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Mass and half-life measurements of neutron-deficient isotopes with $A \sim 100$ and developments for the FRS Ion Catcher and CISE

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Mass and half-life measurements of neutron-deficient isotopes with $A \sim 100$ and developments for the FRS Ion Catcher and CISE

PhD Thesis

to obtain the degree of PhD at the
University of Groningen
on the authority of the
Rector Magnificus Prof. C. Wijmenga
and in accordance with
the decision by the College of Deans.

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Friday 09th of April 2021 at 14.30 hours

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“You think of yourself as a citizen of the universe. You think you belong to this world of dust and matter. Out of this dust you have created a personal image, and have forgotten about the essence of your true origin”

Molana (Rumi)

مولانا (رومی)

Persian Poet
13th Century

Wikipedia: [<https://en.wikipedia.org/wiki/Rumi>]

Contents

1	Introduction	1
1.1	History of mass spectrometry	2
1.2	Mass and binding energies	3
1.3	Mass-precision requirements for different physics studies .	5
1.4	Nuclear structure and decay properties	6
1.5	Thesis layout	12
2	Experiments on exotic nuclei	13
2.1	Isotope production and separation techniques	14
2.1.1	ISOL technique	14
2.1.2	In-Flight technique	15
2.2	Direct mass measurement techniques	19
2.2.1	Penning trap	19
2.2.2	Electromagnetic Storage Ring (ESR)	21
2.2.3	Multiple-Reflection Time-Of-Flight (MR-TOF) spec- trometer	23
3	Ion preparation principles and mass spectrometry	25
3.1	Stopping cell and internal ion sources	26
3.2	Multiple RF ion-guides	34
3.2.1	Quadrupole ion-guide and mass filtering	37
3.2.2	Higher orders of multiples (hexapole and octupole)	44
3.3	Time-of-Flight mass spectrometry	45
3.4	Ion optical simulations	48
4	Chemical Isobaric SEparation (CISE) setup	53
4.1	Chemical isobaric separation technique	54
4.2	CISE setup	58
4.2.1	Gas catcher	59
4.2.2	Coupling ion-guide	62

4.2.3	qToF mass spectrometer	74
4.3	Technical design developments	75
4.4	Proof-of-principle by using electrospray ion source	76
4.5	Conclusion and outlook	83
5	FRS experimental setup and gas cleanliness of the cryogenic stopping cell	85
5.1	Experimental facility at GSI	86
5.1.1	Fragment separator (FRS)	87
5.1.2	FRS Ion Catcher setup	88
	Multiple-Reflection Time-Of-Flight Mass Spectrometer	89
5.2	Ultra-clean Helium gas in CSC	90
5.3	Upgraded gas handling system for the FRS Ion Catcher	91
5.4	Cold Trap gas purifier	93
5.5	Techniques for monitoring low-mass impurities in the gas	103
5.5.1	Extraction-RFQ mass scans	104
5.5.2	Residual gas analyzer (RGA)	104
5.6	Gas purification measurements	105
5.7	Charge-states extracted, latest update	111
5.8	Charge-exchange in the RFQ beamline	114
5.9	Conclusions	118
6	Mass and half-life measurements of the neutron-deficient nuclei	119
6.1	Data evaluation procedure	120
6.1.1	Final mass value and the uncertainty contribution	122
6.1.2	Components of error	123
6.2	Neutron-deficient iodine isotopes ^{114}I and ^{116}I	126
6.2.1	^{116}I mass measurement	127
6.2.2	^{114}I mass and half-life measurements	131
6.2.3	Systematic studies of the binding energies	137
6.2.4	Partial half-life of α decaying iodine isotopes	141
6.3	Isotopes in the vicinity of $N = Z$ line	142
6.3.1	Mass measurement in the vicinity of $N = Z$ line	144
6.3.2	Systematic studies of isotopes in the vicinity of $N = Z$ line	152
7	Conclusions and outlook	155

Nederlandse samenvatting	161
List of Abbreviations	167
List of Figures	169
List of Tables	175
Acknowledgements	187

Chapter 1

Introduction

The mass of an atom can be translated in the binding energy of the nucleons, being one of the most fundamental keys in the study of nuclear structure and decay properties of a nucleus. Several techniques have been developed in the last century to measure the mass of an atom. The precision of the mass measurements has improved down to the value of $\Delta m/m = 10^{-11}$ [1] for stable nuclei and 10^{-9} for some short-lived exotic nuclei [2]. This chapter reviews briefly history of the mass spectrometry and defines the mass and the binding energy of a nucleus together with the physics interests of these measurements.

1.1 History of mass spectrometry

The concept for mass spectrometry goes back to 1897 when the electron was discovered by the British scientist Joseph John Thomson. The so-called "cathode rays" pass between two high-voltage electrodes within an evacuated glass tube. He then measured the charge-to-mass ratio (e/m) of the "cathode rays" (electrons) by the perpendicular deflection in external electric and magnetic fields. Thomson got the Nobel prize in 1906 for his discovery and the measurements. In the early 1900s, the technique then was employed by Thomson and his student Francis William Aston at Cambridge University for the determination of the mass-to-charge ratio of positive ions passing through crossed electric and magnetic fields [3–5]. Aston received the Nobel Prize in Chemistry 1922 for his isotope studies carried out with this type of instrument called "Parabola spectrographs". In 1918, professor of physics A. J. Dempster at the University of Chicago developed a magnetic deflection instrument with radial focusing of the beam of ions by a permanent dipole magnet [6]. The ions with different mass-to-charge ratios (m/e) could then be separated due to the different curvature paths in the magnetic field and used as a mass spectrometer [7–9].

A new technique of mass spectrometry was proposed in 1946 by William E. Stephens at the University of Pennsylvania based on the Time-Of-Flight (TOF) of different ions traveling a straight path with same energy, thus with different velocities that reach a collector at different times [10]. The further improvements toward the commercial TOF mass spectrometers were achieved by the key advances that were made by William C. Wiley and I. H. McLaren [11] for ion's energy and space focusing; together with the help of the sophisticated fast electronics required for the TOF mass spectrometry developed in the mid 1950s. Later, the technique was enhanced by using the reflection mirrors for a better correction of the energy distribution and focusing of the ions in longer flight paths.

The investigations on the other methods of mass spectrometry were also done by Wolfgang Paul and Hans Dehmelt in the 1950s for developing ion traps by using the radio-frequency multiple potentials [12]. Wolfgang Paul and Hans Dehmelt were awarded a shared Nobel prize in 1989 for their efforts. However, these days the "Paul traps" are usually

used for ion transportation and mass filtering rather than mass measurements. Instead, the traps with static quadrupole potential superimposed with a magnetic field called "Penning traps" [13] are used for high-precision mass spectrometry by measuring the cyclotron frequency of the ions oscillating in the trap. Presently, the Penning trap technique provides the highest precision of mass spectrometry among all the available techniques. The third type of ion traps called "Electromagnetic storage Rings (ESR)" with relatively larger scales were developed in the early 1980s in Los Alamos in the USA for confining higher-energy ions. Mass spectrometry is performed by measuring the revolution frequency of ions in a large ring of electromagnets [14, 15].

1.2 Mass and binding energies

Mass is one of the most fundamental properties of particles which can reveal information about the nuclear structure and the decay properties of a bound particle. The mass of a neutral atom is defined as:

$$M = [(Z \times m_p) + (N \times m_n) - B_{nucleus} + (Z \times m_e) - B_{atom}] / c^2 \quad (1.1)$$

where Z and N are the number of protons (electrons) and neutrons, m_p , m_n and m_e are the mass of free proton, neutron and electron, respectively. B_{atom} and $B_{nucleus}$ are, respectively, the binding energy of all electrons and the binding energy of nucleons. The mass of atoms can be determined precisely with an uncertainty of up to 10^{-11} [1] for stable atoms and lower mass uncertainties for short half-lived and rare isotopes of around 10^{-9} with mass measurement techniques. The higher mass-accuracy measurements of atoms give a better determination of nuclear and atomic binding energies $B_{nucleus}$ and B_{atom} which represent the structure and interaction mechanism between nucleons and electrons [1, 16]. Figure 1.1 demonstrates the experimental and extrapolated mass uncertainties achieved so far for more than 3000 nuclei.

Figure 1.1: The mass uncertainties for more than 3000 nuclei measured at various laboratories [17, 18].

The secondary observables like Q -value and the nucleon separation energies derived from the masses are also interesting parameters in the investigation of the decay properties and the shell closure of nuclei. The Q -value is defined as the mass difference between the mother and the daughter nuclei in a nuclear decay, describing if the decay is energetically possible ($Q > 0$). The Q -value of the most common spontaneous nuclear decays are presented here:

$$Q_{\alpha} = [M(A, Z) - M(A - 4, Z - 2) - M(\text{He})] \times c^2 \quad (1.2)$$

$$Q_{\beta^-} = [M(A, Z) - M(A, Z + 1)] \times c^2 \quad (1.3)$$

$$Q_{\beta^+} = [M(A, Z) - M(A, Z - 1) - 2m_e] \times c^2 \quad (1.4)$$

$$Q_{ec} = [M(A, Z) - M(A, Z - 1)] \times c^2 - B_e \quad (1.5)$$

The nucleon separation energy is defined as the energy required to remove a nucleon from a nucleus. The nucleon separation energies are a

reflection of how the nucleons are structured in the different energy levels of a nucleus in the shell model calculations [19]. The two-nucleon separation energy is commonly used in the shell closure studies to avoid the pairing effect of the single nucleons. The two-nucleon separation energies (S_{2n} , S_{2p}) can be defined as:

$$S_{2n} = B(N, Z) - B(N - 2, Z) \quad (1.6)$$

$$S_{2p} = B(N, Z) - B(N, Z - 2) \quad (1.7)$$

where $B(N, Z)$ is the binding energy of a nucleus with Z protons and N neutrons. As an example, figure 1.2 shows the evolution of the nuclear shell closures by showing the two neutron and two-proton separation energies demonstrating a sudden decrease in the separation energies as one crosses shell closures ($N = 82$ and $Z = 50$) for the medium-heavy nuclei.

Figure 1.2: The evolution of the shell closure by plotting the two neutron and two-proton separation energies showing closed shells at $N = 82$ and $Z = 50$ for the medium-heavy nuclei. The raw data are obtained from AME 2016 [20].

1.3 Mass-precision requirements for different physics studies

The needed mass accuracy can be different for probing different aspects of physics. In general, a medium-high level of mass uncertainty is required to study the global nuclear structure, shell evolutions and astrophysical processes whereas a very-high mass accuracy is desired for

more fundamental research like testing the standard model and electroweak interaction, etc. [16]. Table 1.1 summarizes the required mass precision for the different fields.

Table 1.1: The generally required mass-precision for probing different fields [1].

Field	Mass uncertainty
Chemistry: identification of molecules	10^{-5} – 10^{-6}
Nuclear physics: shells, sub-shells, pairing	10^{-6}
Nuclear fine structure: deformation, halos	10^{-7} – 10^{-8}
Astrophysics: r-process, rp-process, waiting points	10^{-7}
Nuclear models and formulas: IMME	10^{-7} – 10^{-8}
Weak interaction studies: CVC hypothesis, CKM unitarity	10^{-8}
Atomic physics: binding energies, QED	10^{-9} – 10^{-11}
Metrology: fundamental constants, CPT	$\leq 10^{-10}$

In the next section, the main physics goals and motivations for nuclear structure, mass models and decay properties of nuclei are presented. The more fundamental research where the ultimate mass precision is required is beyond the scope of this thesis.

1.4 Nuclear structure and decay properties

The Liquid Drop Model (LDM), presented by Weizsäcker and by Bethe [21,22], describes the collective properties of nuclei such as nuclear mass, binding energy and nucleon separation energy in a macroscopic approach. The model is generally described by the well-known Bethe-Weizsäcker formula:

$$B = a_v A - a_s A^{2/3} - a_c \frac{Z(Z-1)}{A^{1/3}} - a_{as} \frac{(A-2Z)^2}{A} \pm \delta(A, Z) \quad (1.8)$$

where the first term is known as the volume term that is proportional to the volume of the nucleus (A). The second term is proportional to the surface of the nucleus as $A^{2/3}$. The third term is the coulomb term ($A^{-1/3}$) for protons (Z). The fourth term is the asymmetry component showing the asymmetry between the number of protons and neutrons

and the pairing term δ including the effects of spin coupling between nucleons.

Soon after its developments, it was realized that the collective model (LDM) generalizes the properties of nuclei and has some limitation in describing the microscopic properties of nuclei. Figure 1.3 shows the deviations between the theoretical nuclear binding energies evaluated by the LDM as shown in equation (1.8) and the experimental values. One can see very large deviations for particular combinations of neutron numbers (2, 8, 20, 28, 50, 82, 126 and ...) showing the magic numbers for the closed shells which were later described by the Nuclear Shell Model (NSM) [23]. The NSM describes the nuclear orbits and individual description of nucleons which move in average potential created by other nucleons, in a microscopic approach. Many other microscopical models have also been developed so far for a more conclusive prediction of the mass and other properties of nuclei [24–34]. However, they are still suffering from some limitations due to the lack of experimental input data. As an example, figure 1.4 shows the comparison between the predictive power of different models for the mass of isotope chains from Rh ($Z = 45$) to Cs ($Z = 55$) as a function of neutron number (N) [16]. One can see that the predictions are quite accurate and close to each other for the region of known masses (stable isotopes) since the parameters of the models are adjusted based on the experimental values from direct mass measurements of the isotopes in this region. However, there is a huge discrepancy between different models for the region where the experimental masses are unknown (isotopes far away from the valley of stability). The mass of isotopes in the most neutron deficient/rich regions are extrapolated due to the difficulties for their production and direct mass measurements. These isotopes, the so-called "exotic nuclei", play a major role in explosive nuclear astrophysical processes [35]. More experimental data on these exotic nuclei are needed as input for mass models and the astrophysics synthesis models [35–39].

Figure 1.3: The deviations between the theoretical nuclear binding energies evaluated by the liquid drop model (LDM) and the experimental values showing a very large discrepancy in certain number of neutron numbers N hinting at the closed-shell structures [1].

Figure 1.4: The predictive power of the mass models from Rh ($Z = 45$) to Cs ($Z = 55$) relative to the experimental values as a function of neutron number N [16]. FRDM12 mass model has been used as a baseline. The black solid points are the experimentally known values and the black hollow points are extrapolated values from AME.

Accuracy of the theoretical descriptions of mass models also strongly depends on the region of nuclei under consideration. This has been investigated for different regions in the nuclear chart: Light: ($8 \leq Z < 28$,

$N \geq 8$), Medium-I ($28 \leq Z < 50$), Medium-II ($50 \leq Z < 82$) and Heavy ($Z \geq 82$) [40]. FRDM12, HFB24 and UNEDF models are among the best models describing the mass of nuclei for the isotopes investigated in this PhD thesis ($44 \leq Z \leq 53$). The finite-range droplet model 2012 (FRDM12) model [41] is a macroscopic-microscopic mass model, with the liquid-drop model used as an initial framework for the macroscopic approach joined with single particle microscopic nuclear structure model. The Hartree-Fock-Bogoliubov (HFB) model [42] itself was developed in the early 2000s and uses phenomenological corrections to the energy-density functional. Many versions have been published, with HFB24 optimized using data from the 2012 atomic mass evaluation. The universal nuclear energy density functional (UNEDF) model [43] is based on the pure energy-density functional models of nucleus. For this, the pairing correlation has been added through an HFB approach to optimize the Skyrme energy-density functional.

Looking at the decay properties of nuclei, α -decay is the major decay channel for the heavy and superheavy elements [44]. However, there is also a small island of α -emitters in the medium-heavy neutron-deficient region above the doubly-magic nucleus ^{100}Sn ($Z = N = 50$), stopping the rp-process in Te-Sb-Sn loop [39, 45]. For any α -decay, the Q_α value has a direct correlation to the partial half-life ($T_{1/2}$) of the decaying nuclei for every chain of isotopes, known as the Geiger-Nuttall law [46]. This has been experimentally verified for a wide range of α emitters and not a significant deviation was observed so far. The Geiger-Nuttall law is given by the following:

$$\log_{10} T_{1/2} = A(Z) Q_\alpha^{-1/2} + B(Z) \quad (1.9)$$

where $A(Z)$ and $B(Z)$ are two experimentally determined coefficients for a chain of isotopes with Z protons. Figure 1.5 shows an example of the linear correlation of the partial half-life with the decay energy in the case of even-even Yb-Ra nuclei [47]. The Branching Ratio ($BR\%$) of the α -decay is then usually reported as the $BR = t_{1/2}/T_{1/2}$ where $t_{1/2}$ is the total half-life of the nuclei. The Q_α value of an α -decay can be determined with a direct mass measurement of the nuclei, subsequently, the branching ratio and the partial half-life (knowing the total half-life); and all can be used as the input parameters in nuclear physics models describing the decay properties of nuclei.

Figure 1.5: The logarithms of partial half-lives for the even-even Yb-Ra nuclei as a function of $Q_{\alpha}^{-1/2}$ described by Geiger-Nuttall (GN) law. The marks are the experimental values and the lines are the description of GN law. The plot is adopted from Ref. [47] and it is modified.

In the medium-heavy region, the isotopes in the vicinity of the $N = Z$ line are of great interest to study the nuclear structure, the decay properties and nucleon interactions [48–50]. This region contains interesting cases to study the nuclear force and binding energies for $N = Z$ isotopes [51], pairing and isospin symmetry in mirror decays [52–54], the neutron-proton interaction [55], Wigner energy [56], rp-process pathline calculations [39], Gamow-Teller β decay properties [57], etc. As it was already mentioned, mass is one of the most fundamental keys in these studies. However, the heavy nuclei in this region are suffering from a poor mass accuracy and most masses have not even been measured so far.

In a β -decay, the transition probability or strength of the decay strongly depends on the underlying shell structure and it is usually distributed among several states. For a single-state transition the strength of the

decay can be calculated [58]:

$$B(\text{GT}) = \frac{2\pi^3 \hbar^7 \ln(2)}{m_e^2 c^4 G_F^2 V_{ud}^2 (G_A/G_V)^2 f t_{1/2}} = \frac{3885 \pm 14 \text{ s}}{f(z, \epsilon_0) t_{1/2}} \quad (1.10)$$

where $f(z, \epsilon_0) t_{1/2}$ value is the comparative half life calculated by knowing the decay energy Q_{EC} , half-life $t_{1/2}$ and the decay scheme. G_A/G_V is weak coupling constant. G_F and V_{ud} are fermi coupling constant and the CKM matrix element [59], respectively. c is speed of light and m_e is electron mass.

The doubly-magic ^{100}Sn is the heaviest self-conjugate ($N = Z$) nucleus with numerous unique properties and nuclear structure effects [60]. A huge resonance in Gamow-Teller (GT) decay ($0^+ \rightarrow 1^+$) is observed for ^{100}Sn (even-even) to only a single state of ^{100}In with largest GT strength ($B(\text{GT}) = 9.1^{+2.6}_{-3.0}$) observed so far for any β -decay named as a "superallowed Gamow-Teller". This is even stronger than the known superallowed Fermi decay ($0^+ \rightarrow 0^+$) [61]. Many other investigations and measurements are done for the neighboring even-odd and odd-odd nuclei which shows, in contrast, a broad distribution of the GT transitions [62,63]. The even-even isotones ($N = 50$), e.g. ^{98}Cd , ^{96}Pd and ^{94}Ru , are of particular interest to observe this quenching or splitting of the GT strength close to ^{100}Sn (even-even). For the case of ^{96}Pd and ^{94}Ru also a quenching of the GT strength is observed [64,65] predicted in the single particle shell models. For ^{98}Cd , a GT decay to four underlying states (1^+) are observed with a summed strength of $B(\text{GT}) = 3.5^{+0.8}_{-0.7}$ with large error bars originated from the extrapolated Q -value [66]. A more precise mass measurement reducing the uncertainty of ^{98}Cd can improve our understanding of the GT strength distribution in this region.

1.5 Thesis layout

This chapter presented an introduction about the mass and other related nuclear properties together with a motivation of the physics studies on the medium-heavy and heavy exotic nuclei far away from the valley of stability.

Chapter two presents the production methods of exotic nuclei and the techniques for the direct and high-precision mass measurements.

Chapter three and four describe the general techniques for the low-energy ion manipulation and the developments for the CISE (Chemical Isobaric SEparation) setup at KVI-CART, Groningen, the Netherlands, for the separation of the isobaric nuclei.

Chapter five describes the FRS experimental setup and also presents the technical developments for the gas distribution system of the Cryogenic Stopping cell (CSC) at the FRS Ion Catcher (FRS-IC) setup at GSI, Darmstadt, Germany.

Chapter six presents the new direct mass measurements of the two neutron-deficient iodine isotopes (^{114}I and ^{116}I) and also isotopes in the vicinity of the $N = Z$ line below ^{100}Sn (12 ground states and 2 isomers) by using the MR-TOF-MS technique at FRS-IC setup.

Chapter seven provides some conclusions of the present study and an outlook of the studies in the future.

Chapter 2

Experiments on exotic nuclei

The production and studies of the exotic nuclei far away from the valley of stability are challenging due to several reasons such as low production cross sections, short half-lives, high background, etc. The production of these nuclei is possible at the large-scale accelerator-based facilities e.g. GSI, GANIL, MSU, RIKEN, Jyvaskyla, TRIUMF, CERN and the future FAIR facility for the most extreme neutron rich/deficient isotopes. In this chapter, the methods used for the production of these nuclei and the techniques for high-precision mass measurement are presented.

2.1 Isotope production and separation techniques

The radioactive isotopes away from the valley of stability are called "exotic nuclei" which are not naturally present on Earth. However, studies on these rare nuclei are one of the basic keys for a better understanding of many questions, e.g. how isotopes are produced in stars and supernova explosions after the Big Bang in the early days of the universe. Nowadays, these exotic nuclei can be artificially produced by nuclear reactions in laboratories. In spite of the difficulties to produce them, more than 3000 isotopes so far have been identified and studied in the laboratories. The production of these exotic nuclei are mainly achieved in two different ways known as ISOL and In-Flight techniques. These methods of production and separation of the exotic nuclei are explained in the following sections.

2.1.1 ISOL technique

In Isotope Separation On-Line (ISOL) technique, usually a beam of protons with high energies (100-1000 MeV) hits a thick solid target with a few 100s g/cm² areal density (see figure 2.1). The exotic nuclei can then be produced in spallation, fission or other reactions [67]. The recoil products stop within the target. The target is held at high temperatures around 2000 K in order to speed up the extraction of products by diffusing out of the target and effusing to the ionization source placed after the target. The extracted atomic or molecular recoils are then ionized by using different techniques: surface ionization, plasma ionization or laser ionization techniques. The ionized particles are subsequently re-accelerated up to a few 10s keV in post-acceleration stage after production, extraction and ionization stages. The re-accelerated ions are filtered out by passing through a dipole magnets towards the experimental halls for the studies of purified exotic nuclei. The advantages of ISOL technique are providing a low energy and low emittance exotic beam re-accelerated from rest and a high selectivity of the exotic nuclei in laser-ionization technique. However, the technique is also limited due to the chemical properties of the elements for efficient extraction of the nuclei and to the relatively long extraction time which can be from a few ms to hours, so no longer suitable for short-lived isotopes in some cases. The ISAC facility at TRIUMF, Canada [68] and the ISOLDE facility at CERN, Switzerland [69, 70] are the two largest working ISOL facilities for the production and research on exotic nuclei.

