and (C) Li [83–85] ions. There is no available experimental data for Be ions.

at the IAEA [76, 77], and with SRIM [75] calculations also for H_2 targets (dash-dot dark-green line). For further comparison, we include Bethe’s analytical formula (dash-dot dark-orange line) from [72–74],

$$S_e = \frac{4\pi e^4}{mv^2} Z_p^2 Z_t \ln \left(\frac{2mv^2}{I_0} \right), \quad (8)$$

where I_0 is the target mean excitation energy. For atomic

hydrogen, $I_0 = 14.9$ eV is used, as reported by Bethe [73, 74] and by Mott and Massey [86]. Note that our results are limited to the bare ion case. Therefore, an accurate comparison with experimental data requires consideration of all other screened ion projectiles, as reported in Ref. [87], where the beam charge fraction is required.

For the coupled trajectories, the Bethe expression (Eq. (8)) matches our S_e results beyond the maxima. At very

TABLE I. Electron capture cross section, σ (10^{-16} cm²), total stopping cross section, S_T (10^{-15} eV cm²), and nuclear stopping cross section, S_n (10^{-15} eV cm²), for H^+ , He^{2+} , Li^{3+} , and Be^{4+} ions colliding with $H(1s)$ as a function of the projectile energy (E in keV/u) for the case of electron-nuclei coupled trajectories.

$E(\text{keV/u})$	H^+			He^{2+}			Li^{3+}			Be^{4+}		
	σ	S_T	S_n	σ	S_T	S_n	σ	S_T	S_n	σ	S_T	S_n
0.1	25.814	3.276	7.55739	2.332	0.196	15.6748	1.00315	32.356	34.8949	15.740981	55.2884	45.8768
0.25	22.782	1.866	3.17662	0.405	3.461	12.3975	1.07430	14.775	20.1815	17.860768	66.5140	28.2684
0.5	20.570	1.456	2.95391	1.739	2.558	3.3956	1.81666	12.531	7.5884	20.704486	74.4218	12.4336
0.9	18.251	1.272	1.04834	4.606	2.582	8.0594	3.79431	1.832	18.2927	20.266769	88.6153	19.4791
1.5	16.261	1.768	0.26016	8.226	3.543	1.1667	5.39327	16.631	3.1981	20.390969	90.2421	14.4162
5.0	11.201	3.730	0.05163	15.079	10.790	0.2158	15.28633	30.334	0.5616	19.317279	103.2013	5.0087
10.0	8.882	6.393	0.01998	15.395	17.914	0.1082	19.65515	48.067	0.2699	19.233950	141.9972	1.0964
15.0	6.851	7.978	0.01115	14.300	22.127	0.0694	19.51015	61.494	0.1794	20.261358	191.7968	0.5270
25.0	4.125	10.550	0.00656	10.912	34.174	0.0386	16.31505	89.340	0.1057	21.790332	191.4832	0.3505
36.0	2.381	10.774	0.00456	7.366	38.883	0.0250	11.87955	87.918	0.0705	20.541394	181.0882	0.2076
50.0	1.281	9.727	0.00321	4.514	40.316	0.0167	7.83414	87.351	0.0479	16.434467	152.1292	0.1408
72.2	0.552	8.162	0.00226	2.199	36.219	0.0107	4.15584	71.937	0.0305	11.682945	143.3466	0.0971
100.0	0.214	6.554	0.00164	0.986	27.841	0.0073	2.01806	58.256	0.0203	6.616649	119.5971	0.0632
225.0	0.014	3.325	0.00073	0.074	13.237	0.0030	0.17858	28.884	0.0075	3.227359	97.8711	0.0425
400.0	0.001	1.963	0.00044	0.008	8.031	0.0018	0.02020	17.814	0.0041	0.301962	49.3949	0.0153
900.0	1.1e-6	0.897	0.00018	0.003	3.791	0.0007	0.00001	8.455	0.0016	0.034990	30.5431	0.0078

high collision energies, both the Bethe expression and the experimental data are in good agreement. However, the S_e results deviate from the Bethe expression for collision energies below the maxima, where the charge exchange process becomes significant (see Fig. 4). For all projectiles, the electronic stopping cross section reaches a minimum near $E_p \approx 0.1$ keV/u and generally peaks around $E_p \approx 50$ keV/u. In the projectile energy range of 0.1 to ~ 1 keV/u, nuclear target recoil becomes the dominant channel contributing to the total stopping cross section.

For the straight-line results (solid purple line), the best agreement with the coupled trajectories, Bethe, and experimental data occurs only at very high collision energies. In the remainder of the energy range, the electronic stopping cross sections derived from the straight-line approximations differ significantly from those obtained from the coupled trajectories. For the H^+ projectile, the straight-line results reach a maximum (beyond the scale of our figure) at a much lower collision energy than the coupled results. This would imply that, at low energies, the target gains more energy than is physically available from the projectile, which violates energy conservation. For He^{2+} , Li^{3+} , and Be^{4+} projectiles, the straight-line electronic stopping cross sections are smaller due to the more pronounced charge transfer process, which reduces the probability of finding the electron in the target (see Fig. 2). This is a consequence of the higher projectile charge. Additionally, there are still regions where S_e exceeds S_T , which is unphysical, particularly at low collision energies. Therefore, it is clear that there is a strong dependence on trajectory for energy and

momentum transfer processes in these collisions.