Figure 2.1: ISOLDE target before irradiation at ISOL facility of CERN [70,71].

Figure 2.2 shows the produced isotopes (in color) so far at ISOLDE facility taken from reference [72] based on the ISOLDE yield database.

Figure 2.2: ISOLDE yields over the chart of isotopes taken from reference [72] based on the ISOLDE yield database.

2.1.2 In-Flight technique

In the In-Flight technique, a high-energy beam (a few 100s MeV/u up to GeV/u) of medium-heavy and heavy ions irradiate a thin target for the production of the nuclei of interest. Projectile fragmentation and projectile fission are two main favorable reactions at high energies and fusion-evaporation at lower energies for the production of exotic nuclei. In contrast to the ISOL technique, the highly-charged reaction's recoils

exit the target with high kinetic energies (30-2000 MeV/u) focused in the forward direction. The isotopes of interests are then separated based on their A/q ratio by the electromagnetic separators behind the reaction targets like FRS@GSI [73]. Figure 2.3 shows an example of the production and the separation of the ^{78}Ni in the in-flight method at the FRS facility. The purified isotopes of interest can be transferred to different experimental areas with high energy e.g. storage rings [14] and the experimental area of R³B (Reactions with Relativistic Radioactive Beams) [74] or cooled down and stopped for low-energy experiments e.g. stopping cells [72]. The latter one is known as a hybrid systems for the high-precision studies of the low-energy exotic nuclei [75]. A few examples of the existing In-Flight facilities are FRS@GSI [73], RIKEN [76,77], FRIB [78] and the future Super-FRS in-flight facility at FAIR [79,80].

In principle, most of the isotopes on the chart of isotopes are accessible when using the in-flight technique at different energies and utilizing different nuclear reactions with a proper beam intensity (figure 2.4). The advantage of the in-flight technique is the chemical independency and fast separation of recoils in flight [81]. However, the technique bears some limitations making it difficult to perform low-energy precision experiments, thus the need for the stopping cells.

Figure 2.3: The in-flight method at FRS facility [73] for the production and the separation of the ^{78}Ni nuclei as an example [73].

Figure 2.4: The predicted isotope yield for the future Super-FRS facility utilizing the in-flight technique (adopted from Ref. [72]). The technique can, in principle, cover the whole nuclear chart.

The nuclear reaction mechanisms mentioned in both ISOL and In-flight isotope production methods can vary based on the requested isotope regions and the center-of-mass energies of the reactions. The fission reaction is the main mechanism for the medium-heavy and neutron-rich isotope productions [82], while the fusion reaction is mainly for the production of the isotopes close to the proton drip-line in the neutron deficient side [83, 84] and for the production of the heaviest nuclei [85]. The fragmentation and spallation mechanisms are rather universal reactions for the production of isotopes on both sides of the valley of stability for neutron rich/deficient isotopes [67]. Figure 2.5 demonstrates the schematic view of the most common reaction mechanisms for the production of the new isotopes.

a) Projectile Fragmentation: **b) Abrasion-Fission:** **c) Coulomb-Fission:** **d) Fusion-evaporation:** **e) Spallation:**

Figure 2.5: The schematic view of the most common reaction mechanisms for the production of the new isotopes [86].

2.2 Direct mass measurement techniques

The direct mass measurements of the exotic nuclei is performed by employing three main techniques with different approaches and advantages: the "Penning Trap", "Electromagnetic Storage Ring" and "Multiple-Reflection Time-Of-Flight" techniques. The techniques vary from the relativistic energies to the low and thermal energies. The precision can also change from high-precision to medium-precision levels based on the physics needs and the experiments; parameters. The techniques can be best for the small number of ions and/or best for the short-lived isotopes and high background contamination situations. A brief overview of these three techniques for direct mass measurements will be presented in the following sections.

2.2.1 Penning trap

This is an electromagnetic trap made from a combination of magnetic field (B) for storing ions in the radial direction and a quadrupole static electric field for the axial confinement of the charged particles [13]. The schematic view of a penning trap and the trajectory of the confined ions are shown in figure 2.6. The confined ions have three independent eigenmotions in the electromagnetic field inside the penning traps: the axial motion with frequency ω_z parallel to the magnetic field and the radial motion with the magnetron ω_- and the reduced cyclotron ω_+ frequencies. The radial oscillations obey the relation $\omega_c = \omega_+ + \omega_-$ where ω_c is known as the cyclotron motion. The direct measurement of cyclotron frequency ω_c allows to determine the mass-to-charge ratio (m/q) of the confined ions obeying the formula $\omega_c = qB/m$. The penning traps provides the highest precision achieved so far for the mass measurements for stable ions (10^{-11}) and exotic nuclei (10^{-9}) [1].

The penning traps are working in main labs around the world, at SHIP-TRAP [87], TITAN [88], LEBIT [89], JYFLTRAP [90] and ISOLTRAP [91]. These Penning traps are usually operated using three different methods of the measurement for the radial frequencies consequently the m/q of the ions described below.

Figure 2.6: The cross cut of a penning trap working at TITAN, TRIUMF [92] and the motion of ions in the trap [93].

The **TOF-ICR** (Time-Of-Flight Ion Cyclotron Resonance) is the "standard" method based on the RF excitation of the ions and ejection from the trap for measuring the time-of-flight to the detector [2,92,94,95]. The nominal frequencies are scanned over the expected cyclotron frequency of the ions. The shortest recorded time-of-flight is at the resonance excitation with the cyclotron frequency, ω_c , of the extracted ions defining the mass-to-charge of ions. However, the scanning mode of operation limit the measurements to only for one ion species at the time and at least 30 ions are needed for the measurements [2,96].

In the most recent method **PI-ICR** (Phase-Imaging Ion Cyclotron Resonance) the phase evolution of the radial oscillations of ions is measured after extraction to a position sensitive detector. The technique has a higher precision and more sensitivity for low number of ions due to the non-scanning mode of operation compared to the TOF-ICR method [2] but limited to a narrow mass window for the measurements.

The **FT-ICR** (Fourier-Transform Ion Cyclotron Resonance) method based on measurement of the induced charges on the trap's electrode from the oscillation of the charged particles inside the trap [97,98]. This is a non-destructive detection method without losing the ions and is suitable for a very small number of ions in the low production-rate experiment (sensitive to a single ion). However, reaching a reasonable low mass uncertainty requires a longer observation time for a small number of ions e.g. mass uncertainty of 3×10^{-7} for 10 ions being measured requires almost 10 s of observation time. The technique is so far only used for the fundamental research on stable nuclei or electrons/protons [2].

2.2.2 Electromagnetic Storage Ring (ESR)

The storage ring is the other non-destructive method of the direct mass measurements operating at high energies (a few 100s MeV/u) with the medium-high level of mass uncertainty. The main advantage of the storage ring is the unique capability to study the highly-charged and even completely stripped ions. The technique provides direct mass measurements of multiple mass species and studies of the reaction experiments of radioactive ions stored in the ring. However, the large size of the construction (≈ 40 m diameter) makes the method applicable only at the large scale facilities e.g. ESR (Electromagnetic Storage Ring) at GSI facility [99]. Figure 2.7 shows the schematic view of ESR consisting of dipole and quadrupole magnets for bending and focusing of the beam stored in a closed orbit, the electron cooler section, the RF accelerating cavity and the detection systems (TOF and Schottky) [100].

Figure 2.7: The Electromagnetic Storage Ring (ESR) at GSI facility, Darmstadt, Germany. The figure is adopted and modified from [100].

The mass measurement using this method is based on monitoring the revolution frequency of stored ions in the ring described by equation (2.1):

$$\frac{\Delta f}{f} = -\frac{1}{\gamma_t^2} \frac{\Delta(m/q)}{m/q} + \frac{\Delta v}{v} \left(1 - \frac{\gamma^2}{\gamma_t^2}\right) \quad (2.1)$$

where f , m/q , v and γ are the frequency, mass-to-charge, velocity and relativistic factor and $\Delta f = f_2 - f_1$, $\Delta v = v_2 - v_1$ and $\Delta m/q = (m/q)_2 - (m/q)_1$ are the corresponding differences of two species of ions stored in the ring. The γ_t factor is an ion optical characteristic parameter (transition energy) in which the revolution frequency becomes independent of the energy for each ion species. The frequency revolutions $\Delta f/f$ are directly corresponding to the m/q if one omits the second term in the formula. This is usually done in two different ways: the Schottky Mass Spectrometry (SMS) method by providing $(\Delta v/v) \rightarrow 0$ and the Isochronous Mass Spectrometry (IMS) method by making $(\gamma^2/\gamma_t^2) \rightarrow 1$ shown in figure 2.8.

The **Schottky Mass Spectrometry (SMS)** method: ions are cooled by the electron cooling technique to have negligible velocity spreads $(\Delta v/v) \rightarrow 0$ [101]. The frequency revolution of the ions are measured with charge pick-up plates called "Schottky noise pickups" sensitive to a single ion. A resolving power of 7×10^5 [102] is achieved for the radioactive nuclei. However, the method is limited to long-lived isotopes due to the required cooling time of the hot fragments (a few seconds).

The **Isochronous Mass Spectrometry (IMS)** method: ions are not cooled since the revolution frequency becomes independent of the velocity spread in the transition energy mode of the operation $(\gamma^2/\gamma_t^2) \rightarrow 1$ [103]. The Time-Of-Flight of the ions are recorded in each path while they are passing through a thin metalized carbon foil. A resolving power of 1×10^5 is achieved at ESR [102]. Since the cooling time is excluded in this method, the technique is capable for mass measurement of the exotic nuclei and short-lived isomeric states down to microsecond half-lives.

Figure 2.8: The Schottky Mass Spectrometry (SMS) and Isochronous Mass Spectrometry (IMS) methods for the mass measurements at ESR, GSI [1].

2.2.3 Multiple-Reflection Time-Of-Flight (MR-TOF) spectrometer

The Multiple-Reflection Time-Of-Flight (MR-TOF) is a technique with a high mass precision level and other capabilities required for the challenging short-lived exotic nuclei. The technique can work as an independent mass spectrometer for the low-energy ions [75, 104–106] and/or as a complementary setup prior to the penning traps for the primary beam diagnostic in a broadband mass range and non-scanning mode of operation greatly enhancing the mass measurement capabilities. The combination is successfully operating at the TITAN facility, TRIUMF, Canada [107]. The setup is more compact and less complicated compared to the storage rings operating with a higher mass precision (achieved for FRS-IC setup) while being fast enough (a few ms) to study the most neutron rich/deficient exotic nuclei [108]. The technique covers a broadband range of masses as the main advantage compared to the Penning trap technique.

The technique is based on the time-of-flight (*TOF*) measurement of a bunch of ions going through a field-free drift tube (at a potential difference of U) with the kinetic energy of E_k . The lighter isotopes with smaller m/q gain higher velocities resulting in shorter *TOF* compared to the heavier isotopes:

$$TOF = \frac{l}{v} = l \cdot \sqrt{\frac{m}{2E_k}} = l \cdot \sqrt{\frac{m}{2qU}} \quad (2.2)$$

where l is the flight path of the ions with m/q and velocity v .

The MR-TOF method is the main technique used for the mass measurements presented in this thesis. It will be described in more technical details and to the full extent of its capabilities in the following chapters.

Chapter 3

Ion preparation principles and mass spectrometry

Most of the isotope production facilities possess low-energy experimental halls for high-precision measurements on short-lived and rare isotopes. High-energy reaction products need to be manipulated before reaching the low-energy areas. The isotope manipulation includes: purification, slowing down, transportation and making a package of low-energy ions for the high-precision studies. In the following sections, the required techniques for the ion manipulation are discussed. These techniques should be developed in off-line studies before any on-line experiments which uses beams from the accelerators.

3.1 Stopping cell and internal ion sources

The "stopping cells" so called "gas catchers" are widely used to slow down the high-energy reaction products in on-line isotope production experiments. A stopping cell is, in general, a chamber filled by noble gases in order to cool down incoming ions from the energy of a few MeV to a few eV for high-precision measurements. The high-energy ions first stop in the gas-filled chamber by ion-atom collisions. Afterward, ions are transported by a combination of DC fields applied to the DC cage electrodes along the main body of the stopping cell and a DC+RF pushing field applied to the RF structure (RF carpet [109] or RF funnel [110]) toward the exit center of the gas catcher. Finally, a super sonic gas flow close to the extraction hole of the RF structure pushes out ions from the stopping cell to the following low-energy beam transportation system and measurement setups. Figure 3.1 shows the forces applied to the ions inside the stopping cell.

Figure 3.1: The arrows show the effective forces acting on the ions inside the stopping cell. The green arrows show the DC gradient force to move ions along the main body of the stopping cell. The red arrows are the RF repelling force originating from the surface of the RF carpet in order to prevent ions from hitting the surface of the RF carpet. Another DC gradient force pushes ions on the surface of the RF carpet toward the extraction hole at the center where a supersonic gas flow guide ions out of the cell [72].

Stopping cells can be operated either in cryogenic or room temperature ranges based on the experimental requirements. The cryogenic stopping cells are used for a better suppression of the background contaminants by freezing them at below condensation temperatures. This effectively increases the ion survival probability due to less molecular formations and charge-exchange reactions. On the contrary, the room temperature stopping cells are ideal setups to investigate the ion-atom molecular formations in the gas. The operation of the room temperature stopping cells are also less complicated due to the normal working temperatures. Figure 3.2 shows the FRS cryogenic stopping cell placed in the low-energy area after the fragment separator at GSI, Darmstadt, Germany [72]. The outer chamber is insulating the cryogenic inner-chamber where it is filled with cooled helium gas. Both chambers have a very thin stainless steel window (100 μm thickness) at the entrance flange in the left side for entering the incoming beams from FRS. The DC cage electrodes and the RF carpet attached to the right-end section of the cell providing the guiding fields for the ion extraction. The offline ions sources are also installed on the entrance flange at the left side on the first DC cage electrode.

Figure 3.2: The FRS cryogenic stopping cell at GSI, Darmstadt, Germany [72, 109, 111].

RF structure

The RF structure used in the stopping cells are usually a combination of 300-500 coaxial ring electrodes centered at the extraction side of the gas catcher and biased to a RF voltage with 180° phase-shift on every second ring. The ring electrodes are ordered in a conical shapes with smaller diameters toward the extraction hole called as RF funnel (figure 3.3, right) or printed on a PCB-board with reduced structure size known as RF carpet (figure 3.3, left).

Figure 3.3: Left: RF carpet at high-density cryogenic stopping cell of FRS [109]. Right: RF funnel at low-density cryogenic temperature SHIPTRAP stopping cell [110].

The advantage of using the new generation "RF carpet" in FRS cryogenic stopping cell comparing to the old generation "RF funnel" structure can be summarized below:

- The applied repelling voltage on the RF structure is limited by the capacitance of the structure, the rings on the RF carpet have a much lower capacitance than the physically larger plates in the funnel. Furthermore, small spacing between reduced structure size of electrodes printed on a PCB-board (4 rings/mm [109]) at RF carpet increases the maximum effective RF repelling field acting on the ions. In contrast, the structure size of RF funnel (1 mm gap between two rings [110]) is limited due to the technical difficulties for construction and alignment of the rings. A high RF repelling force is crucial for extraction of ions at high areal gas density of stopping cells and also extraction of the multiple-charged ions from the stopping cell

with a low effective mass-to-charge (m/q) ratio. The effective repelling RF field of the RF carpet is described as:

$$E_{eff} = \frac{1}{2k_b^2 r_0^3} \cdot \left(\frac{r}{r_0}\right) \cdot K^2 \cdot \frac{m}{q} \cdot V_{rf}^2 \cdot \frac{1}{n^2} \quad (3.1)$$

where V_{rf} is the amplitude of RF voltage applied to electrodes, r_0 is the half distance between the center of two electrodes, n is the gas density, m/q is the mass-to-charge ratio of ions, K is the mobility of ions ($K_0 \cdot P_0/T_0$) with the reduced mobility K_0 in atmospheric condition (P_0, T_0), k_b is the Boltzmann constant and r is the radial coordinate on a surface on top of the RF carpet.

- Less electrical power is required for the RF carpet due to the lower capacitive load of the small structure electrodes compared to the RF funnel. The lower heating power is ideal for the operation of the stopping cells at low temperatures.
- Less complications in construction and the alignment of the electrodes in RF carpet since all the electrodes are printed on a PCB-board with the well designed electrical circuit on the backside of the board.

Internal ion sources

The performance of a stopping cell needs to be characterized and optimized in off-line investigations using the internal ion sources before any on-line (accelerator-based) experiment. Using this technique, a radioactive/stable ion source is installed inside the stopping cell producing the ions of interests. A variety of different ion-source techniques can provide either low or high energy ions and the short-lived/stable isotopes for continuous monitoring of the stopping cell extraction and even as calibrant ions for the mass measurements. These ion sources can be generally categorized using four different techniques:

- Low-energy radioactive ion source

In this technique, a wide range of isotopes and elements can be produced in decay chains of the radioactive ion sources. A sample of a long-lived isotope with a low activity (kBq) is usually coated on a small plate and

installed inside the gas catcher for the off-line measurements. The ^{228}Th [112] and ^{223}Ra [109] sources are two examples of this kind of low-energy ion sources (see tables 3.1 and 3.2 for the isotope chains and the decay properties in figures 3.4 and 3.5).

Figure 3.4: The decay chain of the ^{223}Ra radioactive ion source with medium half-life range.

Table 3.1: The decay properties of the ^{223}Ra radioactive ion source [109].

Isotope	Half-life	Decay mode	Branching ratio	Energy (keV)
^{223}Ra	11.435 d	α	100%	5539.8 5606.7 5716.2 5747.0
^{219}Rn	3.96 s	α	100%	6425.0 6552.6 6819.1
^{219}Po	1.781 ms	α	100%	7386.1
^{211}Pb	36.1 min	β	100%	1373 (end-point)
^{211}Bi	2.14 min	α	100%	6278.2 6622.9
^{207}Tl	4.77 min	β	100%	1418 (end-point)

Figure 3.5: The decay chain of the ^{228}Th radioactive ion source with long half-life range.

Table 3.2: The decay properties of the ^{228}Th radioactive ion source [112]

Isotope	Half-life	Decay mode	Branching ratio	Energy (keV)
^{228}Th	1.91 y	α	100%	5423
^{224}Ra	3.66 d	α	100%	5685.37 5448.6
^{220}Rn	55.6 s	α	100%	6288.08 5747
^{216}Po	145 ms	α	100%	6778.3
^{212}Pb	10.64 h	β	100%	569.1 (end-point)
^{212}Bi	60.55 min	β	64.06%	2251.5 (end-point)
		α	35.94%	6050.78 6089.88
^{212}Po	299 ns	α	100%	8784.86
^{208}Tl	3.05 min	β	100%	4998.5 (end-point)

- High-energy fission ion source

Fission sources can provide a very wide range of fission fragments in the medium mass range of nuclei (3.6). The huge energy released in a fission (around 200 MeV) makes high-energy products inside the gas catcher suitable for investigating the stopping efficiency and element dependence of extraction efficiency of a stopping cell operating at high areal gas density. The FRS stopping cell uses the ^{252}Cf fission source for off-line calibration and also studies on the fission fragments [113].

Figure 3.6: The fission products of the ^{252}Cf source with normalized yields per fission [17, 114].

- Laser ablation ion source

The laser ablation ion source can produce most of the stable/radioactive metallic ions by local heating of a metal target with a laser in order to sputter ions from the surface into the gas [115, 116]. Figure 3.7 shows a schematic view of the laser ablation ion-production principle.

Figure 3.7: Schematic view of the laser ablation ion-production technique.

- Discharge source

The discharge source is another kind of setups for ionizing the buffer gas in the stopping cell (He and other impurities) mainly used also for the gas cleanliness studies of the gas catcher. In this technique a high-current passing through two metal tips (needle and plate with a 0.5 mm gap in between) making local discharge to ionize the gas in the environment. The structure of the discharge source mounted on one of the DC cage electrodes in the FRS ion catcher is shown in figure 3.8 [112].

Figure 3.8: The structure of the discharge source at FRS stopping cell [112].

3.2 Multiple RF ion-guides

Multiple RF ion-guides are the main devices for the low-energy ion transportation from the gas catchers at high pressures ($\approx 30\text{-}200\text{ mbar}$) to the following devices like mass spectrometers working at lower pressure regimes ($\approx 10^{-7}\text{ mbar}$). These devices are not only used for ion transportation, but also for collision-cooling of ions with buffer gas atoms, mass filtering and mass selecting of ions of interest and making a cooled bunch of ions with low-energy and low-space dispersion required for the subsequent precise measurements [117].

A multiple RF ion-guide is generally made by using couples of round-shaped metal rods which are symmetrically arranged around the axis of ion transportation. Figure 3.9 shows a cross-cut (x,y plane) over the axis of ion transportation (z) of multiples (quadrupole, hexapole and octupole).

Figure 3.9: A cross-cut of RF multiples in the (x,y) plane. Quadrupole, hexapole and octupole connected to a pair of RF and DC potentials are shown.

The electrodes are connected to either a pair of 180° phase-shifted Radio Frequency (RF) or a combination of RF and Direct Current (DC) potentials. The half distance between the face of two opposite rods is known as the "field radius" and defined as r_0 . By assuming that the rods are much longer in z direction than the field radius of multiples, the electric

potential in the (x,y) plane of an RF multiple can be generally described by the following equation [118]:

$$\phi_N(x,y) \propto \frac{\text{Re}[(x + iy)^N]}{r_0^N} \quad (3.2)$$

where N is the order of the multiple ($N=2$ quadrupole, $N=3$ hexapole, $N=4$ octupole, etc.). The potential can then be simply derived for the different orders of multiples as following:

$$\text{Quadrupole } (N=2) : \quad \phi_2(x,y) = \phi_0 \frac{(x^2 - y^2)}{r_0^2} \quad (3.3)$$

$$\text{Hexapole } (N=3) : \quad \phi_3(x,y) = \phi_0 \frac{(x^3 - 3x \cdot y^2)}{r_0^3} \quad (3.4)$$

$$\text{Octupole } (N=4) : \quad \phi_4(x,y) = \phi_0 \frac{(x^4 - 6x^2y^2 + y^4)}{r_0^4} \quad (3.5)$$

The different shapes of the normalized potentials in (x,y) coordinates as a function of the relative distance from the center of the multiple are shown in figure 3.10.

Figure 3.10: The normalized potential shapes for quadrupole, hexapole and octupole versus the radial distance from the center of the RF multiples in (x,y) plane.

The characteristics of the different orders of the multiples can be looked at in several aspects:

- The higher order of poles (e.g. octupole) has a flat potential close to the axis while the lower order of poles (e.g. quadrupole) has a steep potential. The flat-shaped potential close to the axes minimizes the space-charge forces since ions are allowed to spread out in larger radial distances. It also gives a wider acceptance for capturing a diverged ion beam which usually comes out of the extraction hole of the gas catchers. On the contrary, the sharper potential in a quadrupole leads to a stronger and linear restoring force in order to make a more focused ion beams close to the axes.
- The potential in x and y directions are independent for quadrupole which causes to have an independent and linear equations of motion of ions in x and y coordinates. In contrast, the motions in x and y directions of the higher orders of multiple are coupled and they are not linear anymore. The linearity and independence of the equations of motions in the quadrupole provide a strong power for mass filtering and mass selection of ions.
- The higher order of poles (e.g. octupole) has higher ion capacity because of wider potential in radial coordinate which decreases the space-charge limitation while the lower order of poles (e.g. quadrupole) has lower ion capacity. The maximum charge per unit of length in a multiple can be generally described as below [119]:

$$Q_{max} = \frac{1}{2} \pi \epsilon_0 N V_{rf} \quad [\text{C/m}] \quad (3.6)$$

where ϵ_0 is the electric vacuum permittivity, N is the number of poles and V_{rf} is the amplitude of RF potential applied to the multiple. One can see that an octupole ($N=4$) has double charge capacity as compared to a quadrupole ($N=2$) with the same parameters.

- In a practical applications of the multiples, there is an optimized ratio between the radius of electrodes, r_e , and the half distance between two faces of the opposite electrodes, r_0 ($r_e/r_0 = 0.355, 0.537$ and 1.147 for octupole, hexapole and quadrupole, respectively [120]). For example, considering the same r_0 for all the multiples would lead to a different radial sizes of the electrodes in order

to make a pure multiple potential. Therefore, the number of electrodes together with the optimized radii in different multiples lead to a more openly-arranged geometry for quadrupole compared to hexapole and octupole in order to have more pumping efficiency for internal areas of the multiples.

The different characteristics of the multiples would help to choose the best order of an ion-guide for different purposes for instance when one requires to have more ion-capacity, more focusing power or mass filtering of the ions. Table 3.3 summarize the main characteristics of the multiple ion-guides.

Table 3.3: Comparison between the main characteristics of the multiple ion-guides.

Multipoles	Focusing power	Ion capacity	Ion radial distribution	Filtering ability	Geometry
Octupole	Small	High	Large		Close
Hexapole	Large	Low	Small		Open
Quadrupole	Large	Low	Small		Open

3.2.1 Quadrupole ion-guide and mass filtering

Defining the ϕ_0 as a combination of the DC and RF potentials in equation 3.3 as following:

$$\phi_0 = U_{DC} + V_{RF} = U_0 + V_0 \cos(\omega \cdot t) \quad (3.7)$$

where U_0 and V_0 are respectively the amplitudes of DC and RF potentials, ω is the angular frequency equal to $2\pi f$, f is the RF frequency and t is the time. The $+\phi_0$ and $-\phi_0$ are actually connected, respectively, to the pairs of electrodes in x and y directions in a quadrupole (see figure

3.11) and ions move through the quadrupole in z direction. Therefore, we will have the quadrupole potential in x and y planes as follows:

$$\phi(x, y) = \phi_0 \frac{(x^2 - y^2)}{r_0^2} = [U_0 + V_0 \cos(\omega \cdot t)] \frac{(x^2 - y^2)}{r_0^2} \quad (3.8)$$

Figure 3.11: Quadrupole geometry. Electrodes are connected to $+\phi_0$ and $-\phi_0$ and aligned in z direction.

One can derive the force acting to the ions by taking the derivative of the quadrupole potential (equation 3.8) in x and y coordinates:

$$\begin{aligned} F_x &= -e \left(\frac{d\phi}{dx} \right)_y = \frac{-2e}{r_0^2} [U_0 + V_0 \cos(\omega \cdot t)] x = m \frac{d^2 x}{dt^2} \\ F_y &= -e \left(\frac{d\phi}{dy} \right)_x = \frac{+2e}{r_0^2} [U_0 + V_0 \cos(\omega \cdot t)] y = m \frac{d^2 y}{dt^2} \end{aligned} \quad (3.9)$$

where e is the elementary charge unit and m is the mass of ions.

With the help of Newton's second law one can write the equations of motion of ions when passing through a quadrupole ion-guide and obtain

the so called "Paul equations" [118, 121]:

$$\begin{aligned}\frac{d^2x}{dt^2} + \frac{2e}{mr_0^2}[U_0 + V_0 \cos(\omega \cdot t)]x &= 0 \\ \frac{d^2y}{dt^2} - \frac{2e}{mr_0^2}[U_0 + V_0 \cos(\omega \cdot t)]y &= 0\end{aligned}\tag{3.10}$$

The equations of motion of ions in a quadrupole are usually expressed by a known second-order differential equation called "Mathieu equation" developed in 1866 by the French physicist named Mathieu [118, 121]:

$$\frac{d^2u}{d\xi^2} + [a - 2q \cos(2\xi)]u = 0\tag{3.11}$$

where u stands for either x or y . The dimensionless parameter ξ is defined as $\omega \cdot t/2$ thus $2\xi = \omega \cdot t$. All the physical properties of the quadrupoles and ions are collected in two dimensionless parameters a and q known as "stability parameters" as follows:

$$a = a_x = -a_y = \frac{8U_0}{\frac{m}{e}\omega^2 r_0^2}\tag{3.12}$$

$$q = q_x = -q_y = \frac{4V_0}{\frac{m}{e}\omega^2 r_0^2}\tag{3.13}$$

The stability parameters define a stable or unstable trajectory of ions passing through a quadrupole based on the finite or infinite solutions of the Mathieu equation. This stability can be demonstrated in a stability diagrams (figure 3.12) in x and y directions, where the colored area shows the stable and white area shows the unstable area for ions in different directions (x, y).

Figure 3.12: The stability diagrams of x and y coordinates of a quadrupole presented by dimensionless stability parameters, a and q , axes. The colored sections show the stable area for motions of ions in x (left) and y (right) directions.

Since the stable path of ions mean the simultaneous stability both in x and y directions, the main overlap of stability diagrams in x and y directions defines the final stability diagram for ions as demonstrated in figure (3.13).

Figure 3.13: The overlap of the stability diagrams in x and y coordinate.

In general and for the simplicity, stability area is only presented for positive values of stability parameter a since the negative values symmetrically refer to the negative U_0 applied to another pair of electrodes. The main intersection of the stability area close to zero is shown in figure 3.14. Most of the commercial quadrupoles are operating in this main intersection.

Figure 3.14: The stability diagram of a quadrupole. Light gray area shows the stability in y direction, light brown area shows the stability in x direction and dark gray/brown shows the overlap of stabilities in x and y directions.

Independent equations of motion of ions in x and y directions together with the linear force acting on the ions make the quadrupole a suitable setup for mass filtering and mass selection of ions based on the mass-to-charge ratio. By considering the stability parameters presented in equation 3.12 and 3.13, one can make a set of parameters in such a way that different mass-to-charge ratios (m/e) either stay within or outside of the stability region in order to select the specific mass-to-charge ratio and filter out the rest. For example, figure 3.15 demonstrates the location of three different singly-charged ions with masses $m_3 > m_2 > m_1$ in the

stability diagram, in which the mass m_2 is the only one sitting in the stability region both in x and y directions. Therefore, the ion with m_2 can travel through the quadrupole in z direction until the end. In contrast, the heavier mass m_1 and the lighter mass m_3 which are located outside of the stability area will have unstable trajectories in y or x direction, respectively, and are subsequently filtered out. All the three masses are placed on a line called the filtering line. The resolving power of this mass filtering depends on the slope of the line " R " shown in figure 3.15. The slope can be changed in order to have more or less resolving power based on the set of ratio of variables (U_0, V_0) in stability parameters presented in equation 3.12 and 3.13. The larger slope of the resolving-power line (R_1) makes the system work more closely to the top triangle shape of the stability area which only covers a narrow mass range for transmission while the smaller slope of the resolving-power line (R_3) makes the system transmit a wider mass range with a poorer resolving power (see figure 3.16).

Figure 3.15: The location of the three masses $m_3 > m_2 > m_1$ in the stability region. Only the mass m_2 is within the xy stability region.

Figure 3.16: The different resolving-power lines $R_1 > R_2 > R_3$ in the stability regions. The top point at stability area is shown at $a = 0.237$ and $q = 0.706$ and also the boundary at the lower right side at $a = 0.0$ and $q = 0.908$ on the q axis is known as the LMCO of the quadrupole at $U_0 = 0$ operation.

The resolving power is, of course, affected by the goodness of construction and alignment of the quadrupole rods and also stability and quality of DC and RF potentials applied to them, but also the maximum mass resolving power is limited by the number of cycles which ions feel in the RF field in their flight through the length of the quadrupole $N^2 = Lf/V_z$ [122,123]. Parameter L is the length of the quadrupole, f is the frequency of RF potential and V_z is the injection velocity in z direction. Therefore, the following equation describes the maximum theoretically-achievable resolving power [122]:

$$R = \frac{m}{\Delta m} = \frac{1}{k} N^2 = \frac{0.05 f^2 L^2 m}{2eE_0} \quad (3.14)$$

where k is a constant which is empirically evaluated to be around 20 [122], f is the frequency of RF potential, m , e and E_0 are the mass, the charge and the injection energy of the ions.

3.2.2 Higher orders of multiples (hexapole and octupole)

By considering the higher order potentials $\phi(x, y)$ from the equations 3.4 and 3.5, one can derive the equations of motion for hexapole and quadrupole as following:

Hexapole ($N = 3$):

$$\begin{aligned} F_x &= -e \left(\frac{d\phi}{dx} \right)_y = \frac{-e\phi_0}{r_0^3} (3x^2 - 3y^2) = m \frac{d^2x}{dt^2} \\ F_y &= -e \left(\frac{d\phi}{dy} \right)_x = \frac{-e\phi_0}{r_0^3} (-6x \cdot y) = m \frac{d^2y}{dt^2} \end{aligned} \quad (3.15)$$

Octupole ($N = 4$):

$$\begin{aligned} F_x &= -e \left(\frac{d\phi}{dx} \right)_y = \frac{-e\phi_0}{r_0^4} (4x^3 - 12y^2 \cdot x) = m \frac{d^2x}{dt^2} \\ F_y &= -e \left(\frac{d\phi}{dy} \right)_x = \frac{-e\phi_0}{r_0^4} (-12x^2 \cdot y + 4y^3) = m \frac{d^2y}{dt^2} \end{aligned} \quad (3.16)$$

The equations of motion of ions show that, in contrast to the quadrupole, they are not linear equations anymore for $N > 2$ of multiples. Furthermore, the motions of ions are coupled in x and y directions and it is not possible to provide a distinct stability diagram, anymore. Therefore, the stability of ions are only described by a stability parameter η [124–126]:

$$\eta = 2N(N-1) \frac{V_0}{\frac{m}{e} \omega^2 r_0^2} \left(\frac{r}{r_0} \right)^{(N-2)} \quad (3.17)$$

where N is the order of multiple ($N = 3$ hexapole, $N = 4$ octupole, etc.), V_0 and ω are the amplitude and angular RF frequency respectively, m/e is the mass-to-charge ratio of the ion, r_0 is the half-distance between the face of two opposite rods and r is the ion radial position at injection time at $z=0$ plane. The stability conditions of ions are evaluated based on the numerical simulations with the following results [124–126]:

$$\eta < 0.3 \quad \frac{r}{r_0} < 0.8 \quad (3.18)$$

Although higher order multiples are not capable of mass filtering, the stability conditions of the multiples cover a very wide range of masses with no effective Low Mass Cut Off (LMCO) for ion transportation. The wide potential together with the larger maximum charge capacity of ions (see equation 3.6) make the higher-order multiple more suitable for accepting extracted ions from the gas catcher with a very wide phase-space.

3.3 Time-of-Flight mass spectrometry

The basic principle of the Time-of-Flight Mass Spectrometry (ToF-MS) is pretty straightforward. A package of ions with a low energy and small spatial distribution will be subjected to an accelerating voltage ΔU and drift over a field-free region with a length of d . The time-of-flight of ions (t) will be recorded at the end of the flight path by a high time-resolution detector e.g. Multichannel Plate (MCP) detector:

$$\frac{1}{2}mv^2 = e\Delta U \quad (3.19)$$

where v is the velocity of the accelerated ions. By substituting $v = d/t$ in the field-free region, we have:

$$\frac{1}{2}m \frac{d^2}{t^2} = e\Delta U \quad (3.20)$$

The formula can be written as the (m/e) of the ions proportional to the square of their time-of-flight (t^2):

$$\frac{m}{e} = \frac{2\Delta U}{d^2}t^2 \quad (3.21)$$

Therefore, ions with lower mass-to-charge ratio reach the detector earlier than ions with higher mass-to-charge ratio. This is the basic concept for mass spectrometry. However, the techniques can be more sophisticated in order to achieve a higher precision. Figure 3.17 demonstrates a general view of three different approaches from low- to high-precision mass spectrometry. The top figure shows a linear ToF mass spectrometer and demonstrates the basic principle as discussed. The performance

of the linear ToF is limited by the length of the flight tube and also by the de-focusing of the diverging ion beam during flight. In addition, the technique is very sensitive to the initial energy and space divergences of the injected bunch of ions. The same masses of ions but with a slightly different injection energy will reach the detector with a wide ToF spectrum and might overlap with the adjacent mass unit (red and green ToF spectra in figure 3.17, top row). A few examples of the linear ToF technique can be found in references [127–129].

Figure 3.17: Three general techniques for the ToF mass spectrometry for low- and high-precision mass spectrometry.

The middle setup in figure 3.17 demonstrates the "Reflection ToF" technique which can improve the performance of the ToF spectrometer with "energy focusing" of ions by using a reflector mirror at the end of the flight tube. The reflector is actually a set of electrostatic potential steps

which reflect ions in a longer path toward the detector in the other direction. The longer path of ion's flight causes to have a more resolved peaks for ions with different masses. But, the more important advantage is the energy focusing of the ions during the reflection which can compensate the initial energy spread of the injected ions. In this technique, ions with the same masses but slightly higher initial energies penetrate in more depth of the reflector and fly over a longer path compared to the lower-energy ions and both reach the detector at the same time. This effect improves the width of the time of flight spectrum (see the red and green spectra in the middle). A few examples of the reflection ToF technique can be found in references [130–132].

The bottom figure in 3.17 shows the technique with the highest precision of mass spectrometry with energy focusing and an extremely long flight path by using two electrostatic mirrors at two ends of the flight tube. The injected ions are trapped in the flight tube in order to have a very long flight of a few hundreds of meters. Ions are then ejected toward the detector by switching a set of extraction potentials. The technique provides the most resolved peaks with a narrow peaks. A few examples of the multiple-reflection ToF technique can be found in references [75, 133–135].

The precision of the mass spectrometry can be identified by two fundamental definitions: "**Mass resolving power**" and "**Mass accuracy**".

- **Mass resolving power:**

The resolving power is an instrument's ability in mass spectrometry of ions and it is independent of the mass being measured. It is defined for a single peak made up from ions with mass m and the Full-Width-Half-Maximum (FWHM), Δm at 50% intensity of the peak height (see figure 3.18):

$$\text{Resolving power} = \frac{m}{\Delta m} \quad (3.22)$$

Since m is proportional to t^2 , one can derive $m = At^2$ and $\Delta m = 2At \cdot \Delta t$ where A is a constant. Therefore, the mass resolution can also be

expressed as follows:

$$\text{Resolving power} = \frac{m}{\Delta m} = \frac{At^2}{2At\Delta t} = \frac{t}{2 \cdot \Delta t} \quad (3.23)$$

where Δt is the FWHM of the time-of-flight of ions.

Figure 3.18: The definition of mass resolving power based on the 50% intensity level of a single Gaussian peak.

- **Mass accuracy:**

The mass accuracy is actually the comparison between the measured mass and the expected value of the mass of the ion. This is describing how well the mass spectrometer measures the mass of an ion. The mass accuracy is usually expressed as part-per-million (ppm):

$$\text{Mass accuracy} = \frac{\text{measured mass} - \text{expected mass}}{\text{expected mass}} \times 10^6 \text{ [ppm]} \quad (3.24)$$

3.4 Ion optical simulations

SIMION [136] and COMSOL Multiphysics [137] are two commonly-used computer codes for the field calculations and ion-optical simulations.

COMSOL uses a numerical method called "Finite Element Analysis" (FEA) in order to solve complicated simulations. It breaks down the main domain into many small parts (meshing into finite elements) and then it sets an equation to each specific element. The mesh size in FEA is determined based on the available memory size and the required CPU time of simulations. At the end, the solver symmetrically re-combines the set of elements in order to make a global system of equations for the final analysis. The technique, in general, can provide a more accurate representation of the complex geometries; specially for fringe-field areas close to the very small geometries with many details. In addition, COMSOL can merge many different physics disciplines into the problem for more complicated and more realistic calculations like ions trajectories affected by the gas flow drag field in presence of the gas jets e.g. close the extraction hole of the RF carpet. On the other hand, SIMION is a programmable software based on solving the Laplace equation for any user-defined geometry. The software calculates the electromagnetic fields and then simulate the ion trajectories in the field. In practice, the technique used in SIMION works much faster than the technique used in COMSOL but less accurate in details of the complicated geometries and not capable to combine several physics calculations.

All the simulations in this thesis are done by using COMSOL Multiphysics software in order to take advantage of multi-physics calculations. Three different modules, namely "AC/DC", "Charged Particle Tracing" and "Viscous drag" modules are used in the simulations. "AC/DC" module can provide all the electrostatic and alternating fields in complex geometries. The combination of the "AC/DC" with "Charged Particle Tracing" can provide the resulting electromagnetic force applied to the charge particles together with the elastic ion-atom collision models for ion transportation in the presence of the buffer gas background. The "Viscous drag" model is also used for the calculations of the pushing field applied to the ions in super-sonic gas flow very close to the extraction hole of the RF carpet.

Collision model

The collision model in COMSOL includes the hard-sphere elastic collisions between the ions and the background gas using Monte Carlo models. Ions have a random chance to collide with background gas based on

the gas density and collision cross section. The probability of the collisions is defined as:

$$P = 1 - e^{-f(\Delta t)} \quad P \in [0, 1] \quad (3.25)$$

where f is the collision frequency and Δt is the time step. The collision frequency can be defined as:

$$f = N_d \sigma |g| \quad (3.26)$$

where N_d is the background gas density, σ is the collision cross section and $g = v - v_g$ is the relative velocity between the velocity of the ion v and the velocity of the background gas v_g in the center of mass reference. The velocity of background gas is assumed to have the Maxwellian distribution at stable (non-flow) background pressure:

$$f(v_g) = \frac{1}{(2\pi k_\beta T / m_g)^{3/2}} \exp\left(\frac{-m_g [v_g - u]^2}{2k_\beta T}\right) \quad (3.27)$$

where:

- u (SI unit: m/s) is the average velocity of the background gas,
- m_g (SI unit: kg) is the mass of the background gas,
- T (SI unit: K) is the temperature of the background gas, and
- k_β (SI unit: J/K) is the Boltzmann constant.

The mass m_g can also be expressed in terms of the molar mass M_g (SI unit: kg/mol):

$$m_g = \frac{M_g}{N_A} \quad (3.28)$$

where N_A (SI unit: 1/mol) is the Avogadro constant.

The collision cross section can be also approximately calculated from the geometrical cross section of ions and the gas atoms (see figure 3.19) by using the Van der Waals radii in elastic collisions:

$$\sigma = \pi(R_{\text{ion}} + R_{\text{gas}})^2 \quad (3.29)$$

where R_{ion} , R_{gas} are the van der Waals radii of the ions and the atoms of the buffer gas mixture.

Figure 3.19: The Van der Waals radii of ions and buffer gas atoms in an elastic collision.

The elastic collisions between the ion and background gas results in a change of the velocity of ion in such a way that the total energy of the system is conserved. The post-collision velocity of the ion is defined by the expression:

$$v' = v - \frac{m_g}{m + m_g} (g - g') \quad (3.30)$$

where m is the mass of the ion and g' is the post-collision relative velocity given by $g' = |g| R$. Here, R is a uniformity-distributed random unit vector.

Chapter 4

Chemical Isobaric SEparation (CISE) setup

High-precision mass measurements of exotic nuclei are of great interest for nuclear structure and nuclear astrophysics. However, studies of these rare isotopes are challenging due to the low production yield and huge amounts of unwanted by-products. A large fraction of the by-products can be suppressed in an electromagnetic separator behind the reaction target. Some experiments even require a second separation step to suppress isobaric contaminants (nuclei with the same mass numbers A). A novel technique with the help of chemistry can be implemented for this isobaric separation while the high-energy reaction products are slowed down in a gas catcher filled by a noble gas and additional amount of reactive gases. The isobaric by-products can chemically react with the reactive gas inside the gas catcher and form heavier clusters. Then, the heavier clusters will be easily separated in the downstream transportation line (e.g. by a quadrupole mass filter) from the other isobars which have not reacted with the reactive gas. The Chemical Isobaric SEparation (CISE) setup has been developed with the aim to understand the chemistry inside the gas catcher and to explore its potential as a new technique for separation of isobars from by-products in on-line experiments. However, such a novel technique first needs to be investigated in off-line tests before being implemented in an accelerator-based experiment.

4.1 Chemical isobaric separation technique

The chemical separation of the isobars should preferably happen within the gas catcher where the high-energy recoils (produced in nuclear reactions) are slowed down. The gas catcher is a suitable place to investigate and even to induce chemical reactions and molecular formations of ions with the reactive gas at room temperature. Subsequently, these chemical reactions will help in the separation of isobars based on their different molecular formations. The molecular formation of the ions with an adduct in a gas cell has already been observed specially for the water impurities. This has been used in an experiment for the separation of $^{32,33}\text{Si}$ and ^{34}Pi isotopes from the other unwanted background contaminants at the Low Energy Beam and Ion Trap (LEBIT) facility at the National Superconducting Cyclotron Laboratory (NSCL) [138]. However, the full potential of chemistry in a gas catcher for the separation of isobars has not been explored, yet. Therefore, the idea for CISE is the development of a technique for the chemical separation of isobars.

A potential application of the new separation technique is for the production and separation of the doubly-magic ^{100}Sn and isotopes in its vicinity close to the proton drip line and $N = Z$ isotopes. ^{100}Sn as the heaviest self-conjugate nucleus [139] with the same number of protons and neutrons ($N = Z = 50$) is a unique isotope for exploring and understanding many aspects of nuclear physics such as the shell structure close to the magic numbers, binding energies, Superallowed GT decay and the path line calculations of rp-process [39, 61, 140]. However, production and purification of ^{100}Sn and isotopes in its vicinity, far away from the valley of stability, are really challenging because of the low production cross sections and high background contaminations. The fusion-evaporation reaction $^{50}\text{Cr} + ^{58}\text{Ni}$ at 5.1 MeV/u projectile energy is one of the favorable reactions for the production of the doubly-magic ^{100}Sn isotope with a relatively high reaction cross section (40 nbarn) [141]. Figure 4.1 shows the expected nuclei produced in this reaction, simulated based on the fusion-evaporation statistical model PACE4 by using LISE++ software. The dashed line called "isobaric line" shows the isobaric nuclei produced in addition to ^{100}Sn isotope with the same mass number $A = 100$.

Figure 4.1: Nuclei produced in fusion-evaporation reaction $^{50}\text{Cr} + ^{58}\text{Ni}$ at 5.1 MeV/u projectile energy, evaluated by using the statistical model PACE4 with the LISE++ software. The dash line indicates the isobaric nuclei with the same $A = 100$.

Producing ^{100}Sn in fusion-evaporation reaction and capability of conducting this reaction at GSI (Germany) with high beam intensity leads to a high production rate. Starting with 6×10^{12} ions/s beam of ^{50}Cr on ^{58}Ni target with $500 \mu\text{g}/\text{cm}^2$ thickness and considering 20% efficiency of SHIP (Separator for Heavy Ion Products [142]; the velocity filter behind the target for the suppression of the most unwanted reaction products), it is expected to have a production rate of 0.25 ions/s of ^{100}Sn at the end of SHIP where ions are entering a gas catcher in the low-energy part of the beam line. The challenging part of this technique is the removal of other isobaric contaminants ^{100}In , ^{100}Cd and ^{100}Ag produced along with ^{100}Sn . Table 4.1 shows the expected production rate of ^{100}Sn and other isobaric contaminants ^{100}Cd and ^{100}Ag and ^{100}In entering the gas catcher at the low-energy part of the beam line based on the experimental cross sections of production [141]. The aim of chemical isobaric separation is developing a technique to let the low amount of produced ^{100}Sn or ^{100}In survive and suppress the other two isobaric contaminants with a few orders of magnitudes higher production rates for ^{100}Cd and ^{100}Ag . This technique allows us to study these rare isotopes in high-precision measurements.