In Table I, we provide the numerical results from the electron-nuclei coupled trajectories for the electron capture, total, and nuclear cross sections for reference purposes.

IV. CONCLUSIONS

In this work, our goal was to determine whether trajectory effects influence inelastic processes such as charge exchange and energy loss in collisions of bare ion projectiles with atomic hydrogen. We used a lattice representation to numerically solve the time-dependent Schrödinger equation with a coupled electron-nuclear dynamics approach as well as a straight-line trajectory approximation for the study. This method provided excellent results for electron capture cross sections, which agree well with experimental and theoretical data. From this, we determined that the charge exchange process is unaffected by the trajectory. However, for energy loss, the straight-line trajectories lead to the projectile inducing a higher energy gain for the target, which is inconsistent with physical principles. Thus, this work asserts that a proper description of the electron-nuclear dynamics is necessary to account for the energy and momentum transfer processes in collisions of bare ions with atomic hydrogen when compared with simpler straight-line trajectory calculations.

We hope our results will encourage further interest from the experimental community to investigate stopping cross sections at low collision energies. Addition-

ally, we intend for this work to be used as a benchmark for other theoretical methods, including classical, semi-classical, and perturbative approaches, particularly in the low energy range where agreement has been difficult to establish. Building on these findings, we aim to apply this method to study collisions involving more complex, multi-electronic systems. Specifically, this method can be applied to investigate charge exchange cross sections of negatively charged ions originating from a positive charge state. This is particularly relevant for low-yield radioactive species where producing ions in the negative charge state through electron capture reactions is the most vi-

able approach.

ACKNOWLEDGMENTS

R.C.T. and M.N. acknowledge support from grants UNAM-DGAPA-PAPIIT IN-109-623 and LANCAD-UNAM-DGTIC-228, as well as to the University of Gothenburg for providing the conditions for a visiting stay. D.H. and M.N. acknowledge support from the Swedish Research Council (2020-03505). This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 861198.

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Paper V

Isotope shift in the stable tin anion with bound-bound electric dipole forbidden transition

M. Nichols,^{1,*} C. B. Adiels,¹ J. Alnis,² U. Bērziņš,² A. Bondarev,³ A. Ciniņš,² B. R. Escobedo,¹ N. D. Gibson,⁴ A. James,¹ D. Leimbach,¹ D. Lu,¹ P. Martini,⁵ J. E. Navarro Navarrete,⁵ D. Pérez Guerrero,¹ R. Poulou, ⁵ H. T. Schmidt,⁵ J. Snikeris,¹ C. W. Walter,⁴ H. T. Zettergren,⁵ and D. Hanstorp¹

¹*Department of Physics, University of Gothenburg, SE-412 96 Gothenburg, Sweden*

²*Institute of Atomic Physics and Spectroscopy, University of Latvia, LV-1586 Riga, Latvia*

³*Helmholtz Institute Jena, 07734 Jena, Germany*

⁴*Department of Physics and Astronomy, Denison University, Granville, OH 43023, USA*

⁵*Department of Physics, Stockholm University, 10691 Stockholm, Sweden*

(Dated: April 15, 2025)

The isotope shift of an electric-dipole forbidden transition in the tin anion (Sn^-) has been measured for the even-mass naturally occurring isotopes. Negative ions are uniquely sensitive to electron correlation, making the specific mass shift, which directly reflects these effects, a powerful probe for many-body atomic structure. Negative ions commonly lack bound excited states, and when such states do exist, they typically share the same parity as the ground state, rendering them optically forbidden. Using a newly developed laser spectroscopy technique at the cryogenic ion-beam storage ring DESIREE, we have successfully probed the electric-dipole forbidden transition $\text{Sn}^- (^4S_{3/2}) \rightarrow \text{Sn}^- (^2D_{5/2})$. This method enables high-precision determination of transition frequencies, lifetimes of the bound excited 2D_J states, and provides sufficient spectral resolution to study isotope shifts. From these measurements of the even-mass isotopes, we extract mass and field shift factors, which are compared with calculations using a combined configuration interaction and all-order method. Our results establish a new frontier for precision studies in anions with optically forbidden transitions and validate state-of-the-art atomic theory, enabling deeper insight into atomic and nuclear structure.

I. INTRODUCTION

Isotope shifts (IS) in atomic spectra offer valuable insights into the interplay between nuclear and atomic structure, containing information about the size of the nuclear charge radius as well as electron-nucleus and electron-electron interactions [1–3]. Advances in precision laser spectroscopy on atomic and molecular systems have enabled detailed studies of nuclear charge radii [4–7], magnetic moments [8–10], and electron-electron correlation [11–14]. These studies serve as benchmarks for many-body theoretical models, which are crucial for relating IS measurements to fundamental nuclear and atomic properties [15–18]. With the combined efforts of precise experiments and accurate theory, a level of sensitivity has been achieved that facilitates sub-atomic particle studies, sparking interest in searches for physics beyond the Standard Model [19–24].

Among the elements suitable for detailed IS measurements, tin (Sn) has been a subject of significant interest due to the neutron shell closures at $N = 50$ and $N = 82$. It is also the heaviest element to have two isotopes with both neutron and proton shell closures, ^{100}Sn and ^{132}Sn , known as doubly magic nuclei. Notably, ^{100}Sn is the heaviest known bound nucleus with $N = Z$, making it ideal for testing nuclear structure models and performing precision spectroscopy near the proton drip line [25]. In

addition, Sn has ten stable isotopes from ^{112}Sn to ^{124}Sn , which is the most of any element. This provides a unique platform for systematically studying isotope shifts across a wide range of proton-to-neutron ratios.