Table 4.1: Experimental cross sections and expected production rates of ^{100}Sn , ^{100}Cd and ^{100}Ag and ^{100}In entering the gas catcher at SHIPTRAP by considering experimental cross sections from Ref. [141] and assuming 20% efficiency of fragment separator SHIP behind the reaction target.

Isobars	Cross section [barn]	Production rate ions/s
Sn	40×10^{-9}	0.25
In	4×10^{-6}	24.6
Cd	8×10^{-4}	4925
Ag	3.9×10^{-3}	24008

For making proper conditions for gas-phase chemistry inside the gas catcher, one can use a gas mixture of helium plus reactive gases (e.g. CH_4 , H_2O , etc.) for chemical isobaric separation in such a way that isobaric contaminants chemically react with the reactive gas and make heavier components whereas the isotopes of interest do not react. The heavier clusters of contaminants can then be filtered out in the ion transportation line based on the different masses. In addition, the charge-state of the ions can be changed by the charge-exchange reaction of the ions during the collisions with the buffer gas atoms with lower ionization potential than helium. This can be also used for the separation of some ions based on the different mass-to-charge ratios m/q in the beam line.

Gas-phase chemistry

A possible option of the gas inside the gas catcher is a mixture of helium and methane (He-CH_4) and/or water ($\text{He-H}_2\text{O}$). Helium is a noble gas with the highest 1st ionization potential (24.58 eV) suitable for thermalizing the high-energy recoils. Methane and water are also two possible candidates as a reactive gas with high tendency to react with some isobaric contaminants and easy to control. The chemical reaction for making the molecular form of ions (X^+) attached to the reactive gas (M) can be shown as:

The rate of the molecular formation is defined as [143]:

$$r = \frac{dn}{dt} = -kn[I] \quad (4.2)$$

where k is the reaction rate coefficient, n is the number of incident ions and $[I]$ is the concentration of the reactive gas. A time constant τ for the given condition can be associated with the reaction as follows:

$$\tau = \frac{1}{k[I]} \quad (4.3)$$

The reaction of metallic ions Ag, Cd, In and Sn with CH₄ [144] and H₂O [145] are experimentally conducted in a room temperature helium bath at 0.46 mbar pressure. The reaction rate coefficients and the molecular formations are reported in the tables below.

Table 4.2: The reaction rate coefficients reported in Ref. [144] for the reaction of Ag, Cd, In and Sn with reactive gas CH₄ in a room temperature helium bath at a pressure of 0.46 mbar.

Ions	Adduct	Reaction rate coefficient k [cm ³ molecule ⁻¹ s ⁻¹]	Primary product	Higher-order products
Ag ⁺	CH ₄	2×10^{-13}	Ag ⁺ (CH ₄)	Ag ⁺ (CH ₄) ₂
Cd ⁺	CH ₄	$< 10^{-13}$	Cd ⁺ (CH ₄)	no reaction
In ⁺	CH ₄	$< 10^{-13}$	no reaction	no reaction
Sn ⁺	CH ₄	$< 10^{-13}$	no reaction	no reaction

Table 4.3: The reaction rate coefficients reported in Ref. [145] for the reaction of Ag, Cd, In and Sn with reactive gas H₂O in a room temperature helium bath at a pressure of 0.46 mbar.

Ions	Adduct	Reaction rate coefficient k [cm ³ molecule ⁻¹ s ⁻¹]	Primary product	Higher-order products
Ag ⁺	H ₂ O	7×10^{-13}	Ag ⁺ (H ₂ O)	Ag ⁺ (H ₂ O) ₂
Cd ⁺	H ₂ O	$< 5 \times 10^{-13}$	no reaction	no reaction
In ⁺	H ₂ O	$< 5 \times 10^{-13}$	no reaction	no reaction
Sn ⁺	H ₂ O	$< 5 \times 10^{-13}$	no reaction	no reaction

A higher tendency of cluster formation of two isobaric contaminants Ag^+ and Cd^+ with reactive gases like CH_4 and H_2O offers the possibility for the separation of the other low-produced isobars In^+ and Sn^+ . Isobaric separation would be then possible according to the higher mass of the ions with an adduct attached to them by using a quadrupole mass filter behind the gas catcher in the ion transportation line (see section 4.2.3).

However, the capability of implementing this technique for isobaric separation still needs to be developed for systematic studies required for finding the most suitable reactive gas. This new technique of isobaric separation is under investigation by developing the CISE (Chemical Isobaric SEparation) setup in off-line measurements by studying the stable isotopes of these exotic nuclei since the chemical behavior of stable and exotic nuclei of the same element will be the same. The details of the work will be described in the following sections.

4.2 CISE setup

The CISE setup is being developed and built at KVI-Center for Advanced Radiation Technology institute. The setup consists of a gas catcher and an ion-guide coupled to a commercial quadrupole Time-of-Flight (qToF) spectrometer from Micromass, United Kingdom (model: qToF2 hybrid). The layout of the CISE setup is shown in Figure 4.2. The chemical isobaric separation technique is under development in several steps of off-line measurements. The off-line measurements are planned by using the laser ablation ion source within the under-construction gas catcher and some preliminary measurements are done by using the electrospray ion source in replace of the gas catcher (section 4.4).

Figure 4.2: Schematic of the CISE setup which consists of a gas catcher and an ion-guide that are coupled to a commercial qToF. The ion-guide system consists of Hexapole 1 and Hexapole 2. The qToF is a quadrupole mass spectrometer (Quadrupole MS) coupled with a reflection Time-of-Flight mass spectrometer (ToF MS).

Ions from the gas cell will be transferred by the ion-guide assembly to the qToF mass spectrometer for detecting chemical mass species either by MS1 (Quadrupole MS) or MS2 (ToF MS). The technical developments and ion optical simulation for the different parts of the CISE setup will be discussed in the following sections in more details.

4.2.1 Gas catcher

The gas catcher in CISE setup is developed by Brankica Andjelic at KVI-CART [PhD thesis in preparation]. The gas catcher is designed in a cylindrically-shaped vacuum chamber with the size of 450 mm in length and 400 mm in diameter. It consists of 16 DC ring electrodes connected to a series of DC potentials with decreasing potentials in steps of 7 V/cm for guiding ions along the main body of the gas catcher and toward the

end, where an RF carpet is placed. The RF carpet is made of thin circular-shaped electrodes printed on a PCB board with 1 mm thickness. A combination of RF ($100 V_{pp}$ at 10 MHz) and DC gradient potential (3 V/cm) applied to RF carpet electrodes provide the fields to guide the ions toward the central hole of the RF carpet. A supersonic gas flow then pushes ions out of the gas catcher through the RF carpet's hole with a diameter of 0.45 mm. Figure 4.3 shows the schematic view of forces applied to the ions within the gas catcher [146].

Figure 4.3: The DC and RF forces applied to the ions inside the gas catcher. The plot is from Ref. [146].

Ion trajectories in the vicinity of the exit hole of the RF carpet are simulated by using COMSOL Multiphysics software (figure 4.4) taken from Brankica Andgelic's thesis [146].

Figure 4.4: Ion trajectories in the vicinity of the exit hole of the RF carpet. The color code refers to the kinetic energy of the ions. The simulation includes gas flow as well as the DC and RF fields calculations. The collisions of ions with helium gas are simulated based on viscous-drag model [137]. A 100% transmission efficiency is obtained in the simulation models [147]. The gas pressure inside the cell is 50 mbar (He/CH₄). Simulations from Brankica Andgelic's PhD thesis [146].

The laser ablation ion source is chosen to be implemented inside the gas catcher for production of stable isotopes of the metallic ions ^{100}Sn , ^{100}Cd and ^{100}Ag and ^{100}In mentioned in the previous section as an example of separation application. The gas catcher is filled with a mixture of helium and methane gases at 50 mbar pressure. The ratios of the gas mixture can be changed for optimizing the chemical reactions. However, all the ion-optical simulations and collision cross sections are done by assuming the ratio of 95% He plus 5% CH₄ reactive gas as the starting values for the gas mixture. These conditions result in a gas concentration of $[I] = 6 \times 10^{16} \text{ 1/cm}^3$ for CH₄ and a reaction time constant of $\tau = 8.3 \times 10^{-5}$ seconds e.g. for Ag ions reacting with CH₄ (see equations 4.2 and 4.3).

4.2.2 Coupling ion-guide

The design of the coupling ion-guide is done in two sections in order to have a sufficient differential pumping behind the gas catcher. The multiple ion-guides are in hexapole configuration for a better acceptance of the extracted ions from the gas catcher and a less RF heating of the ions during the transportation compared to the quadrupole ion-guide systems. A short hexapole is placed in the first section called "hexapole 1" and a longer hexapole in section two called "hexapole 2" where it connects to the qToF spectrometer. Hexapole 2 is designed to be long enough in space to accommodate a strong turbo pumps with large flange diameters. Three electrostatic lenses with reducing size of the apertures are placed between hexapole 1 and hexapole 2. First two lenses with larger apertures (6 mm and 5 mm) are designed for focusing of the ions and the last one with a small aperture (3 mm) acts as a differential pumping barrier. The schematic view of the coupling ion-guide is demonstrated in figure 4.5.

Figure 4.5: Coupling ion-guide assembly including hexapole 1 and hexapole 2 and three electrostatic lenses in between.

Differential pumping

Figure 4.6 shows the schematic view of the differential pumping system of the coupling ion-guide assembly in order to couple the higher pressure gas catcher to the lower pressure qToF mass spectrometer. Since the gas catcher is held at 50 mbar pressure, the two sections of the coupling ion-guide should be capable of decreasing the pressure by more than 6 orders of magnitude required for the qToF spectrometer. The gas catcher

is separated from section one (hexapole 1) by the RF carpet with a hole at the center with a diameter of 0.45 mm. Section one is connected to a turbo pump, Leybold 2300 l/s DN200. Section one and two are separated by one of the electrostatic lenses with a hole size of 3 mm in diameter. Section two is connected to a 250 l/s turbo pump with DN100 flange size. The section two is also separated from the qToF chamber with an aperture with a hole at the center with a diameter of 3 mm.

Figure 4.6: The schematic view of the differential pumping system of the CISE setup.

The mass flow rate Q going through a aperture from a chamber at higher pressure (e.g. P_0) to a chamber at lower pressure (e.g. P_1) can be defined as below [148] assuming ($P_1 < P_0$):

$$Q = 14.2 \frac{d^2}{\sqrt{mT}} \times P_0 \quad \left[\text{mbar} \cdot \frac{1}{\text{s}} \right] \quad (4.4)$$

where m is the mass number of gas (e.g. $m = 4$ for He), d is the diameter of aperture in [mm] and T is the gas temperature in [Kelvin]. Therefore, the pressure at the following chamber which is connected to a pump with pump speed V [l/s] can be calculated as:

$$P_1 = \frac{Q}{V} \quad [\text{mbar}] \quad (4.5)$$

By considering $P_0 = 50$ mbar pressure of the room temperature helium gas ($T = 300$ K) in the gas catcher with $d = 0.45$ mm for the size of the extraction aperture of the RF carpet, the mass flow rate is equal to $Q_1 = 4.2$ mbar·l/s going to section one. The pressure at section one then calculated to be $\sim 3 \times 10^{-3}$ mbar. To calculate this pressure, one needs to evaluate first an effective pump speed V_{eff} which is calculated as:

$$\frac{1}{V_{eff}} = \frac{1}{V} + \frac{1}{C} \quad (4.6)$$

where V is the pump speed of the turbo pump at section one (2300 l/s for air and for this case ~ 2050 l/s for helium) and C is the conductance of flange with DN200 ($C = 11.6 \times A \times c$). Parameter A is cross section of the flange in cm^2 and c is the correction factor for helium gas, $c = 2.64$.

The same calculations for section two give the mass flow rate $Q_2 = 9 \times 10^{-3}$ mbar·l/s and $p_2 \approx 4 \times 10^{-5}$ mbar. The differential pumping calculations then provide a safe pressure of below 10^{-5} mbar required for the operation of the MS1 (Quadrupole MS) and a pressure below 10^{-6} mbar for MS2 (ToF MS) mass spectrometer.

Hexapole 1

Hexapole 1 consists of six stainless steel rods of $r_e = 2.5$ mm radius and 125 mm length. The distance between the face of two opposite rods is $2r_0 = 8.9$ mm and an RF voltage with 120 V_{pp} at 1 MHz frequency is applied to them. Figure 4.7 shows the technical drawing of hexapole 1 together with the simulated 2D cut of the applied RF potential.

Figure 4.7: The technical drawing of hexapole 1 together with the holding assembly in the left and a cut of the RF potential simulated by COMSOL multiphysics in the right.

From the gas catcher, the ions are carried by a supersonic gas jet with a cone shape distribution (see Fig. 4.4) into hexapole 1 in section one. Figures 4.8 and 4.9 show the phase space and the energy spectrum of the extracted ions from the gas catcher at a distance of 2 mm behind the RF carpet where hexapole 1 starts. The diverging extracted ion beam will be perfectly captured by hexapole 1 as it is shown in a simulation presented in figure 4.10. The stability conditions of hexapole 1 and performed simulations show a 100% efficiency of capturing and guiding ions within hexapole 1. The stability parameters satisfy the stability conditions (see equations 3.17 and 3.18) $\eta = 0.12$ for singly charged Ag^+ ions, $\eta = 0.10$ for AgCH_4^+ and $r/r_0 = 0.14$ by considering $r = 0.62$ mm from the simulation (see figure 4.8).

Figure 4.8: The phase space of the extracted ions from the gas catcher at a distance of 2 mm behind the RF carpet. The raw data are taken from the simulations of Brankica Andjelic on RF carpet [146].

Figure 4.9: The energy spectrum of the extracted ions from the gas catcher at a distance of 2 mm behind the RF carpet. The raw data are taken from the simulations of Brankica Andjelic on RF carpet [146].

Figure 4.10: Capturing the diverging ion beam extracted from the RF carpet hole. Simulated ions from the gas catcher are imported at a distance of 2 mm behind the RF carpet where hexapole 1 starts.

Ions entering hexapole 1 will be cooled down by the collisions with the buffer gas atoms while they are traveling through it at a pressure of

$\sim 3 \times 10^{-3}$ mbar. The collision cross sections of atomic ions Ag^+ and ion cluster AgCH_4^+ with the buffer gas (mixture of 95% He + 5% CH_4) are evaluated to be $\sigma = 3.12 \times 10^{-19} \text{ m}^2$ and $8.33 \times 10^{-19} \text{ m}^2$ according to the geometrical cross section approximation of the atomic sizes:

$$\sigma = \pi(R_{\text{ion}} + R_{\text{He}})^2 \times [0.95] + \pi(R_{\text{ion}} + R_{\text{CH}_4})^2 \times [0.05] \quad (4.7)$$

where R_{ion} , R_{He} and R_{CH_4} are the van der Waals radii of the ions and the atoms of the buffer gas mixture. The collision cross section is then implemented in the collision models of the ion-optical simulations (see section 3.4).

The transport of the ions through hexapole 1 has been simulated by using the COMSOL multiphysics software (figure 4.11). The phase space of the ions evolves while they are passing through hexapole 1 by the effect of the oscillations in the RF field and also the collisions with the buffer gas atoms. Figure 4.12 and 4.13 show the evolution of the phase space of atomic ions Ag^+ and the ion clusters AgCH_4^+ in different time steps, respectively. The correlation between the velocity and the position of ions is lost at the end of hexapole 1.

Figure 4.11: Collision cooling of the ions in hexapole 1 at a pressure of $\sim 3 \times 10^{-3}$ mbar.

Figure 4.12: The evolution of the phase space of Ag^+ ions guided by hexapole 1 (figures from a, b, c, ..., j ordered in transmission time steps: 0, 1.2, 3.7, 5.0, 6.4, 8.0, 11.0, 13.0, 86.4, 350.0 μs). The phase space is evolved by the effects of both the RF field and the buffer gas collisions through hexapole 1 at $\sim 3 \times 10^{-3}$ mbar pressure. The correlation between the radial velocity and the position of ions are totally lost at the end of hexapole 1.

Figure 4.13: The evolution of the phase space of AgCH_4^+ ions guided by hexapole 1 (figures from a, b, c, ..., j ordered in transmission time steps: 0, 1.2, 3.7, 5.0, 6.4, 8.0, 11.0, 13.0, 86.4, 350.0 μs). The phase space is evolved by the effects of both the RF field and the buffer gas collisions through hexapole 1 at $\sim 3 \times 10^{-3}$ mbar pressure. The correlation between the radial velocity and the position of ions are totally lost at the end of hexapole 1.

The ions lose energy by collisions with the buffer gas in the first hexapole with a pressure of $\sim 3 \times 10^{-3}$ mbar which in turn leads to a significant broadening of the energy spectrum of ions at the end of the hexapole. The energy spectrum can even extend to energies higher than the initial energy of the entering ions due to the RF heating of ions. The blue and purple histograms in figure 4.14 show the energy of atomic ions (Ag^+) and ion clusters (AgCH_4^+) at the end of hexapole 1 cooled by ion-atom gas collisions. The FWHM is 0.7 eV for both spectra while the ion clusters (AgCH_4^+) are slowed down more due to a higher collision cross section (see equation 4.7). The mean energy of ions are 0.8 eV for Ag^+ and 0.4 eV for AgCH_4^+ at the end of hexapole 1 with a length of 125 mm. The short length of hexapole 1 prevents major losses of the ions due to the collision cooling without any axial DC gradient field based on the simulations in the COMSOL.

Figure 4.14: The energy spectrum of atomic ions Ag^+ (blue) and ion cluster AgCH_4^+ (purple) at the end of hexapole 1 with 0.7 eV FWHM for both spectra and a mean energy of 0.8 eV for Ag^+ and 0.4 eV for AgCH_4^+ ions. The spectra approximated to a Gaussian distribution to get the FWHM values.

Histogram 4.15 shows the number of collisions of Ag^+ and AgCH_4^+ ions with the buffer gas atoms (95% He and 5% CH_4) which travel through hexapole 1 at a pressure of $\sim 3 \times 10^{-3}$ mbar. A higher number of collisions are expected for the AgCH_4^+ ions due to the larger collision cross section.

Figure 4.15: The number of collisions between Ag^+ ions and the buffer gas atoms (left panel) and between AgCH_4^+ ions and the buffer gas atoms (right panel) through hexapole 1 at a pressure of $\sim 3 \times 10^{-3}$ mbar.

Electrostatic lenses and Hexapole 2

At the end of hexapole 1, ions pass through a differential pumping barrier with a small hole of 3 mm in diameter. Figures 4.16 and 4.17 show the radial distribution of Ag^+ and AgCH_4^+ ions at the end of hexapole 1 where ions reach the three focusing electrostatic lenses. The three electrostatic lenses with decreasing size of the diameter of the holes: 6, 5 and 3 mm (the last one with the smallest hole acts as the differential pumping barrier) are connected to a DC potential in decreasing steps ensure the efficient transportation of ions to hexapole 2. A potential difference of 14 V between the first and the second hexapole guarantees the acceleration of the ions towards the qToF (see figure 4.18).

Figure 4.16: The radial distribution of Ag^+ ions at the end of hexapole 1.

Figure 4.17: The radial distribution of AgCH_4^+ ions at the end of hexapole 1.

Figure 4.18: Hexapole 1 (125 mm in length), three electrostatic lenses (with diameters 6, 5 and 3 mm) and hexapole 2 (550 mm in length) in the ion-guide assembly. A potential difference of 14 V between the first and the second hexapole ensures the acceleration of ions to the qToF spectrometer which is positioned after hexapole 2.

The ion trajectory simulations in the ion-guide assembly are shown in figure 4.19 with the overall transmission efficiency of more than 90% for both atomic and ion clusters.

Figure 4.19: Ion-guide assembly with the overall transmission efficiency above 90% for both atomic and ions cluster.

The resulting simulations for the energy spectrum and the phase space of Ag^+ and AgCH_4^+ ions at the end of hexapole 2 are demonstrated in figures 4.20 and 4.21, respectively.

Figure 4.20: Energy spectrum of the ions when they reach the end of hexapole 2 with a mean energy of 14 eV for both ions.

Figure 4.21: Phase space of the ions when they reach the end of hexapole 2.

4.2.3 qToF mass spectrometer

From the ion-guide assembly, the ions are injected into a commercial qToF mass spectrometer from Micromass, United Kingdom (model: qToF2 hybrid). The qToF consists of two mass spectrometers: MS1 (Quadrupole MS) and MS2 (ToF MS); See the dashed box in figure 4.2.

- **MS1 (Quadrupole MS)**

MS1 (Quadrupole MS) includes the quadrupole analyser, the hexapole collision cell and the hexapole transfer lens (figure 4.2). The quadrupole analyser can, in principle, work in three different modes. First: as a quadrupole mass filter; second: an ion-guide for a wide range of masses and third: as a mass spectrometer synchronized with a dinolite point detector afterward for ions with masses from 10 to 4000 m/q (mass-to-charge ratio) with a mass resolving power of $R = m/\delta m = 100$. As an example, the separation of atomic ions $A = 100$ (Sn^+ , In^+) from the ion clusters $A = 116$ (AgCH_4^+ , CdCH_4^+) can be achieved by using the quadrupole mass filter mode (see figure 4.22).

Figure 4.22: The separation of the Sn^+ , In^+ from AgCH_4^+ , CdCH_4^+ in a quadrupole mass filter.

Behind the quadrupole is a hexapole collision cell which is located within an inner chamber with an extra gas inlet for making a local higher pressure in the chamber. The collision cell can be used as an additional step of chemical reactions studies in the ion transportation line for either molecular formations or Collision Induced Dissociation (CID) based on the energy of the ions.

The hexapole transfer lens focuses ions to the MS2 (ToF MS) for higher-precision mass spectrometry.

- **MS2 (ToF MS)**

The pusher plate with a high voltage pulsar initiate the time of flight path of ions in orthogonal direction toward the reflectron lenses at the bottom of MS2 (ToF MS). Ions are then reflected back toward the MCP (Micro-Channel Plate) detector where the time-of-flight of ions are registered. The MS2 (ToF MS) provides mass spectrometry with a resolving power of $R = m/\delta m = 10000$ and a mass range from 50 to 50000 m/q for identifying different chemical mass species.

4.3 Technical design developments

The technical drawings of the gas catcher and the ion-guide have been developed and the components are currently under construction. Figure 4.23 shows the main components of the gas catcher and the ion-guide coupling to the qToF mass spectrometer.

The gas catcher is designed in a way that it can be easily divided by an additional RF carpet (green carpet) into two subsequent sections to avoid problems through plasma formation in the future on-line experiments. Ions will be slowed down in the first section with higher pressure only filled with helium gas with a high ionization potential (24.5 eV). In the following section reactive gases will be introduced at lower pressure for chemical reactions. The pressure difference between the two sections provides the required gas flow to push ions through the carpet hole. For the off-line experiments, two target holders are placed inside the chamber for production of the stable ions with laser ablation technique. A base pressure of 10^{-7} mbar is achieved in the gas catcher with a 400 l/s turbo pump before helium gas injection. The ion-guide assembly is also divided to two inner vacuum chambers for differential pumping purposes. The first chamber for hexapole 1 is pumped through a very powerful turbo pump (2300 l/s) and another smaller turbo (250 l/s) is connected to the second chamber for hexapole 2.