The structure of the Sn anion is particularly interesting as it has a bound excited 2D_J state, which was found to be the case for all negative ions of the carbon group [26]. Excited electronic states are uncommon for negative ions because the valence electron is bound by a shallow dipole potential and therefore experiences very weak nuclear attraction. As a result, the behavior of the valence electron is strongly influenced by electron-electron correlation, which is enhanced by inner-electron screening effects [27, 28].

These correlation effects are central to IS studies in anions, which have most often been measured across electron affinity (EA) values [12, 29, 30]. While this remains the dominant approach, one study utilized a bound-bound transition within the negative ion to measure the IS in Os^- [13]. Although rare, there are five known negative ions (Os^- [31], Ce^- [32], La^- [33], Th^- [34], and U^- [35]) that have bound states of opposite parity, rendering them optically accessible via electric dipole ($E1$) transitions. These systems are particularly promising for laser cooling applications, especially in the context of sympathetic cooling of antiprotons [36].

However, many atomic negative ions possess excited states that are $E1$ -forbidden and instead decay via higher-order magnetic dipole ($M1$) and electric quadrupole ($E2$) transitions. While IS measurements using forbidden transitions have been performed in neutral

* miranda.nichols@physics.gu.se

atoms [37, 38] and positive ions [39, 40], such a systematic study in an anionic system has yet to be conducted. However, some $M1$ and $E2$ transitions within negative ions have been observed using multiphoton schemes [26, 41, 42]. With most negative ion laser spectroscopy studies limited to bound-continuum excitations, precision is compromised mainly due to large background contributions from all excited states below the photodetachment continuum. It is clear that it would be beneficial to develop a method that suppresses this background, allowing for the resolution of effects that are otherwise too small.

The recent developments of cryogenic electrostatic storage rings have allowed for significant improvements in vacuum conditions and ultracold environments [43–45]. These developments have dramatically extended the storage times of atomic and molecular ions, paving the way for high-precision studies of negative ions [46]. Building on this progress, we introduce a novel approach for IS measurements by leveraging an optically $E1$ forbidden bound-bound transition in the Sn anion, conducted at the Double ElectroStatic Ion-Ring ExpEriment (DESIREE) [43].

In this work, we present IS measurements of the $\text{Sn}^- (^4S_{3/2}) \rightarrow \text{Sn}^- (^2D_{5/2})$ transition for the stable Sn isotopes. We report the transition frequencies for the even-mass isotopes, extracting both mass and field shift factors. These results are compared with theoretical calculations using a combined configuration interaction (CI) and all-order approach, which treats electron correlation to all orders [47]. Our findings not only validate this theoretical approach but also establish methodology and introduce a new experimental frontier in probing bound excited states in negative ions that have the same parity as the ground state. With newfound access to forbidden anionic transitions, our method allows for deeper insights into electron correlation and facilitates broader investigations of fundamental atomic and nuclear structure.

II. EXPERIMENTAL METHODS

A. Setup

The present method builds on the high-precision electron affinity (EA) measurement technique developed in [46], and was implemented at the DESIREE facility located at Stockholm University. The facility consists of two cryogenic ion-beam storage rings, an asymmetric ring with two-fold quadrupole doublet symmetry and a symmetric ring with four-fold quadrupole doublet symmetry. The entire apparatus is maintained at a temperature of 13 K. For this experiment, we used only the symmetric ring, which contains four 10° and two 160° electrostatic deflectors and four quadrupole doublets, as seen in Fig. 1.

The negative ions were created using a National Electrostatics Corp. cesium sputter ion source (SNICS II)

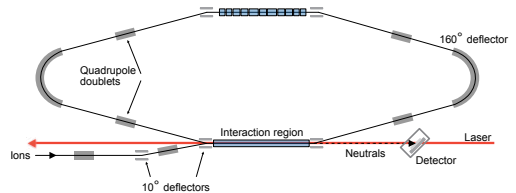


FIG. 1. Schematic of DESIREE. Only the symmetric ring is shown, which was exclusively used in the present work. For the isotope shift measurements, the OPO and diode laser were aligned collinearly and anti-collinearly, respectively.

from a cathode of SnO_2 . The extracted ions were accelerated to a kinetic energy of 30 keV, mass-selected by a 90° double-focusing bending magnet, and then injected into the storage ring. To ensure the entire ring fills up with ions in a single injection, the beam was bunched to a length of approximately $38 \mu\text{s}$.

The injected ion beam, with a current of $\sim 1 \text{ nA}$, was then collinearly overlapped with photons at 1200 nm produced with an optical parametric oscillator (OPO). This served to deplete the electronic population in the 2D_J excited states. Simultaneously, a diode laser was aligned in the anti-collinear geometry and continuously illuminated the ions, implementing a two-step excitation scheme. It first drives the resonant transition from the ground state in the negative ion to the $^2D_{5/2}$ state, and subsequently photodetaches the excited electron, serving as a probe for the resonant transition. This process is shown in Fig. 2.

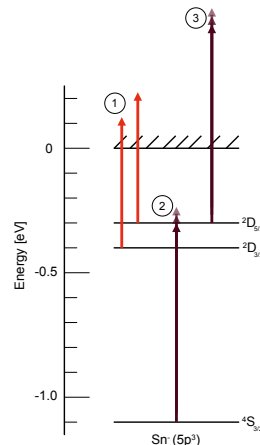


FIG. 2. Energy level diagram of Sn^- and the applied laser transitions. The circled numbers represent the excitation steps: 1 corresponds to the excited state depletion, 2 is the selective state repopulation, and 3 is the final detachment into the continuum.

The depletion process occurred for the first 20 seconds post-injection. Five seconds after the OPO is blocked ($t=25$ s), the diode laser started a scan. Each diode laser scan was performed once per ion injection cycle, typically lasting about 90 seconds depending on the isotope. A stepper motor controlled the diode laser scan speed, set at 0.002 nm/s. This timing sequence is illustrated in Fig. 3.

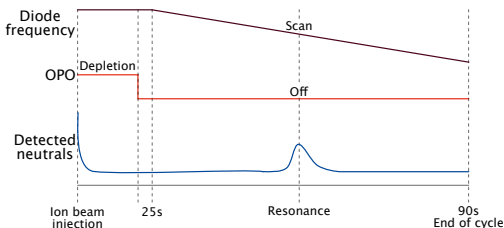


FIG. 3. Timing scheme for the measurement. After ion injection, the OPO depletes the 2D_J states for the first 20 s. At 25 s, the frequency of the diode is scanned, selectively repopulating and probing the $^2D_{5/2}$ state, showing a resonance by detecting the photodetached neutral atoms.

The resulting neutral atoms were then measured with a resistive anode encoder, which consists of a graphene-coated quartz plate that produces secondary electrons upon neutral Sn impact. The electronic signals were amplified and detected by a microchannel plate (MCP) stack [48].

B. Lasers and calibration

The lasers used in this experiment were a Toptica Photonics CTL 1550 continuous-wave diode laser and an EKSPLA NT240 integrated diode-pumped Nd:YAG tunable laser and OPO with a repetition rate of 1 kHz. To measure the frequency of the diode laser, an HP/Keysight 86120C wavelength meter was used, with an absolute accuracy of ± 2 ppm and a fixed resolution of 100 MHz.

The calibration of the wavelength meter was done using absorption spectroscopy of the acetylene (C_2H_2) spectrum in the region around 1535 nm. A reference cell with a nominal pressure of 50 Torr was used. In this region, there are three well-known transitions that were used. The calibration was performed on an average of every four hours.

C. Measurements and data analysis

The experimental procedure enabled us to measure the excitation energy of the $^2D_{5/2}$ bound excited state, lifetimes of the $^2D_{3/2,5/2}$ states, and isotope shift (IS) values across the chain of stable isotopes.

The excitation energy of the $^2D_{5/2}$ state in $^{120}Sn^-$ was determined from 40 independent measurements, each obtained from a Voigt fit of the resonance profile. A weighted average was calculated using the inverse square of the individual fitting uncertainties as weights. The given uncertainty is purely statistical, obtained by combining the weighted fit error and the standard deviation of the mean in quadrature.

For determining the lifetimes of the 2D_J states, we leveraged the fact that the longer-lived $^2D_{5/2}$ state can be selectively isolated by laser-driven repopulation or by waiting 55 seconds for the population in the shorter-lived $^2D_{3/2}$ state to be sufficiently small. This approach is advantageous, as fitting a single exponential decay function is significantly more robust than fitting a two-component combined signal. Once the lifetime of one state is known, the parameters can be fixed in subsequent fitting procedures to extract the lifetime of the other state more precisely. Measurements of both the isolated $^2D_{5/2}$ state and contributions from both states were performed with different laser powers, and the resulting lifetimes were linearly extrapolated to zero power to account for power-dependent effects and obtain the true lifetimes of the states.

The absolute frequency of the $Sn^-(^4S_{3/2}) \rightarrow Sn^-(^2D_{5/2})$ transition was measured for all stable even-mass isotopes. The most abundant isotope, ^{120}Sn ($\sim 33\%$ natural abundance), was used as the reference in determining the IS. The IS frequencies were calculated relative to ^{120}Sn , following $\delta\nu^{A,A'} = \nu^A - \nu^{A'}$. A total of ten sets of data were collected, with each set containing an average of one resonant transition frequency per isotope for $^{116}-^{124}Sn$. The reference isotope, ^{120}Sn , was measured an average of three times per set to reduce statistical uncertainty. The shift $\delta\nu^{A,120} = \nu^A - \nu^{120}$ was extracted individually for each isotope, where ν^{120} was typically taken as the average of the two reference frequencies if measurements were made both before and after. The IS values were then averaged across all data sets, and the associated uncertainties were calculated as the standard error of the mean.

Due to their low natural abundances, ^{112}Sn and ^{114}Sn (0.97% and 0.66%, respectively) were each measured twice over many hours, as more time was required to accumulate sufficient statistics.

After the IS values were obtained, King-plot analysis was used to extract mass and field shift factors. King-plot analysis is commonly used to relate isotope shifts between two electron transitions of the same element. While *ab initio* calculations are required to extract M_{SMS} and F due to their sensitivity to electron correlation, increasing the number of electrons in a system complicates these calculations. Some computational approaches have begun to address this [12, 17, 47]. In the case of Sn^- , which has five correlating electrons in its open-shell structure, King-plot analysis provides a practical alternative for extracting these parameters. The validity of this approach extends to complex molecular systems [49] and across dif-

ferent charge states [50] where the linearity of the King plot still holds, allowing for mean-square charge radii to be extracted without the need for detailed calculations.