Figure 4.23: The technical design of the gas catcher and the coupling ion-guide in the CISE setup.

4.4 Proof-of-principle by using electrospray ion source

Since the first two components of the CISE setup (gas catcher and ion-guide assembly) are still under construction, the proof-of-principle of isobaric separation technique can be investigated within the hexapole collision cell and by using an electrospray ion source (z-spray) in replace of the gas catcher attached to the qToF mass spectrometer (see figure 4.24).

The electrospray ion source is a source in which the aqueous solutions of the elements are transformed into the gas-phase ions. The desired solid crystal of ions (ion's salt) is dissolved in a proper solvent with a proper evaporation characteristics like methanol plus water. The sample solution is pumped and sprayed through a capillary needle biased to a high voltage (e.g. 3kV) and heated up to a few hundreds of centigrade. The HV together with the heat help to evaporate the droplets of spray into the gas-phase ions; and the ions are then attracted through the cone to the ion beam line. Figure 4.25 shows the main components of the electrospray ion source.

Figure 4.24: The qToF mass spectrometer with the z-spray ion source in the beginning of the setup to replace the gas catcher for the production of Ag, In, Cd and Sn ions. The chemical reactions are then investigated within the hexapole collision cell.

The sample solutions of Ag, In, Cd and Sn are prepared by dissolving the corresponding salts in water and methanol with different concentrations shown in table 4.4. The samples will be separately pumped to the electrospray source for production of ions of interest.

Figure 4.25: Electro spray ion source attached to the qToF for the production of Ag, Cd, In and Sn ions. A sketch of the system is shown on the right while a photo of the device is presented on the left.

Table 4.4: Sample solution preparation with different concentrations.

Salt	Solvent	Concentration [mg/ml]
AgNO ₃	methanol+water	2×10^{-2}
CdI ₂	methanol+water	1.2×10^{-2}
InCl ₃	methanol+water	1.7×10^{-2}
SnCl ₂ 2H ₂ O	methanol+water	1.6×10^{-1}

Table 4.5 shows the natural abundances of Ag, In, Cd and Sn stable isotopes. The positively-charged ions of Ag⁺, In⁺, Cd⁺ and Sn⁺ have been successfully identified by the qToF spectrometer, and the gas-phase chemistry has been investigated in the hexapole collision cell by applying a gas mixture of 90% Ar and 10% CH₄ with 25 and 10 VPM (Volumes Per Million) contamination of O₂ and H₂O at a pressure of 2.8×10^{-3} mbar. The left column in figure 4.26 shows the mass spectra of positively-charged ions produced by the electro spray ion source and sent through the empty (6×10^{-5} mbar) hexapole collision cell to be subsequently identified by the qToF mass spectrometer.

Table 4.5: The natural abundance of the Ag, In, Cd and Sn elements on earth.

Isotope	Natural abundances
¹⁰⁷ Ag	51.84 %
¹⁰⁹ Ag	48.16 %
¹¹³ In	4.29 %
¹¹⁵ In	95.71 %
¹⁰⁶ Cd	1.25 %
¹⁰⁸ Cd	0.89 %
¹¹⁰ Cd	12.49 %
¹¹¹ Cd	12.8 %
¹¹² Cd	24.13 %
¹¹³ Cd	12.22 %
¹¹⁴ Cd	28.73 %
¹¹⁶ Cd	7.49 %
¹¹² Sn	0.97 %
¹¹⁴ Sn	0.66 %
¹¹⁵ Sn	0.34 %
¹¹⁶ Sn	14.54 %
¹¹⁷ Sn	7.68 %
¹¹⁸ Sn	24.22 %
¹¹⁹ Sn	8.59 %
¹²⁰ Sn	32.58 %
¹²² Sn	4.63 %
¹²⁴ Sn	5.79 %

In the next measurements, the hexapole collision cell is filled with the reactive gas mixture with a pressure of up to 2.8×10^{-3} mbar for investigation of the chemical reactions in the hexapole collision cell. The right column in figure 4.26 shows the mass spectra for ions passing through the hexapole collision cell filled with background reactive gas for inducing the cluster formations in the collisions. One can see that the Ag^+ isotopes mostly reacted with the H_2O contaminants in the buffer gas in hexapole collision cell and made heavier clusters of $\text{Ag}^+(\text{H}_2\text{O})$ and $\text{Ag}^+(\text{H}_2\text{O})_2$. In addition, some less dominant peaks are also identified for the reaction of Ag^+ ions with CH_4 gas in the hexapole collision cell. Table 4.6 shows a list of the positively-charged clusters of Ag ions identified by the qToF mass spectrometer based on the mass-to-charge ratio of the components. Total reaction yield is calculated for each isotope.

Figure 4.26: The left column shows the mass spectra for ions produced by the z-spray source and sent through the hexapole collision cell at 6×10^{-5} mbar that have subsequently been identified by the qToF spectrometer. The right column shows the same measurement but the hexapole collision cell is filled up to 2.8×10^{-3} mbar by a gas mixture of Ar/ CH_4 with O_2 and H_2O contaminants.

Table 4.6: The positively-charged clusters formed by Ag ions and the buffer gas atoms in the hexapole collision cell at a pressure of 2.8×10^{-3} mbar filled with a gas mixture of Ar/CH₄ with O₂ and H₂O contaminants. The last column shows the reaction yield for each identified peak (N_A/N_{total}) and bold values represent the total reaction yields for each isotope.

<i>A</i>	Products	N_A/N_{total} (%)
124	$^{107}\text{Ag}^+\text{OH}$	1.5 ± 0.1
125	$^{107}\text{Ag}^+\text{H}_2\text{O}$	30.6 ± 0.7
139	$^{107}\text{Ag}^+(\text{CH}_4)_2$	2.0 ± 0.2
142	$^{107}\text{Ag}^+(\text{H}_2\text{O})\text{OH}$	1.3 ± 0.1
143	$^{107}\text{Ag}^+(\text{H}_2\text{O})_2$	18.2 ± 0.5
157	$^{107}\text{Ag}^+(\text{CH}_4)_2\text{H}_2\text{O}$	1.2 ± 0.1
Total reaction yield for ^{107}Ag		54.7 ± 1.1
126	$^{109}\text{Ag}^+\text{OH}$	1.9 ± 0.2
127	$^{109}\text{Ag}^+\text{H}_2\text{O}$	31.5 ± 0.8
141	$^{109}\text{Ag}^+(\text{CH}_4)_2$	2.2 ± 0.2
144	$^{109}\text{Ag}^+(\text{H}_2\text{O})\text{OH}$	1.5 ± 0.1
145	$^{109}\text{Ag}^+(\text{H}_2\text{O})_2$	17.5 ± 0.5
159	$^{109}\text{Ag}^+(\text{CH}_4)_2\text{H}_2\text{O}$	1.2 ± 0.1
Total reaction yield for ^{109}Ag		55.9 ± 1.2

The spectrum for In⁺ shows that it has not reacted with any components in the gas mixture in the hexapole collision cell and still are detected as atomic ions at qToF (see figure 4.26 for In). In contrast, for the case of Cd⁺, it is seen that they also chemically reacted with H₂O and two CH₄ molecules in the hexapole collision cell and reached qToF as heavier clusters (see figure 4.26). The cluster formations and the reaction yields are listed below (table 4.7):

Table 4.7: The positively-charged clusters formed by Cd ions and the buffer gas atoms in hexapole collision cell at a pressure of 2.8×10^{-3} mbar filled with a gas mixture of Ar/CH₄ with O₂ and H₂O contaminants. The last column shows the reaction yield for each identified peak (N_A/N_{total}).

A	Products	N_A/N_{total} (%)
124	$^{106}\text{Cd}^+\text{H}_2\text{O}$	22.2 ± 10.0
126	$^{108}\text{Cd}^+\text{H}_2\text{O}$	35.0 ± 15.4
128	$^{110}\text{Cd}^+\text{H}_2\text{O}$	21.5 ± 3.3
129	$^{111}\text{Cd}^+\text{H}_2\text{O}$	27.3 ± 3.5
130	$^{112}\text{Cd}^+\text{H}_2\text{O}$	25.7 ± 2.5
131	$^{113}\text{Cd}^+\text{H}_2\text{O}$	31.5 ± 3.9
132	$^{114}\text{Cd}^+\text{H}_2\text{O}$	23.9 ± 2.2
134	$^{116}\text{Cd}^+\text{H}_2\text{O}$	17.4 ± 3.5
142	$^{110}\text{Cd}^+(\text{CH}_4)_2$	2.1 ± 1.0
143	$^{111}\text{Cd}^+(\text{CH}_4)_2$	3.5 ± 1.1
144	$^{112}\text{Cd}^+(\text{CH}_4)_2$	2.8 ± 0.8
145	$^{113}\text{Cd}^+(\text{CH}_4)_2$	3.3 ± 1.1
146	$^{114}\text{Cd}^+(\text{CH}_4)_2$	3.8 ± 0.8
148	$^{116}\text{Cd}^+(\text{CH}_4)_2$	6.0 ± 1.9

The left spectrum for Sn⁺ in figure 4.26 shows that the different stable isotopes of Sn have been identified by the qToF spectrometer, however the low efficiency for the number of ions produced in electrospray ion source did not allow to study the chemical reactions with the buffer gas in the hexapole collision cell. A different kind of Sn⁺ salt would help to achieve a higher ion-production rate by electrospray ion source and a better condition to study the chemical reactions of Sn⁺ isotopes in the future.

The presented results suggest the proof-of-principle for isobaric separation technique with the help of chemical reactions. The measurements show a clear tendency of two elements Ag⁺ and Cd⁺ to have a larger probability of chemical reactions with the buffer gas to form ion clusters. The heavier cluster can, therefore, be separated from the other species living as atomic ions. However, the

technique needs to be investigated in more details and many systematic studies such as pressure dependence of reaction, longer collision times and different gas types and gas mixtures still need to be done for further developments.

With this technique, proper chemistry conditions are investigated by using stable isotopes of these four elements. The same chemistry can be implemented for the separation of exotic nuclei with the same mass numbers $^{100}\text{Ag}^+$, $^{100}\text{Cd}^+$, $^{100}\text{In}^+$ and $^{100}\text{Sn}^+$ in on-line experiments.

4.5 Conclusion and outlook

The CISE setup was developed at KVI-CART for investigation of a novel technique for the chemical isobaric separation. It consists of a gas catcher and an ion-guide assembly coupled to a commercial qToF mass spectrometer. The ion-optical simulations have been performed for the coupling of the gas catcher to the qToF mass spectrometer in the CISE setup. The simulations for the current design of the coupling ion-guide show an efficiency of better than 90% for the ion transportation. This high efficiency is achieved by a proper differential pumping system desired for the coupling and operation of the qToF mass spectrometer with a goal of final pressure below 10^{-6} mbar.

Since the gas catcher and the coupling ion-guide are under construction, the first step of measurements are performed by using an electrospray ion source attached to the qToF instead of the gas catcher and the chemical reactions are investigated within the hexapole collision cell in the beamline. The positively-charged Sn^+ , Ag^+ , In^+ and Cd^+ are produced by the electrospray ion source and are measured with the qToF mass spectrometer. The chemical reactions have been studied within the hexapole collision cell and suggest the proof-of-principle for chemical isobaric separation technique based on the different cluster formations. The final results presented in table 4.8 show a high tendency of two isobars Ag and Cd to have cluster formations with the reactive gas contaminants in the hexapole collision cell.

Table 4.8: The final results show the reaction yield of Ag, In, Cd ions chemically reacting with the buffer gas at the hexapole collision cell. The data for Sn ion are not presented because of low production efficiency.

Isotopes	Total count (N_{total})	Reacted with gas (N_1)	Reaction yield $N_1/N_{total}(\%)$
Ag	14450	7986	55.3 ± 0.8
In	1300	0	0 %
Cd	2101	597	28.4 ± 1.3
Sn	—	—	—

The studies of the chemical reactions performed within the hexapole collision cell were limited due to the maximum allowed pressure applied to the hexapole collision cell below 2.8×10^{-3} mbar and also limited to the low reaction time of ions passing through the hexapole collision cell. For example, the calculation shows a very small expected reaction rate $r = 1.35$ molecules/s (see formula 4.2) for the cluster formation of Ag^+ and CH_4 in the hexapole collision cell with 10% concentration of the CH_4 in the gas. Considering a reaction time of $t = 50 \mu\text{s}$ for an ion passing through the hexapole collision cell would yield a very low number of collisions under the current conditions, $r \times t = 6.5 \times 10^{-5}$. However, these studies will serve as a guidance for future experiments with the gas catcher and coupling ion-guide attached to the qToF for investigation of chemical reactions within the gas catcher at higher pressures ($p \approx 50$ mbar) and higher reaction times ($t \approx 40$ ms) for the ions reacting inside the gas catcher before extraction. The higher pressure and longer reaction time at gas catcher even for 5% concentration of CH_4 ($[I] = 6 \times 10^{16} \text{ 1/cm}^3$) provide a high reaction rate of $r = 1.21 \times 10^4$ molecules/s and a reaction time constant of $\tau = 8.3 \times 10^{-5}$ s (see equations 4.2 and 4.3). These conditions allow for more systematical studies and the full commissioning of the technique for the chemical isobaric separation.

The chemical isobaric separation technique developed in off-line measurements opens the door to establish the CISE technique for experimental studies of short-lived and rarely-produced isotopes in accelerator-based experiments. One potential application will be the challenging capture of the doubly-magic ^{100}Sn isotope for high-precision mass measurements.

Chapter 5

FRS experimental setup and gas cleanliness of the cryogenic stopping cell

In this chapter, the experimental setup of FRS at GSI will be outlined. Furthermore, the gas cleanliness of the Cryogenic Stopping Cell (CSC) at FRS Ion Catcher setup will be discussed.

The high-energy fragments from the FRS are slowed down and thermalized in the gas-filled stopping cell of the FRS Ion Catcher at GSI. One of the main challenges with this type of cells is the buffer gas, which can strongly influence the ion survival and the extraction efficiency of the stopping cell. Minute impurities in the buffer gas can lead to the formation of molecules, charge-exchange reactions and even neutralization of the ions of interest. Molecular formations also change the mobility of the ions which can pose more limitations on the RF carpet operation for extracting different atomic and molecular ions. Therefore, the impurities in the buffer gas of the FRS cryogenic stopping cell must be controlled (to the levels below ppb) and continuously monitored using different techniques. The techniques will be also used in future in the helium recovery unit at the Super-FRS Ion Catcher for recycling of the helium gas required for the high-density operation of the gas cell.

5.1 Experimental facility at GSI

The GSI Helmholtz Center for Heavy Ion Research placed at Darmstadt, Germany focuses on research with exotic nuclei and their applications. In the facility, a very wide range of ions can be produced and accelerated from protons up to $^{238}\text{U}^{n+}$ ions at the UNiversal Linear ACcelerator (UNILAC) [149] and used for many experimental investigations from fundamental physics to the medical and the space science applications. Figure 5.1 shows the schematic overview of the GSI facility.

Figure 5.1: The GSI Helmholtz Center for Heavy Ion Research located at Darmstadt, Germany.

The primary ion beam from UNILAC can be also injected to the heavy-ion synchrotron (SIS-18) [150] for further acceleration of the ions to relativistic energies. Figure 5.2 shows the high-energy beam-line of GSI capable for accelerating the ions from 3-20 MeV/u up to 1-2 GeV/u and production of the secondary exotic beams in the FRagment Separator (FRS) [73]. The secondary exotic beam can then be delivered to different experimental areas such as Electromagnetic Storage Ring (ESR) [99] or the experimental area of R³B (Reactions with Relativistic Radioactive Beams) [74] for experiments with the exotic nuclei.

Figure 5.2: The high-energy beam-lines of the GSI facility.

5.1.1 Fragment separator (FRS)

The FRagment Separator (FRS) is a high-resolution in-flight mass spectrometer/separator for the isotopes produced in projectile fragmentation and projectile fission reactions [73]. The main part of the FRS consists of four 30° dipole magnets as the main separators and a set of quadrupole and hexapole magnets before and after them for the first-order and the second-order ion focusing and the ion-optical aberration corrections. The FRS operates at a momentum resolving power of 1500.

Thanks to the different degraders (flat and wedge shapes) and the flexible optic layout the FRS can also work in different operation modes, e.g. as an energy loss spectrometer. As a separator (figure 5.3), it works in two different modes of operation [73]. **Achromatic mode:** where the ions are focused on the final focal plane with a minimum spatial distribution but having a large energy/momentum spread; **Monochromatic mode:** where the energy/momentum spread is reduced by up to a factor of 10 but the ions have a large spatial spread in the final focal plane [151]. The latter mode is more favorable to stop the major part of the fragments in the limited thickness (areal density) of the gas stopping cell.

A set of different Particle IDentification (PID) detectors are placed in the FRS beam line for identifying the fragments and also measuring and monitoring the intensity, the time-of-flight and the energy loss of the fragments. These also

Figure 5.3: The FRS (Fragment Separator) [73] is a high-resolution in-flight mass spectrometer/separator for the isotopes produced in the projectile fragmentation and the projectile fission reactions [152].

allow proper tuning of the magnets and different components of the separator. The plastic scintillators (SCI) are used for measuring the time-of-flight and for monitoring the intensity of the fragments at the different steps of the FRS. The Time Projectile Chamber (TPC) detectors are used for monitoring the position and angle of fragments providing their track lengths through the magnets. The combination of the SCI and the TPC is used for the identification of the fragments based on the calculated A/Q from the time-of-flight and the distance they travel. The Multiple Sampling Ionization Chamber (MUSIC) detectors are installed for measuring the energy deposition of the fragments in the gas. A SCI and a MUSIC detector in front of the stopping cell provide the ion count rate entering the stopping cell together with the energy deposition translation of the ions to the center of the gas cell.

5.1.2 FRS Ion Catcher setup

The FRS Ion Catcher (FRS-IC) is located at the final focal plane of the fragment separator (FRS) for stopping the high-energy fragments for high-precision measurements on the low-energy exotic ions (see figure 5.4). The main parts of the FRS-IC are the Cryogenic Stopping Cell (CSC) for stopping and thermalization of ions in the gas, the RFQ beamline for transporting the low energy ions and the Multiple-Reflection Time-of-Flight Mass Spectrometer (MR-TOF-MS) for the high-precision mass spectrometry and the isomeric separation. The FRS-IC setup is also a test facility for the future Low Energy Branch (LEB) at the Super-FRS of the FAIR facility [153, 154].

Figure 5.4: The FRS ion-catcher setup at final focal plane of the fragment separator FRS at GSI for the high-precision mass measurements and isobaric separation [152].

Multiple-Reflection Time-Of-Flight Mass Spectrometer

The FRS Ion Catcher is one of the most powerful setups in the world for the precision mass measurements and isobaric separations of the short-lived exotic nuclei with the Multiple-Reflection Time-Of-Flight Mass Spectrometer (MR-TOF-MS) technique. The technique is well suited to the most challenging experiments of the short-lived nuclei far away from the valley of stability, because it allows for exceptionally fast and broadband mass measurements with a high mass accuracy.

The low-energy ions (a few eVs) from CSC (figure 5.4) are guided by the RFQ beamline and the RFQ switchyard toward the injection trap system of MR-TOF-MS (figure 5.5). The ions are further cooled and bunched in the multi-stage trap system and then the potential of the last trap is lifted up to increase the potential energy of the bunched ions (to 1.3 keV/q) and subsequently inject them to the main mass analyzer with a repetition rate of 50 Hz. The ions then travel several Isochronous Turns (IT) in the analyzer with the electrostatic reflectors at the entrance and exit of the analyzer. The reflectors switch during the injection and ejection of the ions from the analyzer. The mass range selector (MRS) at the center of the analyzer is designed for the beam alignment and cutting a certain range of the m/q of the ions traveling in the analyzer. The lighter (smaller m/q) and the heavier (larger m/q) ions will get spatially separated in their multi-turn pathline in the main analyzer. Afterward, the exit reflector switches for the ejection of the ions from the analyzer. The ions are then reflected and energy-focused toward the TOF detector by the time focus shift reflector (TFS) at the bottom of MR-TOF-MS. The TOF detector then register the time-of-flight of the

incoming ions with different m/q values triggered by the initial injection time from the trap system. The analog signal from the detector is then converted to the digital data by the TDC (time-to-digital converter) and recorded on the PC. The data are then translated to the m/q values in the data-acquisition software. Figure 5.5 shows the MR-TOF-MS at the FRS Ion Catcher setup in more details [108]. The differential pumping stages at MR-TOF-MS also provides a proper vacuum condition for the trap system at 5×10^{-3} mbar for the collision cooling of the ions and a pressure of 5×10^{-8} mbar in the analyzer.

Figure 5.5: The Multiple-Reflection Time-Of-Flight Mass Spectrometer MR-TOF-MS at FRS Ion Catcher setup [108, 155].

5.2 Ultra-clean Helium gas in CSC

Operation of the Cryogenic Stopping Cell (CSC) of FRS-IC at relatively high areal gas density (a factor of 10 higher than other operating cells, e.g. SHIP-TRAP cell [156]) and a factor of two longer extraction times [156] makes the FRS-IC setup much more sensitive to the gas impurities due to the higher number of collisions between the ions and the buffer gas atoms.

The quality and the cleanliness of the gas filling CSC (Cryogenic Stopping Cell) is a very important topic, which strongly influence the ion survival and the extraction efficiency of ions from the stopping cell. Within a non-perfect gas condition ions-of-interest form molecules with the impurities in the gas or do the charge-exchange reaction or even neutralization. The latter will cause the loss of the ions in the CSC. The molecular formation and the unexpected charge-state of the ions also cause a significant change of the ion mobility resulting in a reduction of the extraction efficiency of the ions specially on the RF carpet [157]. The impurities in the gas cell can be also ionized by the deposited energy of the beam or in the charge-exchange reactions, and get extracted from the stopping cell as an additional unwanted space-charge in the RFQ beamline and the trap system reducing the ion-transport efficiency. Extracted impurities can also overlap with the ions-of-interest with the same m/q values in the MR-TOF mass spectrum influencing the mass data evaluations with the higher background contamination.

The FRS-IC stopping cell is filled with pure Helium 6.0 gas and operated at the cryogenic temperature providing clean gas conditions for the stopping and the extraction of the ions. The gas quality, however, should be still improved and continuously monitored to guarantee a stable and reliable operation of CSC at ultra-clean gas conditions. Considering a gas cell operating at 100 mbar and 80 K, ions with an average extraction time of 25 ms [152] undergo $\approx 10^8$ collisions with the buffer gas atoms before extraction from the gas cell. This means a gas cleanliness of 1 ppb is needed to guarantee a maximum ion survival and extraction from the stopping cell. Beside the already mentioned high gas quality and cryogenic operation, the techniques for further improvement of the gas condition are gas purifiers, LN₂ cold trap, the collision cleaning of the gas line [158] and a proper cleaning and baking of the gas line components in ultrasonic bath, etc. which will be discussed in the following sections.