III. THEORETICAL METHODS

A. Electronic structure calculation

Electronic structure calculations are performed using an approach that combines the configuration interaction (CI) method with the linearized coupled cluster single-double (all-order) method [47]. The neutral atom Sn I and the anion Sn^- are treated as systems with the same $[\text{Kr}]4d^{10}$ frozen core and four and five outer valence electrons, respectively. CI is used to describe the valence electrons, while the coupled-cluster method accounts for the core-valence correlations. This approach has been successfully applied to studies of transition energies and rates in negative ions [42, 51, 52] and was recently used to calculate multipole transition rates in Sn II [53]. Further details on the methodology and numerical implementation can be found in Ref. [54].

To construct the configuration space for the Sn^- calculation, we first use single (S) and double (D) excitations from the $5s^25p^3$ and $5s^25p^26p$ reference configurations to the $20spdfg$ basis set (i.e., all orbitals up to $n = 20$ are included for the $spdfg$ partial waves). Expanding the basis to $25spdfg$ leads to negligible changes. However, we find a substantial contribution of the h partial waves when extending the basis set to $20spdfgh$. Next, we iteratively incorporate additional configurations that include the most important triple and quadruple excitations from $5s^25p^3$. At this stage, we observe a considerable impact from configurations where one or two electrons are excited from the $5s^2$ shell. This explains why the initial attempt to treat $5s^2$ as a core shell resulted in poorer agreement with the experimental results and justifies the five-valence-electron treatment of Sn^- . The leading quantum electrodynamics (QED) corrections are taken into account following [55]. The CI+MBPT approach [56] is used to estimate the contribution of higher-order (HO) core-valence corrections, defined as the difference between the CI+all-order and CI+MBPT results.

B. Transition rates and lifetimes

We calculate the magnetic dipole ($M1$) and electric quadrupole ($E2$) reduced matrix elements using the obtained many-electron wave functions and use the experimental values of the transition energies to compute the transition rates listed in Table II.

C. Isotope shifts

The total change in the atomic frequency of a transition is parameterized in the standard way as a sum of the mass- and field-shift contributions,

$$\Delta\nu^{A,A'} = \nu^{A'} - \nu^A = k_{\text{MS}} \frac{m_{A'} - m_A}{m_{A'} m_A} + F \delta \langle r^2 \rangle^{A,A'} \quad (1)$$

For the calculation of isotope shift factors k_{MS} and F , we use the finite-field method. We add a perturbation H_{IS} to the initial many-electron Hamiltonian H with an arbitrary coefficient λ : $H \rightarrow H_\lambda = H + \lambda H_{\text{IS}}$. According to the Hellmann-Feynman theorem,

$$\langle \Psi | H_{\text{IS}} | \Psi \rangle = \left. \frac{dE_\lambda}{d\lambda} \right|_{\lambda=0}. \quad (2)$$

The derivative is then calculated numerically using the 5-point formula. More details can be found in Ref. [54].

The mass shift is calculated using the relativistic recoil Hamiltonian [57] as a perturbation.

$$H_{\text{MS}}^{\text{rel}} = \frac{1}{2M} \sum_{i,j} \left[\mathbf{p}_i \cdot \mathbf{p}_j - \frac{\alpha Z}{r_i} \left(\boldsymbol{\alpha}_i + \frac{(\boldsymbol{\alpha}_i \cdot \mathbf{r}_i) \mathbf{r}_i}{r_i^2} \right) \cdot \mathbf{p}_j \right]. \quad (3)$$

It can be further separated into normal mass shift (NMS) and specific mass shift (SMS). In the Hamiltonian (3) the former is given by terms with $i = j$ and the latter by terms with $i \neq j$.

IV. RESULTS

A. Excitation energies

The excitation energy for $^4S_{3/2} \rightarrow ^2D_{5/2}$ transition in $^{120}\text{Sn}^-$ was measured to be $6512.4183(2) \text{ cm}^{-1}$, where the uncertainty corresponds only to the statistical component. Fig. 4 shows a typical spectrum for $^{120}\text{Sn}^-$. When comparing with the work of Scheer *et al.* [26], we find that our measured resonance is approximately 50 times narrower, achieving an average linewidth of 200 MHz. This improvement in spectral resolution is due to significantly reduced Doppler and pressure broadening, enabled by the cryogenic environment of DESIREE, extended interaction times, and a reduced laser linewidth by three orders of magnitude.

We present the calculated excitation energies of the Sn^- $5s^25p^3 \ ^2D_{3/2,5/2}$ states relative to the $5s^25p^3 \ ^4S_{3/2}$ ground state in Table I. The $5s^25p^3 \ ^2P_{1/2,3/2}$ states are found to be unbound, consistent with previous studies [26, 58, 59]. The theoretical predictions and experimental measurements show excellent agreement, with less than 2% relative difference.

The HO core-valence and QED corrections for both states are small compared to the contributions from additional configurations beyond the SD excitations, particularly those that include triple and quadruple excitations

TABLE I. Calculated excitation energies (in cm^{-1}) of Sn^- bound states relative to the $5s^25p^3\ ^4S_{3/2}$ ground state. The theoretical results are compared with the measured $^2D_{5/2}$ value from this work and the values from Ref. [26]. Further, the relative differences between final and experimental values are presented.

Level	20spdfg	+h	QED	HO	Extra conf.	Final	Exp.	Ref. [26]	Rel. diff.
$5s^25p^3\ ^2D_{3/2}$	6241	-30	2	24	-315	5898	-	5762.50(10)	2.4%
$5s^25p^3\ ^2D_{5/2}$	6931	-30	4	4	-278	6626	6512.4183(2)	6512.37(10)	1.7%

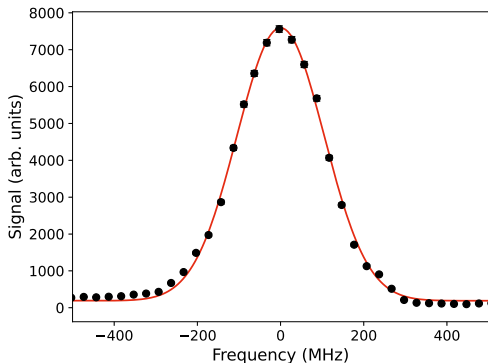


FIG. 4. Example spectral resonance of the bound-bound $^4S_{3/2} \rightarrow ^2D_{5/2}$ transition in $^{120}\text{Sn}^-$. The data is fit with a Voigt profile (solid red line) and centered at 0 MHz. Error bars, which are barely visible, represent square root of the signal.

from the ground one. Increasing the parameter l_{max} , which defines the maximum orbital angular momentum of the partial waves included in the all-order part, from 5 to 6, results in a 2-3 cm^{-1} shift in the energy levels. This suggests that the observed 2% discrepancy with the experiment originates from unaccounted valence-valence correlation in CI, while the core-valence correlations have converged.

The calculated fine-structure splitting of $^2D_{5/2} - ^2D_{3/2}$ is 728 cm^{-1} , showing closer agreement with the experimental value of $749.95(15)\text{ cm}^{-1}$ than the individual energy levels. This suggests that correlations for the ground state $^4S_{3/2}$ are more accurately accounted for than those for the $^2D_{3/2,5/2}$ states. The agreement between the calculated fine structure of the $5s^25p^2$ ground configuration in Sn I and the experimental values is significantly better, with discrepancies of only 30 and 10 cm^{-1} for the 3P_1 and 3P_2 levels, respectively. This highlights the strong configuration mixing in the negative ion.

B. Transition rates and lifetimes

Using calculated magnetic dipole ($M1$) and electric quadrupole ($E2$) transition rates, the lifetimes of the

$^2D_{3/2}$ and $^2D_{5/2}$ states were determined to be $8.6(3)$ and $67.6(14)\text{ s}$, respectively. The uncertainties are derived from the differences in the reduced matrix elements between the CI+all-order and CI+MBPT calculations. The calculated $M1$ and $E2$ transition rates are summarized in Table II. For most transitions, these values agree well with the revised relativistic CI results of O'Malley and Beck [59], as presented in Ref. [26]. The only exception is the rate for the $M1\ ^2D_{3/2} \rightarrow ^4S_{3/2}$ transition, which is about 40% larger than the result reported in Ref. [26]. The rate for the $E2\ ^2D_{5/2} \rightarrow ^2D_{3/2}$ transition is negligible and is therefore omitted. The decay of the $^2D_{3/2}$ state is dominated by the $M1$ transition to the $^4S_{3/2}$ ground state, while for the $^2D_{5/2}$ state, both $M1$ and $E2$ channels to the ground state, as well as the $M1$ channel to the low-lying $^2D_{3/2}$ state, play significant roles.

TABLE II. Rates for transitions between the ground-configuration $5p^3$ states in Sn^- in comparison with the results of Ref. [26].

Transition	Type	Rate (s^{-1})	Ref. [26]
$^2D_{3/2} \rightarrow ^4S_{3/2}$	M1	0.1127(41)	0.0791
$^2D_{5/2} \rightarrow ^4S_{3/2}$	M1	0.00462(13)	0.00431
$^2D_{5/2} \rightarrow ^2D_{3/2}$	M1	0.00407(1)	
$^2D_{3/2} \rightarrow ^4S_{3/2}$	E2	0.00315(17)	0.00349
$^2D_{5/2} \rightarrow ^4S_{3/2}$	E2	0.00610(28)	0.00591

TABLE III. Total theoretical decay rates and lifetimes of the $\text{Sn}^-\ ^2D_J$ states, compared with experimental values.

Transition	$\Gamma_{\text{tot}}\ (\text{s}^{-1})$	$\tau\ (\text{s})$	$\tau_{\text{exp}}\ (\text{s})$
$^2D_{3/2} \rightarrow ^4S_{3/2}$	0.1158(44)	8.6(3)	12(4)
$^2D_{5/2} \rightarrow ^4S_{3/2}$	0.01479(31)	67.6(14)	64(4)

The lifetimes of the $^2D_{3/2,5/2}$ states were experimentally determined to be $12(4)$ and $64(4)\text{ s}$, respectively. An example measurement and exponential decay fit is given in Fig 5, which measures only the lifetime of the longer-lived $^2D_{5/2}$ state in Sn^- .