5.3 Upgraded gas handling system for the FRS Ion Catcher

Figure 5.6 demonstrates the upgraded gas distribution system developed for the FRS Ion Catcher setup for providing an ultra-pure He gas condition. The recent upgrades in this thesis includes the new gas lines for the different gas purification systems, the cold trap gas purifier, the helium bundles with larger capacity and also a completely new trace gas line for the charge-state manipulations of the ions in the gas. The He 6.0 gas can go through the different gas purifiers from different gas line to CSC and also to the RFQ beamline and the MR-TOF trap system.

Figure 5.6: The upgraded gas-handling system of the FRS Ion Catcher setup.

5.4 Cold Trap gas purifier

Cold trap (CT) is a gas purifier developed in house (as a part of the present work) and used in addition to the standard gas purifiers (SAES Microtorr and Monotorr) for further improving the gas conditions. The main advantage of the cold trap is suppressing the noble gases in the helium which is not, in principle, possible to be removed by the standard gas purifiers. The cold trap is a dewar filled with liquid nitrogen LN_2 (77 K) surrounding the helium gas line as shown in figure 5.7. The helium gas line is also filled with activated carbon adsorbents (charcoal) and operated at 2 Bar helium pressure.

Figure 5.7: The cold trap (CT) gas purifier cooled with liquid nitrogen down to 77 K. The helium gas line is filled with activated carbon material.

The suppression of impurities by the cold trap is mainly happening in two ways:

- **Condensation of impurities:**

The helium gas surrounded by liquid nitrogen at a temperature of 77 K can freeze out the impurities with relatively high condensation temperature. Figure 5.8 shown the partial pressure versus the condensation temperature of the different gases. For example, decreasing the temperature of the gas from 200 to 77 K can suppress the partial pressure of the CO_2 by 9 orders of magnitude down to $P_{\text{par.}} = 10^{-6}$ mbar. Considering the fact that a pressure of 2 bar is used for the helium in the gas line, a contamination level of $P_{\text{par.}} / P < \text{ppb}$ level can be achieved for the case of CO_2 .

- **Surface adsorption by activated carbon:**

The molecular sieve material like "Activated charcoal" and "Zeolites" are very powerful gas adsorbents due to their huge surface areas ($\approx 10^3 \text{ m}^2/\text{g}$), used widely in the industrial applications. The physical surface adsorption can capture the noble gases like Kr and Xe [159] (not chemically reactive) more effectively than the regular gas purifiers. Cooling of the adsorbents materials to the cryogenic temperature can also massively increase the adsorption capacity. However, the activated carbon will be saturated after certain amount of adsorption and need to be regenerated. The regeneration is done by baking the charcoal up to 130 °C while pumping the gas line for a few hours.

Figure 5.8: The vapor pressure curves of different gases [160]. The plot is adopted from I. Pohjalainen's PhD thesis [161].

Xe and Kr suppression with cold trap

Although the Xe and Kr contamination levels are not specified in the impurity compositions of the helium 6.0 gas bottles, they are present in the gas due to the history of the gas bottles. The gas bottles are long-lived components which are refilled and reused many times for different gases in their lifetime. Therefore, a trace amount of the noble gases can be present in the gas bottle filled with helium. Table 5.1 shows different levels of Xe contamination in two random helium gas bottles for FRS-IC setup used in a similar conditions while the fission fragments (from offline source inside CSC) are identified with the same count rates, both measured with MR-TOF-MS.

Table 5.1: The measured Xe contamination levels from two random helium gas bottles used for FRS-IC in a similar operational condition while the fission fragments FF (from offline source inside CSC) are identified with a stable count rate with MR-TOF-MS. Xe are ionized by charge-exchange reaction with He^+ and then are extracted from CSC.

A	Bottle No. 1		Bottle No. 2	
	Xe ⁺ (Counts/h)	FF (Counts/h)	Xe ⁺ (Counts/h)	FF (Counts/h)
131	130	97	827	136
132	180	153	1034	181
134	72	304	404	243
Sum	382	554	2265	560

Suppressing these noble gases as heavy impurities present in the gas is quite challenging but really important for the mass-measurement experiments at FRS Ion Catcher. The contamination level can be high enough to strongly affect the gas cleanliness and operation of CSC during the online experiments. They can be ionized either by the deposited energy of the high-energy entering ions or be ionized in the charge-exchange reactions with ions-of-interest/ He^+ and subsequently even form adducts at cryogenic temperatures (e.g. KrN_2^+ or XeO_2^+). In all cases, the ionized noble gases can be extracted from the stopping cell and make some additional space-charge in the beam line and also for the MR-TOF-MS mass measurement. The noble gas impurities are more problematic comparing to other usual light impurities like H_2O and N_2 due to the difficulty for removing them and also having higher masses close to most of the interesting medium-heavy and exotic isotopes in $N = Z$ mass measurements.

For investigating the noble-gas suppression of the cold trap, CSC was filled with 50 mbar helium gas pressure with and without the cold trap in the gas line. The extracted-ion count rate of Xe^+ and Kr^+ are then monitored with MR-TOF-MS in both conditions of the gas. For these measurements, the noble gases present in the gas are mainly ionized in the charge-exchange reactions with

He^+ ions produced by the deposited energy from offline sources (^{252}Cf fission source and ^{228}Th α -source installed inside CSC) and are extracted from CSC and are identified by MR-TOF-MS. Table 5.2 (column a) shows the ion count rate for different Xe^+ isotopes with and without the cold trap. An average improvement factor of **6.5 times** for all natural abundant isotopes by using the cold trap is observed. Figure 5.9 shows the logarithmic mass spectrum for the same measurement time with and without the cold trap. The dominant ^{133}Cs peak is the calibration peak from the MR-TOF-MS ion source. SF_5 and $m/q = 139$ are other impurities coming from the gas in the gas cell which also decrease by the use of the cold trap.

Figure 5.9: The Xe^+ count rates coming from the CSC filled without (top plot) and with (bottom plot) the cold trap in the gas line. The ions are identified with MR-TOF-MS.

One should take into account that only a fraction of the Xe atoms are ionized by using the offline sources inside CSC. Indeed, the Xe^+ count rate can be much higher during the online experiments when the deposited energy by the high-energy fragments are orders of magnitude higher than the offline sources. For the online experiments, every single high-energy entering ions can, on average,

produce 10^7 He^+e^- pairs [72] during the stopping process in the gas (the number of directly-ionized impurities is usually negligible due to low concentrations). Therefore, the charge-exchange collisions resulting the ionization of Xe as a small fraction of the He gas will be also much higher and more problematic during the experiments. It is important to estimate the Xe concentration in the gas and also estimate the expected Xe^+ rate during the online experiments. A technique has been used [162] to estimate these two parameters by measuring the electron current on the entrance flange of CSC. By applying a weak electric field along the CSC body one can collect the electrons produced during the stopping of the high-energy ions; see figure 5.10.

Figure 5.10: Electron-current measurement on entrance flange produced by deposited energy from stopping of the high-energy ions.

The electron current has been measured on the entrance flange for the different pressures of CSC in Ref. [162]. The higher the pressure, the higher the stopping power of the gas resulting in a higher current on the entrance flange. A current of 33 pA is measured at 50 mbar gas pressure (Ref. [162]) which corresponds to 2×10^8 He^+e^- pairs produced by stopping of the off-line source recoils installed inside CSC [112] in which each of the He^+ ions undergoes about 10^8 collisions with the buffer gas atoms before extraction/neutralization. By detecting the Xe^+ ions on MR-TOF-MS and considering the extraction and the detection efficiencies (CSC extraction efficiency of 50%, the beamline and MR-TOF efficiency of 10% and the detection efficiency of 80%), one can trace back and calculate the number of Xe^+ produced inside CSC in the charge-exchange reactions from the total number of collisions ($2 \times 10^8 \times 10^8$). By taking the number of Xe^+ ions over the total number of collisions, one can calculate the ratio of Xe/He concentration in the gas. This is shown in column b of table 5.2.

The Xe/He ratio can be used to estimate the expected number of Xe^+ for the online experiments where the amount of ionization is much higher and more problematic for the measurements. During the online experiments a rate of $\approx 10^4 \text{ s}^{-1}$ fragments are hitting CSC on average. In this case, the deposited energy can produce 10^{11} s^{-1} He^+e^- pairs resulting 10^{19} s^{-1} number of collisions in total. This rate corresponds a higher expected number of Xe^+ reaching MR-TOF-MS (table 5.2 column c) during the experiments with beam.

Table 5.2: Column a: the Xe^+ count rates coming from the CSC filled with and without the cold trap in the gas line; column b: the Xe/He contamination level in the gas cell; column c: the expected Xe^+ count rate identified in MR-TOF-MS during the online experiments assuming 10^4 s^{-1} fragments stopping in the gas on average; The last column shows the improvement factor on average for all natural abundant isotopes by using the cold trap in the gas line.

		Without cold trap			With cold trap			
		a	b	c	a	b	c	
Isotope	Natural ab. (%)	Identified (counts/s)	[Xe/He]	Beam Ionization (counts/s)	Identified (counts/s)	[Xe/He]	Beam Ionization (counts/s)	Improvement factor
^{128}Xe	1.9	0.06	7.5×10^{-17}	30	0.008	1.0×10^{-17}	4	7.5
^{129}Xe	26.4	0.66	8.0×10^{-16}	320	0.09	1.1×10^{-16}	44	7.3
^{130}Xe	4	0.13	1.6×10^{-16}	62	0.02	2.8×10^{-17}	11	6.5
^{131}Xe	21.2	0.60	7.8×10^{-16}	312	0.09	1.1×10^{-16}	44	6.7
^{132}Xe	26.9	0.58	7.0×10^{-16}	280	0.08	9.5×10^{-17}	38	7.3
^{134}Xe	10.4	0.17	2.0×10^{-16}	81	0.03	4.0×10^{-17}	16	5.7
^{136}Xe	8.8	0.18	2.2×10^{-16}	88	0.04	4.6×10^{-17}	19	4.5
								Average
								6.5

In the case of Kr isotopes, it is much more difficult to remove them due to the lower condensation temperature compared to Xe (more than 2 orders of magnitude higher partial pressure at 77 K compared to Xe; see figure 5.8). However, the Kr level was also much less in the gas compared to Xe. Therefore, the discharge source was kept on during the Kr measurements to get a significant count rate for comparison. An average gain factor of 1.7 for the Kr^+ reduction was obtained for all different Kr^+ isotopes when using the cold trap in the He gas line (table 5.3).

Table 5.3: The Kr^+ count rate identified on MR-TOF-MS with and without the cold trap in the gas line (discharge source was on to ionize the gas inside CSC).

Isotope	Natural abundance (%)	Without cold trap (counts/s)	With cold trap (counts/s)	Improvement (ratio)
^{80}Kr unresolved molecule	2.2	0.50	0.42	1.2
^{82}Kr	11.59	0.32	0.17	1.9
^{83}Kr	11.50	0.22	0.12	1.8
^{84}Kr	56.98	0.83	0.40	2.1
^{86}Kr	17.27	0.30	0.23	1.3
				Average 1.7

Impurities over the long-term operation of CSC

It is always necessary to keep the cold trap in the gas line to freeze out most of the impurities before going to CSC. The impurities in the gas can be accumulated inside CSC if a proper gas purification system is not running. For instance, the heavy gases like Xe and Kr have a significantly lower pumping speed through the nozzle compared to He. Therefore, it can take a while until the system reaches the equilibrium gas condition resulting in a gradual increase of the noble gases in CSC during the operation.

In order to monitor the gas contamination over the long-term operation of CSC, the Xe count rates were monitored over about 10 hours during the measurements for the fission fragments at $A/q = 132 - 134$ with MR-TOF-MS operating at 64IT. CSC was continuously filling with a He gas kept at 165 mbar without

the cold trap in the gas line. Figure 5.11 shows how the huge Xe peaks originating from the gas impurities are overlapping with ions of interest (fission fragments) at the same m/q values. It has been observed that Xe was accumulating in the gas cell and increasing overtime, however the rates of the fission fragments were rather stable during the 10 hours of measurement (figure 5.12). The ^{132}Xe with larger natural abundance ratio (26.9%) started with a count rate of 3 counts/s and increased to more than 15 counts/s over 10 hours. The ^{134}Xe with 10.4% natural abundance also started from 1 count/s and increase up to 5 counts/s while the count rate for the well resolved fission fragments (^{133}Sb and ^{134}Sb) were rather stable (on average 0.07 counts/s) over the measurement time.

Figure 5.11: The logarithmic mass spectra of ions with $A/q = 132$ and 134 for the fission-fragment measurements over 10 hours. CSC was operated at 165 mbar and filled without the cold trap in the gas line.

Figure 5.12: The ions rates for ^{132}Xe and ^{134}Xe coming from the impurities of the gas without using the cold trap in the gas line and the Sb fission fragments ($A = 133 - 134$) from the ^{252}Cf source. The rates are normalized to the initial count rate to show the increase in time.

A measurement with exactly the same gas conditions (same gas bundle and the same Micro-torr gas purifier) but the cold trap in the gas line was done over four days of the continuous operation of CSC at 165 mbar to monitor the changes in the Xe and Kr and other impurities in the gas. Figure 5.13 shows a low and a stable contamination level for the Xe isotopes coming from the gas while the Pb ions from the offline source stayed rather stable over four days of monitoring. The Xe contamination level initially starts with a high rate in the beginning of the measurements when CSC is just filled with a large gas flow but it gradually decreased while the input gas flow stabilized. The resulting contamination level for ^{132}Xe isotope after four days of operation remained stable and it is almost a factor of **47 times** less compared to the maximum count rate observed in figure 5.12. Therefore, using the cold trap for freezing the Xe impurities in the gas line before entering CSC significantly helped to avoid the accumulation of the Xe in the helium gas during the operation of CSC. In the same measurements, the Kr contamination is also monitored showing the same behavior as the Xe measurements presented in figure 5.13.

Figure 5.13: The Xe^+ contamination identified in MR-TOF-MS over four days of continuous operation of CSC operating at 165 mbar. The cold trap was used in the gas line to suppress the impurities. The blue and green symbols are $^{208}\text{Pb}^{2+}$ and $^{212}\text{Pb}^{2+}$ ions coming from the Th source installed inside CSC showing a stable ion extraction over long operation time. The black and red symbols are the Xe^+ isotopes. The rates are normalized to the initial count rate to show the trends over time.

Figure 5.14 shows also monitoring of: a) the temperature of the helium gas inside the CSC, b) the RF carpet temperature, c) the helium gas consumption from the gas bundle, and d) the LN_2 level of the cold trap over four days of continuous operation of CSC kept at 165 mbar. The higher temperatures (shown in a) and b)) in the beginning of the operation are due to the large gas flow entering CSC for the initial filling of the CSC to 165 mbar. After the first filling of CSC, the gas flow will be limited to the gas going through the RF carpet nozzle to the pumping section afterward. The temperatures then slowly decreases to an equilibrium low temperature. However, operation of CSC at high gas densities requires a huge amount of gas going to the CSC. The estimated gas consumption from plot c) is around 4 [bar·l/min] for the operation of CSC at 165 mbar. This gas consumption means that a full gas bundle (a pack of 12 interconnected 50 l gas bottles) can only survive for 20 days of the operation. This is the main reason for the need for a Helium Recovery Unit (HRU) which is under development at FRS Ion Catcher group together with the Finnish in-kind contribution to FAIR for recycling the helium gas under the clean condition in future. Figure 5.14 d) is also showing the drop of the LN_2 level mainly evaporated due to the heat load from the room temperature helium gas flow going through the LN_2 . The cold trap should be also re-filled with LN_2 every week of the continuous

operation to make sure that the section filled with the activated carbon stays at low temperature (see figure 5.7).

Figure 5.14: a) The helium gas temperature, b) the carpet temperature, c) the remaining gas pressure at helium gas bundle, and d) the LN₂ level of the cold trap over 4 days of continuous operation of CSC operating at 165 mbar.

5.5 Techniques for monitoring low-mass impurities in the gas

Most of the impurities in CSC are thought to be low-mass molecules like H₂O, N₂, O₂, CO₂, etc. However, it is quite challenging to identify them by MR-TOF-MS due to the difficult tuning of the RFQs and the trap system for transportation of the very low-mass ions. In addition, the heavier impurities (e.g. N₄) may dissociate during their transport to and through the MR-TOF-MS. Therefore, some techniques have been developed and implemented for monitoring of the impurities coming directly out of the CSC nozzle. The techniques are

used to monitor both the neutral contamination present in the gas and also the ionized contamination extracted from CSC.

5.5.1 Extraction-RFQ mass scans

The extraction RFQ is used for monitoring the ionized impurities extracted from the CSC. The extraction RFQ operated as a mass spectrometer in mass-scanning modes of operation. In the scan operation mode, the transmitted ions are detected by the channeltron detector on the movable sled detector (figure 5.4). The channeltron detector was operated in the conversion dynode mode to increase the detection efficiency [163]. The detected signal is then amplified with the ORTEC 572A amplifier. The peaks are discriminated from the noise level by the ORTEC 935 discriminator and are subsequently registered in the ORTEC 994 dual counter/timer synchronized with the extraction RFQ scans.

5.5.2 Residual gas analyzer (RGA)

The residual gas analyzer (RGA) is a commercial and automated quadrupole gas analyzer (Hiden Analytical HMT100) installed at the extraction-RFQ section after CSC. It is not technically possible to monitor the gas condition directly inside CSC due to the maximum operating pressure of a typical RGA (10^{-4} mbar). However, it can be used as an indirect gas analyzer to monitor the gas coming from CSC through the carpet nozzle to the RFQ section afterward (figure 5.15).

Figure 5.15: The RGA installed in the extraction-RFQ section after CSC.

5.6 Gas purification measurements

The Cryogenic Stopping Cell can be filled from different gas lines with different gas purification systems as shown in the gas handling system (figure 5.6). The gas cleanliness condition of CSC is monitored by using the techniques mentioned above when it is filled with the usage of three different gas purification lines. CSC was filled with the helium 6.0 gas: (a) directly from the helium 6.0 bundle without any gas purifier in the line, (b) helium 6.0 gas going through the passive getter (SAES Microtorr gas purifier), and (c) helium 6.0 going through the passive getter and also the cold trap in the gas line. CSC was operating at 85 K temperature and filled up to 18 mbar pressure not to exceed the maximum allowed pressure in the RFQ section for operation of the RGA. The pressure in the RFQ section was kept below 5×10^{-5} mbar for safe operation of the RGA.

Figure 5.16 shows the RGA scans coming from CSC filled by using the three gas purification lines (a, b and c). The background without helium in CSC was measured (figure 5.16 d) and subtracted from the scans with gas in CSC. The dominant peaks presented in the spectra are labeled by using the molecular compositions identification software of RGA. In case (a) the dominant impurities are H_2O , CO , N_2 , CO_2 and hydrocarbons C_mH_n . Using the passive getter in case (b) could effectively remove the heavy hydrocarbons (C_mH_n) from $m/q = 40 - 100$ in the gas. However, this is not effectively suppressing e.g. CO_2 at $m/q = 44$ although it has been specified in the specifications of the getter [164]. By adding the cold trap to the purification gas line (case c) the gas contamination significantly improved by freezing out the impurities in the gas. The CO_2 is also removed by the cold trap due to the relatively high condensation temperature (figure 5.8). The cold trap is placed before the passive getter in the gas line to freeze out the impurities before going to the other gas purifiers. This prevents the saturation of the gas purifiers in the gas line while the cold trap itself can be easily regenerated after the saturation.

While the RGA scans revealed the neutral impurities in the gas, the ionized impurities extracted from CSC are also measured by the extraction-RFQ scans. For this, CSC pressure is increased to 30 mbar in each step to have a stable operation of CSC fields for the extraction of the ions. CSC is also pumped down to a pressure of 5×10^{-6} mbar after every step of the measurements before switching to the different gas purification line for filling CSC. The corresponding extraction-RFQ scans are shown in figure 5.17. One can see the improvements and changes in the gas cleanliness of CSC by using the passive getter and cold trap in the gas line. An interesting point is the ionized nitrogen cluster (N_4^+) as the dominant peak (not seen in the RGA scans in the neutral gas state). The N_4^+ is formed in

Figure 5.16: The RGA scans for three different gas purification lines filling the Cryogenic Stopping Cell. CSC is filled with a He 6.0 gas: (a) directly from the bundle, (b) purified with passive getter, (c) purified with passive getter and the cold trap both in the gas line in series. Panel (d) shows the base pressure scan in RFQ section before filling CSC, subtracted from RGA spectra (a, b and c) in order to plot the impurities only in the gas. The minor negative values (due to the fluctuations) during the subtraction are not shown in the logarithmic plots.

ion clustering reactions predicted by the following two different models based on the different appearance potential for the formation of the N_4^+ by using the electron-impact ionization technique in the nitrogen gas. The appearance energy (also known as appearance potential) is the minimum energy that must be supplied to a gas-phase atom or molecule in order to produce an ion:

model 1:	$N_2^+ + N_2 \rightarrow N_4^+$	14.74 eV appearance potential [165]
model 2:	$N_2^* + N_2 \rightarrow N_4^+ + e^-$	15.03 eV appearance potential [166]

The mass spectrum (figure 5.17) covers the low masses from $m/q \approx 28$ to 100. The lower masses than $m/q = 28$ were not effectively extracted due to technical limitations of the operation of the RF carpet and also the extraction RFQ. A rate of 10^6 counts/10s is the maximum handled rates of the data-acquisition system of the channeltron detector. The heavier impurities like N_4^+ and CF_3^+ and Br^+ and Kr^+ have been also identified more accurately by MR-TOF-MS at high resolving powers (128IT). However, the count rates in the case of N_4^+ significantly decreases since it only exists in the cryogenic environments and could easily break apart in the RFQ beamline and in the trap system due to a very low molecular binding energy.

Figure 5.17: The extraction-RFQ scans corresponding to the gas conditions a, b and c presented in figure 5.16.

Active getter for removing nitrogen in the gas

The passive getter (Micro-torr gas purifier) used in the gas line is not capable of removing nitrogen and CH_4 in the gas. Installing an active (heated) getter (Mono-torr gas purifier) in the gas line can effectively suppress the nitrogen and the other impurities in the gas. Figure 5.18 shows the specification of the passive and active getter for removing the contamination from the He 6.0 gas input.

Figure 5.18: The specifications of the SAES gas purifiers.

The extraction-RFQ scan with active getter in the helium gas line shows a further improvement in the gas cleanliness and also an effective suppression of the N_4^+ of almost 4 orders of magnitude. However, it is not quite straight forward to directly calculate the nitrogen concentration level in the gas similar to what has been performed to achieve the numbers listed in table 5.2 for the Xe concentration. The reason for that is the complexities and unknown parameters for the existence and forming of the N_4^+ clusters in the cryogenic environment from N_2 collisions. Figure 5.19 is the extraction-RFQ scan showing the difference between passive and active gas purifiers in the gas line. Figure 5.20 also shows the subtracted RGA scan demonstrating the impurities removed by the active getter.

Figure 5.19: The extraction-RFQ scan for CSC filled at 75 mbar with the gas purifying from passive and active getter lines.

Figure 5.20: The subtracted RGA scan shown to demonstrate the difference between passive and active getters in the gas line. The minor negative values (due to the fluctuations) during the subtraction are not shown in the logarithmic plots.

^{228}Th products extracted from CSC

An overall comparison of the mass spectra obtained before and after the upgrades and improvements on the gas handling system of the FRS-IC Cryogenic Gas Cell is presented in this section. Figure 5.21 shows an example of the influence of the gas cleanliness on the extraction of the ^{228}Th products from the FRS-IC setup. The top plot shows the identified ions by MR-TOF-MS using the He 6.0 gas in CSC before the upgrades of the gas handling system, and the middle plot shows CSC operating at ultra-clean gas condition by using the gas purifiers and a proper cleaning of the gas lines after the improvements. The background impurities are clearly suppressed. The bottom plot shows the ultra-clean gas condition and also the background filtering technique (IDI [167]) in the RFQ beamline to provide purified ions of interest reaching the MR-TOF-MS in real situations. The survival of the ^{228}Th recoil products is clearly enhanced, as seen in the middle/bottom figures.

Figure 5.21: The overall gas cleanliness condition for extraction of the products from ^{228}Th offline source. The results shown with CSC filled with the clean He 6.0 gas in the top plot. In the middle plot, the results are shown when CSC is filled with the ultra-clean gas by using the gas purifiers and a proper cleaning of the gas lines. Finally, the bottom plot shows the results using the background filtering technique (IDI [167]) in the RFQ beamline to send a pure beam to MR-TOF-MS.

5.7 Charge-states extracted, latest update

Nitrogen as the dominant contamination in the cell is also considered as the main charge carrier inside CSC undergoing charge-exchange reactions with other ions. The charge-exchange reaction takes place when N_2 with low ionization potential (IP=15.5 eV) hits highly-charged ions (e.g. Ra^{n+} from ^{228}Th offline source) at low collision energy. The highly-charged ion picks up the electron in the collision and ionizes N_2 . The classical view of the charge-exchange reaction is shown in figure 5.22.

Charge exchange reaction (classical model):

Figure 5.22: The classical model for the charge-exchange mechanism at low-energy collisions.

An ultra-pure helium gas without any contamination suppresses the charge-exchange reactions in the gas due to the very high ionization potential of helium (IP of 24.58 eV for He and IP of 22.22 eV for He_2). In this case, most of the ions are extracted from CSC as a 2+ and 3+ ions [112]. However, introducing some contamination in the gas, with a relatively lower ionization potential, like N_2 with an IP of 15.5 eV can play a role as the main charge carrier in the gas. The final charge-state of the extracted ions from CSC is then defined based on the

ionization potential of the impurities dominating the charge-exchange reactions [72]. Figure 5.23 shows the latest update for the expected and experimentally measured charge state of the extracted ions in the case of N_2 as the dominant charge carrier in the gas at FRS-IC setup. The extracted charge state of the ions in the experiments can give a very good vision for the kind of impurities present in CSC based on their ionization potentials and their influence on the charge-state of the extracted ions.

Figure 5.23 displays a periodic table with color-coded charge states for each element. The top panel shows the expected charge state (N, +1, +2) and the bottom panel shows the experimentally identified charge state (N, +1, +2, Unknown, Not measured).

Color code

N	+1	+2	Unknown	Not measured
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Figure 5.23: The color code in the top panel of each element shows the expected charge state of the element evaluated based on adding at least 1 ppb N_2 with an IP of 15.5 eV to the helium gas, the color code in the bottom panel of each element shows the experimentally identified charge state of the element at the FRS-IC setup.

Table 5.4 shows the ionization potential of He and other possible contaminations in the gas cell which can contribute in the charge-exchange reactions.

Table 5.4: The ionization potential of He and different possible contaminations in the gas cell obtained from standard IP indexes [168, 169].

A	Impurity	1 st IP (eV)	A	Impurity	1 st IP (eV)
4	He	24.586±0.002	44	CO ₂	13.769±0.03
8	He ₂	22.223±0.002	69	CF ₃	10.10±0.05
14	N	14.53±0.12	44	N ₂ O	12.94±0.01
28	N ₂	15.6±0.1	17	OH	13.17±0.1
78-86	Kr	13.999±0.002	79, 81	Br	11.85±0.03
124-136	Xe	12.129±0.002	158-162	Br ₂	10.53±0.03
38, 40	Ar	15.76±0.01	30	NO	9.250±0.005
16	O	13.9±0.2	16	CH ₄	12.704±0.008
32	O ₂	12.063±0.001	wide range	C _m H _n	9.4 - 11.4
18	H ₂ O	12.614±0.005			
28	CO	14.013±0.004			

Table 5.5 shows the ionization potential and the identified charge state of the ²²⁸Th products at the FRS-IC gas cell.

Table 5.5: The atomic ionization potentials of the ²²⁸Th products [168, 169] and the identified charge state at FRS-IC gas cell.

Atoms	Charge state	1 st IP (eV)	2 nd IP (eV)	3 rd IP (eV)
Ra	2+	5.27	10.14	34
Rn	1+	10.74	21	29
Po	1+	8.41	19	27
Pb	1+, 2+	7.41	15.03	31.93
Tl	1+	6.10	20.42	29.83

The rate capability of gas cells are also correlated with the main charge carrier in the gas cell due to the different ion mobility. During the stopping process of the high-energy ions in gas cell, He⁺ and e⁻ are produced at the center of the stopping cell. The e⁻ are immediately removed due to their very high mobility (almost 3 orders of magnitude larger mobility than ions [170]). In contrast, the positive He⁺ ions with a smaller mobility create a positive field at the center of gas cell, pushing ions toward larger radii and ultimately limiting the rate

capability of cell. For the gas cells operating at room temperatures and low densities, considering the N_2 in the gas can pick up the charge from He^+ ions after very short distance and remove the positive plasma at the center of gas cell more quickly due to the higher ion mobility in the gas (N_2^+ has almost two times higher mobility compared to He^+). However, in the cryogenic and high density condition where the helium is mainly forming clusters (He_2^+ and He_3^+) there is no significant difference in the ion's mobility specially at ($E/N \rightarrow 0$) e.g. for CSC at FRS-IC setup. Figure 5.24 shows the ions mobility for He^+ and different ions in the He gas.

Figure 5.24: The reduced mobility of the main possible charge carriers in the He gas [171]. The x-axis is the field strength E over the helium gas density N . The unit employed is the Townsend (Td), $1\text{Td} = 10^{-17} \text{ V-cm}^2$.

5.8 Charge-exchange in the RFQ beamline

It has been demonstrated that the change in the charge-state of the ions can also happen in the RFQ beamline. At the FRS Ion Catcher setup this can possibly happen in the RFQ transportation line, at the RF Switchyard and also at the MR-TOF-MS trap system where the ions are cooled in relatively higher pressures (10^{-2} mbar). This can occur e.g. in a charge-exchange collisions:

The charge-exchange mechanisms could be magnified if the gas purifiers are saturated or the encapsulated RFQs are exposed to atmosphere during the venting of the setup. To avoid these problems, the RFQ sections in the FRS-IC setup are designed to have the capability of baking them by the heat power generated from the DC voltage on the RFQ resistive rods after each venting.

The unexpected charge-exchange reactions in the MR-TOF-MS system is already investigated and the problem is solved by the procedure described at [172] PhD thesis. However, for the following measurements, it was not fully implemented due to the technical problems. By using a saturated gas purifier at the RFQ beamline at a pressure of 5×10^{-2} mbar and MR-TOF switchyard at a pressure of 1×10^{-2} mbar, it has been observed that the extracted Pb^{2+} ions from CSC can have a large number of charge-exchange reactions in the RFQ beamline and reach the MR-TOF-MS as $q = +1$ ions. The low ionization potential of e.g. H_2O (12.61 eV) and O_2 (12.06 eV) as contaminants can change the charge-state of the Pb^{2+} ions in the ion-gas collisions. Thanks to the two mass filters in the FRS Ion Catcher beamline, it is possible to localize the charge-exchange reactions along the RFQ beamline. In figure 5.25 (a) the extraction RFQ is set to only transfer the +1 ions extracted from CSC and MR-TOF-MS mass window is also set to the corresponding m/q for +1 ions. One can see that $^{208}\text{Pb}^{+1}$, $^{208}\text{Tl}^{+1}$ and $^{212}\text{Pb}^{+1}$ are clearly identified on the MR-TOF-MS spectrum. In figure 5.25 (b) the extraction RFQ was changed to only transfer the $q = +2$ ions from CSC but the MR-TOF-MS was kept to identify the +1 ions which are produced in the charge-exchange reactions in the RFQ beamline or MR-TOF-MS. One can see that the major part of the $^{212}\text{Pb}^{+1}$ and $^{208}\text{Pb}^{+1}$ are extracted as the +2 ions from CSC but undergo a charge-exchange reaction in the beamline and end up as +1 ions at the MR-TOF-MS. However, there is no $^{208}\text{Tl}^{+1}$ identified in MR-TOF-MS due to the very high ionization potential (2nd IP= 20.42 eV) suppressing the charge-exchange reactions for this element. In figure 5.25 (c) the extraction RFQ and also the Mass Filter at DU2 are set to only transfer the +2 ions to the MR-TOF-MS. In this configuration, the Pb count rates are decreased by almost a factor of three. Therefore, 2/3 of Pb ions undergo a charge-exchange in the beamline before MF2 and are, subsequently, filtered out by MF2 while the other 1/3 of the ions pass through MF2 as +2 ions and undergo a charge-exchange reaction afterward.

Figure 5.25: The effect of charge-exchange reactions in the beamline and MR-TOF-MS: a) the extraction RFQ was set to only transport +1 ions extracted from CSC; b) the extraction RFQ was set to only transport +2 ions extracted from CSC. There is no $^{208}\text{Tl}^{+1}$ in the spectrum since it only extracted $q = +1$ due to the high ionization potential. However, there is still a significant amount of Pb which means they are coming as $q = +2$ ions from CSC and undergo a charge-exchange reaction in the beamline and end up as $q = +1$ ions in MR-TOF-MS, and c) both extraction RFQ and the mass filter at DU2 were set to only transport $q = +2$ ions. One can see almost 2/3 of charge-exchange reactions are taking place before MF2 and 1/3 afterward. A CID potential step of 60 V [167] is used in the RFQ beamline for breaking the molecular ions apart. IT is the isochronous turns of the ions in analyzer.

In order to suppress the charge-exchange reactions in the RFQ beamline the saturated gas purifier at DU2 is replaced with a fresh gas purifier to provide a cleaner gas condition. The RGA scan shows a cleaner gas spectrum afterward (figure 5.26). The removal of H_2O , O_2 and $\text{C}_m\text{H}_n/\text{CO}_2$ with relatively lower ionization potentials could cause the suppression of the charge-exchange reactions in the RFQ beamline for Pb ions. The charge-exchange reactions at the DU2 beamline are suppressed from 2/3 to 1/3 (see table 5.6). It means that, now, only 1/3 of charge-exchange reactions are taking place before MF2. However, the total count rate for the charge-exchange reactions in the MR-TOF-MS remained the same since ions are undergoing charge-exchange reactions in the next step at MR-TOF switchyard and the trap system. A next step would be to bake the RFQs of the MR-TOF-MS according to the procedure discussed in Ref. [172]. But due to technical problems, this was not possible within the timeline of the present work.

Figure 5.26: The subtracted RGA scan demonstrating the difference between the old gas purifier and the new one at DU2 RFQ beamline. The minor negative values (due to the fluctuations) during the subtraction are not shown in the logarithmic plots.

Table 5.6: The usage of a fresh gas purifier at RFQ beamline resulting in a reduction of the amount of charge-exchange reactions taking place at the beamline before the RFQ mass filter (shown in figure 5.4) from 2/3 to 1/3.

Mass Filter (MF2)	$^{208}\text{Pb}^{+1}$ (counts)	Ratio (%)	$^{212}\text{Pb}^{+1}$ (counts)	Ratio (%)	Gas Purifier	Comment
Passes $q = +1, +2$:	219	36%	537	37%	Saturated	"2/3 of charge-exchanges happened before mass filter"
Passes $q = +2$:	79		199			
Passes $q = +1, +2$:	207	64%	610	73%	Fresh	"1/3 of charge-exchanges happened before mass filter"
Passes $q = +2$:	133		444			

5.9 Conclusions

The gas handling system of the FRS-IC setup was upgraded (as a part of this PhD project) with a new gas purifiers including the Micro-torr (passive) and Mono-torr (active) gas purifiers and the cold trap for further improvement of the gas cleanliness required for the Cryogenic Stopping Cell (CSC). The different techniques that have been developed will be implemented in the future gas recycling unit of the cryogenic stopping cell of the low-energy branch of the Super-FRS at FAIR. In addition, a complete new gas-line is installed for adding trace gases into CSC required for the experiments involving charge-state manipulations of ions. The trace gases with low ionization potentials like NO (IP of 9.25 eV) and CH_4 (IP of 12.70 eV) can be used, in future, for charge-state manipulation of the extracted ions from CSC.

The cold trap was constructed and tested successfully for the suppression of noble gases like Xe and Kr present in the He gas. A suppression factor of 6.5 and 1.7 were achieved for the Xe and Kr atoms, respectively. The measurements were used to estimate the number of expected Xe^+ produced in the case of beam with much larger ionization in CSC compared to the offline sources. The cold trap was tested for long term operation of CSC over 4 days. It was shown that for a long operation time ($\approx$ week), the Xe level can be reduced by about two orders of magnitude.

The charge-exchange reactions were studied and localized in the RFQ beamline for the ions extracted from CSC, showing the presence and importance of charge-exchange reactions even in the RFQ beamline.

Chapter 6

Mass and half-life measurements of the neutron-deficient nuclei

The Multiple-Reflection Time-Of-Flight Mass Spectrometer (MR-TOF-MS) at the FRS Ion Catcher, with the maximum achieved resolving power of $R = 1,000,000$ [173] and the mass accuracy down to 4.5×10^{-8} [155], is a powerful tool for the precision mass measurement of exotic nuclei. The setup provides a fast (a few ms cycle times), sensitive (a few detected ions), accurate, broadband (simultaneous measurements of many nuclei) and non-scanning operation as a unique technique for mass measurements of short-lived and rare nuclei.

This chapter presents the data evaluation and the mass measurement of the medium-heavy nuclei close to the $N = Z$ line (masses of 12 ground states and 2 isomers) and the light alpha-emitters in the medium-mass range of isotopes (masses of two iodine isotopes); together with the systematic studies evaluated from the new direct mass measurements.

6.1 Data evaluation procedure

The general characteristics of the Multiple-Reflection Time-Of-Flight Mass Spectrometer at FRS-IC were described in the last chapter (section 5.1.2). The current section reviews the data evaluation technique for the high-precision mass measurements. The data evaluation technique for mass measurements with MR-TOF-MS has been developed in the past years by the IONAS group at the Justus-Liebig-University Giessen. The general procedure is presented in Ref. [172] and schematically shown in the algorithm below in figure 6.1.

Figure 6.1: The data evaluation algorithm for the MR-TOF-MS mass and uncertainty evaluations [155]. Here, IOI, MAC, R, TOF, LS and wMLE stand for Ion Of Interest, Mass Acquisition software, R programming language, Time-Of-Flight, Least Square fit and weighted Maximum Likelihood Estimation, respectively.

A brief description of the data evaluation procedure, used for the mass analysis in this chapter, is presented in the following:

1. MAc [174] is the software developed for the data taking and processing of the MR-TOF-MS data acquisition system. The TOF data of ions with different m/q are recorded and shown as a TOF histogram in MAc. The TOF histogram can be then converted to the m/q histogram by using equation (6.1) and two stages of calibrations to determine the constant parameters (t_0 , c and b):

$$\frac{m}{q} = \frac{c(t_{tof} - t_0)^2}{(1 + Nb)^2} \quad (6.1)$$

where t_{tof} is the time-of-flight of ions with N number of turns in the analyzer. The first step of the calibration is done to determine t_0 and c with at least two known calibrants as the TOF references in the path-through mode of MR-TOF-MS ($N = 0$) called as the 0-turn calibration. These two constants will be stable for all the mass measurements as far as there was no modification made on the power supplies, cable lengths, etc. A more precise c -determination can be also done in the multiturn calibration ($N \neq 0$) if any calibrant ion has a different turn number than IOI (Ion Of Interest) in the mass spectrum. The second stage of the calibration is called Time-Resolved calibration (TRC) to determine the b constant, describing the flight path during the reflections in the analyzer. This can vary with time e.g. the fluctuations of the voltages and also the thermal expansion of the electrodes. The TRC calibration is usually performed with calibrant ion which has a high statistics in the mass spectrum. At the end, the time-resolved calibrated m/q spectrum is exported from the MAc software for further mass analysis.

2. The final analysis on the data is performed by using the R programming language for statistical analysis. The first step is the peak shape determination of the ions by fitting a calibrant peak with high statistics (usually the same peak which is used for the TRC calibration as well). The analytical formula describing the peak shapes is called the Hyper Exponentially Modified Gaussian function (Hyper-EMG) which is a Gaussian function with a given number of exponential functions describing the tails on the sides of the peak [175]. This code was specially developed for the MR-TOF-MS mass analysis. The parameters used in the Hyper-EMG function are: μ and σ describing the mean and the standard deviation of the Gaussian function; $\tau_{L,R}$ and $\eta_{L,R}$ the growth constant and the weight of the exponentials on the sides (Left, Right); A and θ the total area and the weight of the areas on the left and right exponentials of the EMG, respectively. The Least Square (LS) minimization method of the data and the initial suggested fit parameters are used for fitting of the

calibrant peak and resulting in the peak shape parameters. At the end, the Kolmogorov-Smirnov (KS) test [176] is used for comparison of the data and the fit function to check how well the data are described by the model ($0 < P\text{-value} < 1$).

3. All the peak shape parameters obtained from the high-statistic calibrant are fixed (σ and τ need to be also scaled; see step 4) after the previous step for all the further analysis. Subsequently, the wMLE (weighted Maximum Likelihood Estimation) is done on the Ion-Of-Interest (IOI) where the only free parameters are μ_{IOI} and the area, A . The weighting is used to minimize the influence of outliers on the determined center of the peak. However, the peak shape uncertainties can influence the IOI mean estimation which leads to the determination of the mass. For considering this, several IOI mean estimations are done by changing every peak shape parameter with 1σ (its uncertainty) and obtaining the IOI mean value while all other peak parameters are fixed. The resulting differences are quadratically added for all the different peak shape parameters and will be used to estimate the final errors in the determination of the mass.
4. The scaling of σ and τ are done due to a different m/q values for calibrant and IOI by using the scaling factor $S = [(m/q)_{IOI} \times R_{Cal}] / [(m/q)_{Cal} \times R_{IOI}]$ where R_{Cal} and R_{IOI} are the resolving power (FWHM) of the calibrant and IOI peaks.

6.1.1 Final mass value and the uncertainty contribution

The final mass value of IOI is defined as follows:

$$m_{Final_IOI} = R(m_{IOI_wMLE} - MRS_{Shift_IOI}) \quad (6.2)$$

where R is the precision calibration factor considering the difference between the literature mass of the calibrant ($m_{Cal_Lit.}$) and the fitted mass of the calibrant (m_{Cal_wMLE}):

$$R = \frac{m_{Cal_Lit.}}{(m_{Cal_wMLE} - MRS_{Shift_Cal})} \quad (6.3)$$

The MRS_{Shifts} is also the mass shift caused due to the switching of the Mass Range Selector (MRS) in the middle of the analyzer influencing the TOF of the ions. The mass shift consideration does not appear if both IOI and calibrant are experiencing together the same MRS field distortion. However, sometime MRS is switched off to have the calibrant in the spectrum and is switched on

to provide a clean spectrum only for IOI. In this case one needs to consider the mass shift caused by the MRS operation:

$$MRS_{shift} = \frac{2 \times A_{mrs} \times \Delta IC}{TOF} \times (m/q)^{3/2} \quad [u] \quad (6.4)$$

where ΔIC is the isolation cycles for MRS and A_{mrs} is a fitting constant, which was determined for $^{133}\text{Cs}^+$ to be 0.011 in offline investigations.

The final atomic mass (M_{Final}) can be written as:

$$M_{Final} = m_{Final_IOI} + m_e + (\text{electron binding energy}) \quad (6.5)$$

where m_e is the electron mass, 548.579909 [μu]. The electron binding energy ($\approx eV$) is usually negligible for medium-high mass precision measurements in the range of keV level.

In the case of several independent mass measurements for an IOI, the following weighting functions are used for the final reported mass value and uncertainty:

$$\langle \overline{M} \rangle = \frac{\sum_{i=1}^n M_i / \sigma_i^2}{\sum_{i=1}^n 1 / \sigma_i^2} \quad \langle \overline{\sigma^2} \rangle = \frac{1}{\sum_{i=1}^n 1 / \sigma_i^2} \quad (6.6)$$

where M_i and σ_i are the mass and uncertainty for each individual measurement, respectively, and the sum is over n measurements.

6.1.2 Components of error

The different mass-uncertainty components are considered as independent errors and they are quadratically added up for the final mass uncertainty. Some uncertainties e.g. background/contamination error, are linearly added to the statistical error with a weighting factor. The main sources of all these mass uncertainties are shortly described here:

- Statistical error

The statistical uncertainty for the pure Gaussian function is calculated from $\sigma / \sqrt{N}$ where N is the number of samples (counts) and σ is the standard deviations of the normal distribution. In the case of using Hyper-EMG function in the wMLE fit, an empirical approach is used for the determination of the statistical uncertainty. A sample of events (same as number of counts in the peak) with a random-position distribution but following the probability distribution determined from the peak shape conditions are generated. Then, a fit to the sample events is done to obtain the mass deviation from the original mean

value. This procedure is repeated several times and the standard deviation is, at the end, calculated from the fit results.

- Peak shape error

The peak shape uncertainties determined for the calibrant peak shape can influence the IOI mean estimation in wMLE method. The procedure for estimating the peak shape error is described in the previous section in the third step of the analysis. The peak shape error is usually translated to around one keV in mass uncertainty.

- Time-Resolved Calibration (TRC) error

The method used for the TRC calibration splits the measurement to the several blocks for the determination of the parameter b for each block. An interpolation of b in all segments is then used for the final TRC calibration. However, this interpolation can cause some peak broadening of the peak and add some uncertainty to the measurements. The TRC error is formulated as the square root of the quadratic difference between the rms of the mean m/q deviation for each calibration block (σ_{rms_block}) and the rms value of the statistical uncertainty in each block ($\sigma_{rms}/\sqrt{N_{blocks}}$):

$$\sigma_{TRC} = \sqrt{(\sigma_{rms_block})^2 - \left(\frac{\sigma_{rms}}{\sqrt{N_{blocks}}}\right)^2} \times \frac{(m/q)_{IOI}}{\sqrt{N_{blocks}}} \quad (6.7)$$

where N_{blocks} is the effective number of blocks in the measurements. Details of this source of error are presented in Ref. [155]. The TRC error contribution is usually in the range of a few keV in mass uncertainty.

- MRS shift error

Alternative switching of the Mass Range Selector (MRS) in the middle of the analyzer can create some field distortions influencing the time-of-flight of the ions. The MRS uncertainty is assumed to be up to 50% of the MRS shift corrections in the final mass value (equation 6.4). The MRS error is usually translated to a few tens of keV in mass uncertainty.

- NPE error

During the ejection of ions from the analyzer, the exit reflectors have to switch the high-voltage electrodes (switches in less than 200 ns). However, switching of the high voltages create a ringing fluctuations on the voltages (a few μ s ringing) until the voltages stabilize. During this time, ions with different m/q (spatially separated) might feel a different field during the ejection and cause a

Non-Perfect Ejection (NPE) uncertainty in the measurements. This uncertainty is calculated by:

$$\sigma_{NPE} = \frac{2\Delta t_{NPE}}{t_{tof_IOI}} \sqrt{\frac{(m/q)_{IOI}}{(m/q)_{ref}}} \left(\frac{m}{q}\right)_{IOI} \quad (6.8)$$

where Δt_{NPE} is the experimentally determined time shift measured for the reference $(m/q)_{ref}$ ions in offline investigations. The NPE error is usually translated to a few keV in mass uncertainty.