The measured and calculated values are compared in Table III. The slightly shorter experimental lifetime observed for the $^2D_{5/2}$ state could potentially indicate additional higher-order decay channels or systematic uncertainties not yet fully accounted for in the experimental data analysis. Overall, the comparison between experiment and theory indicates a strong consistency within error bars. These results validate the theoretical models

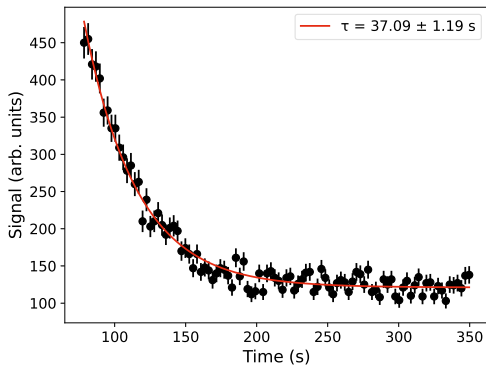


FIG. 5. Lifetime measurement and exponential decay fit of the longer-lived ${}^2D_{5/2}$ state in Sn^- .

employed, with minor discrepancies highlighting areas for potential improvement and more careful analysis of the experimental data.

C. Isotope shifts

The average isotope shifts are presented in Fig. 6. The data exhibit a linear trend with increasing mass number. However, the ${}^{112}\text{Sn}$ data point deviates noticeably from this trend. To quantify this, linear fits were performed with and without mass 112, and the goodness of fit was assessed using reduced χ^2 and R^2 statistics. When all isotopes were included in the fit, the reduced χ^2 and R^2 were 21.74 and 0.9453, respectively, indicating poor agreement with the linear model given the uncertainties. Excluding mass 112 in the fit yields 0.18 and 0.9993 for the reduced χ^2 and R^2 , respectively. This suggests that the results of ${}^{112}\text{Sn}$ significantly deviate from the linear trend seen in the rest of the data and motivate its exclusion from further analysis to extract the mass and field shift factors. A summary of the data is presented in Table IV.

Isotope	$\delta\nu^{A,120}$ (MHz)
112	-200(4)
114	-105(7)
116	-70(6)
118	-37(5)
120	0
122	34(4)
124	64(6)

TABLE IV. Isotope shifts for the ${}^4S_{3/2} \rightarrow {}^2D_{5/2}$ transition in Sn^- .

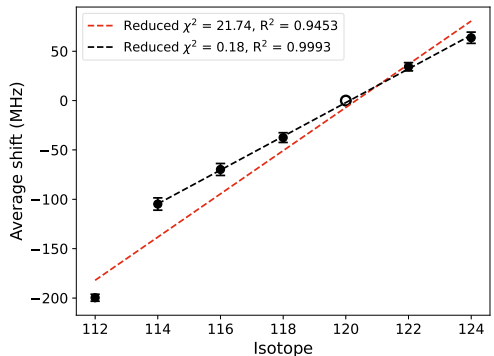


FIG. 6. Measured isotope shifts $\delta\nu^{A,120} = \nu^A - \nu^{120}$ for the ${}^4S_{3/2} \rightarrow {}^2D_{5/2}$ transition in Sn^- . Error bars represent the standard error of the mean. The reference isotope ${}^{120}\text{Sn}$ is shown as a hollow circle for context. Linear fits are shown including (dashed red line) and excluding (dashed blue line) ${}^{112}\text{Sn}$ data point, with the goodness of fit evaluated using reduced χ^2 and R^2 statistics. Average shift values are summarized in Table IV.

V. DISCUSSION

The experimental data presented here constitutes the first measurement of isotope shifts across an extensive chain of stable isotopes in a negative ion. These results enable a detailed analysis of the sensitivity of anions to changes in nuclear charge radii and specific mass shifts. To investigate the feasibility of such a procedure, we perform a King-plot analysis based on the linear dependence of the IS on nuclear mass and charge radius, as described in Eq. 1. By normalizing both sides of the equation by the reduced mass coefficient $\mu^{A,A'} = \frac{m_A - m_{A'}}{m_A m_{A'}}$, we obtain

$$\delta\nu_i^{A,A'} (\mu^{A,A'})^{-1} = k + F \delta \langle r^2 \rangle^{A,A'} (\mu^{A,A'})^{-1}. \quad (4)$$

This transformation removes the dominant mass dependence and allows for a more direct extraction of the constants. To compare the anionic transition measured in this work with well-known electronic transitions in neutral Sn, as reported in Ref. [60], we construct King plots to relate the isotope shifts of two different transitions across the isotope chain. Since the transitions share the same nuclear configurations for a given isotope, this eliminates the dependence on the nuclear charge radii. The resulting linear relationship between the two transitions can be described as

$$\delta\nu_i^{A,A'} (\mu^{A,A'})^{-1} = a \cdot \delta\nu_j^{A,A'} (\mu^{A,A'})^{-1} + b, \quad (5)$$

where

$$a = \frac{F_i}{F_j}, \quad (6)$$

$$b = k_i - a \cdot k_j. \quad (7)$$

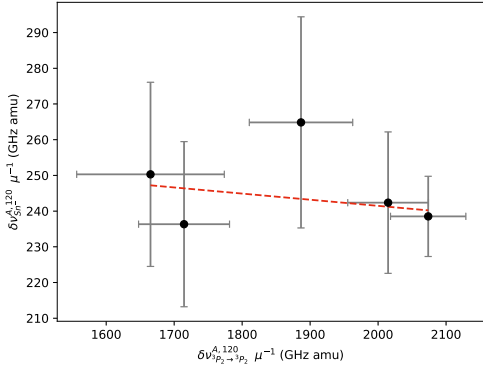


FIG. 7. Example King plot comparing the measured anionic transition with the $^3P_2 \rightarrow ^3P_2$ transition in neutral Sn.

An example King plot is shown in Fig. 7, where our transition in the anion is plotted against the $5s^2 5p^2 \ ^3P_2 \rightarrow 5s^2 5p 6s^3 \ ^3P_2$ transition in neutral Sn. We are encouraged to find that, despite some scatter in the data, an orthogonal distance regression fit can be drawn through all points within their error bars. This shows that the quality of the data supports a reliable preliminary analysis of the system using the initial King plot results.

The calculated isotope shift factors for the $^4S_{3/2} \rightarrow ^2D_{3/2,5/2}$ transitions are given in Table V. For transitions within the same $5p^3$ ground configuration, the FS factors are, as expected, small. In particular, they are an order of magnitude smaller than those for the $5p^2 \rightarrow 5p 6s$ transitions in neutral Sn [60]. We estimate the uncertainties of the FS factors as 20%, primarily due to the numerical uncertainty in the calculation of the derivative in Eq. (2).

The calculated NMS factors for both transitions are close to the value obtained using the approximation $k_{\text{NMS}} \approx m_e \nu$, where m_e is the electron mass and ν is the transition frequency. This approximation yields values of 98.3 and 107.5 GHz u for the $^4S_{3/2} \rightarrow ^2D_{3/2}$ and $^4S_{3/2} \rightarrow ^2D_{5/2}$ transitions, respectively. The absolute value of the SMS factor for the $^4S_{3/2} \rightarrow ^2D_{3/2}$ transition is approximately 4 times larger than for the $^4S_{3/2} \rightarrow ^2D_{5/2}$ transition, resulting in the total MS factors having opposite signs for these transitions. Consequently, for the $^4S_{3/2} \rightarrow ^2D_{3/2}$ transition, the FS and MS contributions to the total IS partially cancel out. In contrast, for the $^4S_{3/2} \rightarrow ^2D_{5/2}$ transition, FS and MS contributions have the same sign. We estimate the uncertainties of the MS factors to be 10%.

The extracted value of $F = -0.03(2)$ GHz/fm², obtained from Fig. 7, is an order of magnitude smaller than the theoretical value of 0.24 GHz/fm². This could suggest that electron correlation effects in Sn⁻ reduce the sensitivity to changes in the nuclear charge radius.

However, further analysis is required to confirm this interpretation. Here, the mass shift is the dominant contribution to the field shift, which is to be expected, especially in negative ions. Sign differences between the theoretical and experimental values are a result of different conventions. Uncertainties have yet to be assigned to the extracted IS parameters.

VI. CONCLUSION AND OUTLOOK

We have presented the first experimental measurement of isotope shifts in an electric dipole forbidden transition in an atomic negative ion. Utilizing the DESIREE cryogenic storage ring, we developed a novel laser spectroscopy method based on laser-driven population manipulation of electronic states. This enabled high-resolution spectroscopy of the $^4S_{3/2} \rightarrow ^2D_{5/2}$ transition in Sn⁻ across the chain of stable isotopes.

In this work, we reported results from the even-mass isotopes, while data for the odd-mass isotopes $^{117,119}\text{Sn}^-$, where the hyperfine structure was resolved, will be presented in a forthcoming publication. The measured transition frequencies and lifetimes show good agreement with both earlier experiments and theoretical predictions using the CI+all-order approach, also detailed here.

The observed isotope shifts confirm the capability of our technique to resolve subtle atomic-scale effects with high precision. A preliminary King-plot analysis demonstrates that the data quality is sufficient for extracting initial mass and field shift factors. These results establish our method as an ultra-sensitive probe for electron-electron correlation and nuclear charge distribution in anionic systems.

Looking ahead, this method opens the door to future precision studies of bound-bound transitions in negative ions, offering new opportunities to explore electron correlation with unprecedented detail. Beyond expanding the experimental frontier of negative ion spectroscopy, this work lays the foundation for accessing forbidden transitions in high-precision measurements. Such approaches hold promise for improving the determination of changes in nuclear charge radii and providing valuable benchmarks for many-body atomic theory.

ACKNOWLEDGMENTS

This work was performed at the Swedish National Infrastructure, DESIREE (Swedish Research Council Contracts No. 2021-00155 and No. 2023-00170). H. Z., H. T. S., and D. H. thank the Swedish Research Council for individual project grants (with Contracts No. 2020-03437, No. 2022-02822, and No. 2020-03505). This material is based upon work supported in part by the National Science Foundation under Grants No. PHY-1707743 and No. PHY-2110444. Financial support was obtained from

TABLE V. Field-shift (in GHz/fm²) and mass-shift (in GHz u) factors for transitions between the ground-configuration $5p^3$ states in Sn⁻.

Transition	F	$F_{\text{exp.}}$	k_{NMS}	k_{SMS}	$k_{\text{SMS,exp.}}$	k_{MS}	$k_{\text{MS,exp.}}$
$^4S_{3/2} \rightarrow ^2D_{3/2}$	0.26	-	98.3	-181.3	-	-83.0	-
$^4S_{3/2} \rightarrow ^2D_{5/2}$	0.24	-0.03(2)	107.5	-44.5	164.8	63.0	272(52)

the Fundamental and Applied Research Project (Nr. lzp-2023/1-0199) from the Latvian Science Council. The au-

thors would also like to thank Dr. Michail Athanasakis-Kaklamanakis for valuable discussions and private communication regarding King-plot analysis.

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