- Background and Contamination error

In the case of background events (usually dark counts from detector) overlapping with the peak of IOI, the number of background events per 1 amu are measured for a wide range of masses in the mass spectrum and then normalized to the area under the peak of IOI. The background contribution is considered as an additional error to the statistical-error calculations, using the methods of random-generated samples. The contamination error also takes into account the possibility that the IOI peak was contaminated from an unknown source as investigated in Ref. [177]. The average height of the non-identified/unexpected peaks in the mass spectrum and the possibility of their appearance under the peak area of the IOI are considered for the estimation of the contamination error. For these calculations, a simulated peak with an average height of the contamination peaks is moved stepwise through the IOI and a mass fitting was done in each step to determine the deviation of the resulting mass compared to the original value. At the end, the standard deviation of the fit results after taking into account a weighting factor (for possibility of having the contamination peak under the peak area of IOI) is used as the contamination error linearly added to the statistical error.

- Error of calibration parameters (Δt_0 , Δc)

The uncertainties in the calibration parameters (t_0 , c) are directly influencing the mass values in the m/q conversion formula (see equation 6.1). The formulation for the mass uncertainty originating from Δt_0 is described in Ref. [177], and usually has a very-small contribution to the final mass uncertainty. The mass error caused by the other calibration parameter c is calculated empirically in MAc by changing the c parameter by its uncertainty and obtaining a new b parameter and a new mass value from them. The mass deviation is then considered as the mass uncertainty originating from Δc . The uncertainty of c is theoretically zero if the calibrant and IOI have the same turn number in the analyzer [172]. The error of calibration parameters are usually translated to around one keV or less in mass uncertainty.

A complete list of errors discussed above with their corresponding values for the presented measurements can be found in the following sections. The very

small uncertainties ($< 1 \times 10^{-8}$ u) caused by effects such as the earth magnetic field [155], TDC dead-time [172], the space-charge effects [178], etc. are neglected in the data presented in this work. The space-charge uncertainty is evaluated to be $\sim 10^{-8}$ u per detected isobaric ion per MR-TOF cycle [178]. For this, a great care has been taken to have less than one detected ion on the mass unit of interest in the data that are used for the mass evaluations.

6.2 Neutron-deficient iodine isotopes ^{114}I and ^{116}I

α -decay is the major decay channel for the heavy and superheavy elements [44]. However, there is also a small island of α -emitters in the medium-heavy neutron-deficient region above the doubly-magic nucleus ^{100}Sn ($Z = N = 50$) containing Te, I, Xe, Cs and Ba isotopes [45] (the yellow labeled isotopes in figure 6.2). This island is also the endpoint of the rp-process due to a higher α -decay rate compared to the process taking place in the rp-process during the X-ray burst of the neutron stars [39]. The studies on mass and decay properties

Figure 6.2: The primary decay modes in the chart of isotopes and the island of the α emitters in the medium-heavy neutron-deficient region. The α -emitter nuclei are labeled with a yellow color. The iodine isotopes which have been measured in this thesis are circled. The chart is exported and modified from Ref. [179].

of the nuclei in this region can improve our understanding about the nuclear structure and the shell closure in this special area. Although there are some direct [180, 181] and indirect [182–184] mass measurements for the more exotic iodine (more neutron-deficient) isotopes down to the $A = 108$ iodine, the mass of the iodine isotope with $N = 61$ (^{114}I) has never been measured and the mass of the isotope with $N = 63$ (^{116}I) was measured only indirectly before, resulting in a large uncertainty in the decay properties of the isotope.

In order to measure the mass of neutron-deficient iodine isotopes (^{114}I and ^{116}I), they were produced at relativistic energies through In-flight projectile fragmentation at the FRagment Separator (FRS) at GSI (figure 5.3). The isotopes are then thermalized in the Cryogenic Stopping Cell (CSC) of the FRS Ion Catcher (figure 5.4) and transported through the RFQ beamline to MR-TOF-MS (figure 5.5) for the high-precision mass measurements.

6.2.1 ^{116}I mass measurement

The previous mass evaluations of ^{116}I ground state ($t_{1/2} = 2.91$ s) were performed indirectly from the β^+ end-point energy measurements (Q -value of 7760 ± 130 keV [185] and 7710 ± 200 keV [186]). For the direct mass measurements performed in the present work, the ^{116}I isotope was produced by in-flight projectile fragmentation of the ^{238}U with 300 MeV/u on a beryllium target of 0.270 g/cm 2 with the intensities of up to 2.5×10^8 ions per spill and a typical spill length of 1 s. The production cross section on target is 1.2 mb according to EPAX [187]. CSC was operated at a helium pressure of 64 mbar at a temperature of 77 K, corresponding to an areal density of 4.2 mg/cm 2 . The mass measurement was performed on the $q = +1$ ions with the $^{86}\text{Kr}^{14}\text{N}_2^+$ serving as the reference calibrant extracted from CSC.

The isomeric state of ^{116}I cannot be measured in MR-TOF-MS due to its short half-life ($t_{1/2} = 3.27$ μs). The ^{116}I ions underwent 570 isochronous turns (IT) in the mass analyzer of MR-TOF-MS. They were then ejected from the analyzer, passed through the Time-Focus-Shift (TFS) reflector and impinged on the detector (see figure 5.5). The total time-of-flight amounted to about 19 ms with a resolving power at FWHM of about 350,000. The Mass Range Selector (MRS) was used to isolate ions with the mass number $A = 116$ from a total of about 30 background species detected in MR-TOF-MS, in the full mass spectrum. Figure 6.3 (top panel) shows the background mass spectrum without using MRS. Figure 6.3 (bottom panel) shows the suppression of the background species with MRS switched on. The zoom region shows ^{116}I ($A = 116$) and how the adjacent peak with $A = 114$ is removed. A total of 506 counts were recorded for ^{116}I isotope for a 1-hour measurement. The reference calibrant ion used for the precision calibration and for the time-resolved calibration (TRC) was the molecule $^{86}\text{Kr}^{14}\text{N}_2^+$ ($A = 114$) with a high statistics ($\approx 10^4$ ions), which was formed in

CSC and ionized by the beam. The calibrant underwent 575 IT in the analyzer of MR-TOF-MS. The number of turns is higher than the one for the IOI due to the slightly lower m/q . This reference ion was included in the spectrum by temporarily switching off the MRS. Due to an unfavorable operation of MRS in this measurement, the MRS shift error is the main source of uncertainty in this mass measurement. Other individual components of the total uncertainty are: peak shape, statistical, calibrant, time-resolved calibration and non-perfect ejection uncertainty (see section 6.1.2).

Figure 6.3: Top) the mass spectrum without using MRS. Most of the peaks are the impurities in the gas ionized by the beam hitting CSC. Bottom) the mass spectra with MRS turned on for isolating $A = 116$ ions from other background species. The y-scale of both panels is kept the same to show the effects.

The next step is applying the Time-Resolved Calibration (TRC) on data before analysis. Figure 6.4 shows how the peak shape was improved in TRC calibration after correcting the peak broadening during one hour of measurement (see section 6.1).

Figure 6.4: The Time-Resolved Calibration (TRC) for improving the peak broadening in the measurement. The peak shape and mass resolving power at FWHM improved from 250,000 to about 350,000.

After applying the corrections, the data need to be binned for LS fitting as the next step. The "Freedmann-Diaconis Rule" is used for determining the bin width [188]. The peak shape parameters and the precision calibration factor R were obtained by fitting a Hyper-EMG function and using the Least Square (LS) fit on the binned data for the calibrant ion $^{86}\text{Kr}^{14}\text{N}_2^+$ (figure 6.5). The resulting precision calibration factor is $R = 1.00000100 \pm 10^{-8}$ (see equation 6.3).

After obtaining the peak shape parameters from the high-statistics calibrant peak, one can fix all the peak shape parameters except the mean value and the area A to do the wMLE fit on the unbinned data for IOI events $^{116}\text{I}^+$ (figure 6.6). The fit on unbinned data for IOI avoids additional errors due to the bin size and position of the bins specially in low-statistics measurements. The unbinned data are shown in the lower part of figure 6.6.

Figure 6.5: The LS fit on the calibrant ion $^{86}\text{Kr}^{14}\text{N}_2^+$ to obtain the peak shape parameters and the precision calibration factor R . The yellow fit shows the initial suggested fit parameters and the red fit shows the final fit obtained in Least Square (LS) minimization method ($\chi^2 = 0.99$ on 88 degrees of freedom).

Figure 6.6: The wMLE fit on the unbinned data for $^{116}\text{I}^+$. The peak parameters were fixed and only the mean and the area A were allowed to vary in the analysis. The unbinned data are shown in the lower part of the figure.

After applying the precision calibration factor and correcting for the MRS shift in the mass, the atomic mass value for ^{116}I is obtained: $(115.916967 \pm 1.46\text{E-}4) \text{ u}$. As mentioned before the main error contribution resulted from the operation of MRS ($\sigma_{\text{MRS}} = 145 \mu\text{u}$). Figure 6.7 shows the comparison of the direct mass measurement of this experiment consistent with the indirect masses as measured by Beck et al. [185] and Gowdy et al. [186].

Figure 6.7: The comparison of the direct mass measurement in this experiment compared to the indirect measurements of Beck et al. [185] and Gowdy et al. [186] obtained from the β -decay end-point energy.

6.2.2 ^{114}I mass and half-life measurements

The mass of the ^{114}I is not measured so far and only an extrapolation value is available in the literature [20] with a large uncertainty of $\pm 150 \text{ keV}$. The ^{114}I also has a long-lived isomeric state with $t_{1/2} = (6.2 \pm 0.5) \text{ s}$ [189] and an excitation energy of 265.9 keV [190] which lies almost within the uncertainty range of the extrapolated ground state mass given in the literature. Therefore, if only a single state is detected for this nucleus, the assignment to ground or isomeric states cannot be confidently made solely based on its mass. The half-life of this isotope is also measured.

For the production of the ^{114}I , a 600 MeV/u beam of ^{124}Xe of up to 1×10^9 ions per spill and a typical spill length of 4 s was used on a beryllium target with a density of 1.622 g/cm^2 . The production cross section on the target is 0.55 mb according to EPAX [187]. CSC was operated at a helium pressure of 75 mbar

and a temperature of 82 K, corresponding to an areal density of 4.6 mg/cm². The mass measurement was performed on the $q=+1$ ions and with the reference calibrant $^{86}\text{Kr}^{14}\text{N}_2^+$ similar to the ^{116}I measurements. MRS was always on and set to isolate the mass number $A = 114$ from the other species. A resolving power of 350,000 (FWHM) was achieved for this measurement with a total time-of-flight of 19 ms for ^{114}I isotope. Three different measurements were performed with two different IT numbers (575, 574 IT). In total, 2376 counts of ^{114}I were identified in 96 minutes of measurements.

The data evaluation was performed similar to the ^{116}I case for all three measurements and a weighted average (equation 6.6) was taken for the final mass value. Table 6.1 summarize the mass values and the statistics in the three independent measurements. Figure 6.8 shows one of the mass measurements, as an example, representing the data evaluation: red solid line which is the sum of the two Hyper-EMG functions fitted to the calibrant and ion of interest ^{114}I , separately. The individual contributions to the total uncertainty are the same as for ^{116}I with the exception of the MRS error. This is zero as the MRS is always on. In this case the TRC contribution is the dominant source of error. For a complete list of individual errors, see table 6.3.

Table 6.1: Three measurements performed for the ^{114}I isotope and the resulting weighted average of the independent measurements.

Exp. No.	^{114}I (counts)	Calibrant	^{114}I atomic mass (u)	Weighted average (u)
1	1444	$^{86}\text{Kr}^{14}\text{N}_2^+$	$113.922017 \pm 1.0\text{E-}5$	$113.922015 \pm 8.0\text{E-}6$
2	755	$^{86}\text{Kr}^{14}\text{N}_2^+$	$113.922017 \pm 1.3\text{E-}5$	
3	177	$^{86}\text{Kr}^{14}\text{N}_2^+$	$113.921972 \pm 4.0\text{E-}5$

Figure 6.8: Measured mass-to-charge ratio spectrum including the calibrant $^{86}\text{Kr}^{14}\text{N}_2^+$ ($A = 114$) and the ion of interest $^{114}\text{I}^+$. The Hyper-EMG functions with one exponential on each side were used for fitting the data, the shape parameters of which were obtained from the calibrant data. The (red) continuous line represents the sum of the two Hyper-EMG functions obtained after fitting the data on unbinned data shown in lower section.

For all three mass measurements performed for this nucleus, the data evaluation procedure revealed the presence of only a single peak in the mass spectrum. A detailed investigation of the smallest detectable isomeric ratio was performed by generating and analyzing synthetic data for the given measurement conditions regarding the mass resolving power, distance between the peaks, and the total number of events and by using the techniques developed for the evaluation of the overlapping peaks of Ref. [155]. The analysis shows that only a single state can be detected by MR-TOF-MS if the relative abundance of one of the states is smaller than 10% at the given resolving power (see figure 6.9). Figure 6.10 shows the results of the simulations as how the different contributions of the ground state (GS) and the isomeric state reflect the mass deviation from the pure ground state. The maximum 10% isomeric contribution correspond to a $20\ \mu\text{u}$ (18.6 keV) additional uncertainty in the mass measurement of the ^{114}I nucleus. The final atomic mass value for ^{114}I is reported as: $(113.922015 \pm 2.1\text{E-}5)\text{u}$.

Figure 6.9: The synthetic data generated with the same resolving power, peak shape and total count rate of the data obtained for ^{114}I and a fixed excitation energy known in AME16 [20]. a) up to 90% for the ground state (GS) and 10% for the isomeric state (IS), accepted by the KS-test as a single peak identification with a normal peak width. b) 75% for the GS and 25% for the IS, rejected by the KS-test as a single peak identification. Here, a significant peak broadening was observed.

Figure 6.10: The estimated mass deviation from the pure ground state (GS) peak for the different contributions of GS and the Isomeric State (IS). The maximum 10% IS contribution correspond to a $20 \mu\text{u}$ (18.6 keV) additional uncertainty in the mass measurement of the ^{114}I nucleus.

The obtained result of $113.922015 \pm 2.1\text{E-}5 \text{ u}$ is between the extrapolated ground-state and the isomeric-state masses with their large uncertainties as reported in AME16 [20]. The mass value is even closer to the extrapolated isomer mass

(mass excess difference of -112 ± 151 keV) than to the extrapolated ground-state mass (mass excess difference of $+154 \pm 151$ keV). If only the mass value is used, both assignments would be possible since the uncertainty of the literature ground-state mass is comparable to the excitation energy of the isomer. Therefore, to unambiguously assign the state of the detected single peak, another nuclear property has to be measured. In this case, the well-known half-lives of both the ground and the isomeric states, (2.1 ± 0.2) s and (6.2 ± 0.5) s [20], respectively, were used.

The half-life can be measured by counting the surviving nuclei via mass spectrometry after a certain storage time, either in CSC [191] or the RFQ beamline [75]. The ^{114}I ions injected in CSC were extracted (ms) and transferred through the RFQ beamline (μs) towards MR-TOF-MS. At the entrance of MR-TOF-MS, the potential of an aperture was switched to block the ions at the start of the spill injected into CSC. After a selectable time, the potential was switched back to its normal value. This caused the extracted ions from CSC to be stored in the RFQ in front of the aperture for an average storage time given by the blocking time of the aperture minus half of the spill length. Note that the ions were always stored for a time longer than the spill length. The average storage times of 0, 3, 5 and 7 seconds were selected to cover at least one half-life of the longer-lived state, namely the isomer with $t_{1/2} = 6.2$ s (91% β^+ -decay and 9% Gamma-decay). The spill length was (4 ± 0.2) s. The uncertainty from the spill length takes into account the uniformity and asymmetry of the spill structure and contributes to the uncertainty of the determined half-life. The extraction time from CSC is negligible ($\approx$ ms) in comparison with the average storage time in the RFQ.

The RFQ that was used for the storage of the ions had an inner diameter of 7 mm and was operated with a pseudopotential of about 43 eV and at a pressure of about 0.01 mbar of helium. Therefore, for the ^{114}I ions, the survival efficiency during storage in the RFQ can be assumed to be the same for the different storage times. However, due to their high recoil energy after the β^+ decay, the daughter ions ^{114}Te could not be captured in the RFQ and were lost. The total number of nuclei delivered by the FRS was recorded for each acquisition period and used as a normalization factor for the number of ^{114}I nuclei produced. The number of ^{114}I ions after the storage was determined via high-resolution mass measurement using MR-TOF-MS. An exponential function was fitted to the normalized counts for the different average storage times in order to determine the half-life (figure 6.11). The uncertainty of the half-life was calculated as the quadratic sum of the statistical uncertainty of the fit (± 0.20 s) and the propagated uncertainty from the spill length (± 0.1 s). The obtained value for the half-life of (1.83 ± 0.22) s is in a good agreement with the literature value for the ground state. Thus, the measured mass value could be assigned to the ground state.

Figure 6.11: The half-life measurements of the ^{114}I by storing the ions in the RFQ beam-line for a certain time and subsequently measuring the remaining counts by MR-TOF-MS. The resulting half-life is compatible with the ground state.

Table 6.2 summarizes the resulting mass and half-life measurements and uncertainties for both iodine isotopes together with the resulting Q_α calculated from the new mass measurements and AME16 masses for $M(A-4, Z-2)$.

Table 6.2: A summary of the resulting mass and half-life measurements for the ^{114}I and ^{116}I nuclei together with the new evaluated Q_α value calculated from the new direct mass measurements. The # sign indicates the extrapolated value.

^{116}I					
	Half-life (s)	Atomic mass (u)	Mass excess ME (keV)	No. of events	Q_α (keV)
FRS-IC	-	$115.916967 \pm 1.46\text{E-}4$	-77345 ± 136	506	1829 ± 138
AME16	2.91 ± 0.15	$115.916810 \pm 1.0\text{E-}4$	-77490 ± 100	-	1680 ± 100
^{114}I					
FRS-IC	1.83 ± 0.22	$113.922015 \pm 2.1\text{E-}5$	-72642 ± 20	2376	2383 ± 21
AME16	2.1 ± 0.2	$113.921850\# \pm 1.6\text{E-}4\#$	$-72800\# \pm 150\#$	-	$2230\# \pm 150\#$

Finally, table 6.3 shows the different error components calculated for the iodine mass measurements. For the case of ^{114}I , three different measurements were performed. For the case of ^{116}I , only a single measurement was performed.

Table 6.3: A list of various components of error to the mass uncertainty of the iodine mass measurements. For the case of ^{114}I , three different measurements were performed while for the case of ^{116}I , only a single measurement was done. An error of 18.6 keV is added to the weighted average of the three measurements of ^{114}I to account for the contribution of non-resolved isomeric state.

Error [u]	^{114}I (1)	^{114}I (2)	^{114}I (3)	^{116}I
Statistical	3.4E-6	4.7E-6	1.4E-5	1.2E-5
Calibrant	2.0E-6	3.0E-6	1.6E-5	3.0E-6
Peak shape	1.0E-6	2.0E-6	2.0E-6	2.0E-6
TRC	7.4E-6	1.0E-5	3.2E-5	2.0E-5
MRS	00	00	00	1.4E-4
NPE	5.6E-6	5.6E-6	5.6E-6	5.7E-6
Contamination	1.8E-6	1.8E-6	1.8E-6	7.0E-6
Calibration parameters	<E-7	<E-7	<E-7	<E-7
Total [u]	1.0E-5	1.3E-5	4.0E-5	1.46E-4

6.2.3 Systematic studies of the binding energies

The influence of the two new iodine masses (^{114}I and ^{116}I) can be observed in the nucleon separation energies which are important in the study of nuclear structure [192–194]. These observables can also be used to cross check the masses since unexpected changes in the trend of the observables can hint to errors or deviations in the extrapolations of the mass surface. Figure 6.12 shows the two-neutron separation energies (S_{2n}) of the iodine ($Z = 53$) isotopes. The black color shows the AME16 values from the previously measured masses. The red color shows the influence of the new mass measurements for iodine isotopes from this work. The new mass measurement of ^{114}I makes it possible to present the new separation-energy values for $N = 61$ and 63. The new mass measurement for ^{116}I is also now resulting in a much weaker knee at $N = 65$ in the trend line. The smooth trend line is in a better agreement with the expected binding energies in the mid-shell closure.

Figure 6.12: The two-neutron separation energies of the iodine ($Z = 53$) isotopes. The comparison between AME16 [20] (black) and AME16 plus new evaluations including the new ^{114}I and ^{116}I masses (red) are presented.

The influence of the two new iodine masses ^{114}I and ^{116}I are magnified in the calculation of another nuclear observable called the double difference of the two-proton separation energy in the Z direction ($d_{2Z}[S_{2p}(N, Z)]$):

$$d_{2Z}[S_{2p}(N, Z)] = \frac{S_{2p}(N, Z+2) - 2 \cdot S_{2p}(N, Z) + S_{2p}(N, Z-2)}{4} \quad (6.9)$$

When $d_{2Z}[S_{2p}(N, Z)]$ is calculated with the masses reported in the literature [20], anomalies in the trend are seen in those nuclei where the binding energy of the iodine isotopes (^{114}I and in particular ^{116}I) is included (top panel of Figure 6.13). The trend of the $d_{2Z}[S_{2p}(N, Z)]$ values affected by the new mass measurements of the iodine isotopes, shows a smoother behavior as compared with the literature values of the same nuclei (filled symbols in the middle panel), in particular for ^{116}I , hinting to a mass discrepancy in the previous indirect mass measurement. A comparison for the $d_{2Z}[S_{2p}(N, Z)]$ values for the iodine chain calculated with different mass models (FRDM12 [41], UNEDF [43] and HFB24 [42]) and the experimental data obtained in this work is shown in the bottom panel of figure 6.13. The HFB24 model shows a progressive decrease from $N = 62$ to $N = 65$ and the FRDM12 model shows

a sudden change at $N = 63$. The UNEDF model seem to best describe the general trend of the experimental data. All the models agree in the overall constant trend for the observable if we take into account a substantial uncertainty from the binding energies provided by the mass models. Despite the smoother behavior of this observable with the new data included, there are still some remaining points where the $d_{2Z}[S_{2p}(N, Z)]$ presents some anomalies in the trend, such as its value for ^{114}Sb . There are also remaining large uncertainties, which prevent accurate identification of the trend, e.g. for the cesium and lanthanum isotopes ($\approx 300\#$). The main remaining anomaly seen at ^{114}Sb can be addressed by checking the binding energies of the following nuclei included in this observable: ^{114}Sb , ^{112}In (previously measured with a storage ring [195]), ^{110}Ag (previously measured with indirect methods [196, 197]) and a more precise determination of ^{116}I . The large uncertainties of the cesium and lanthanum $d_{2Z}[S_{2p}(N, Z)]$ values are caused by the mass uncertainties of the lanthanum isotopes together with the mass uncertainties of ^{115}Cs and ^{116}Cs , for which only extrapolated mass values are available in the literature [20].

Figure 6.13: The double difference of the two-proton separation energy in the Z direction $d_{ZZ}[S_{2p}(N, Z)]$ (see Eq. 6.9) for different isotopic chains calculated with: top panel) literature mass values [20]; middle panel) literature values including the mass measurement of ^{114}I and ^{116}I presented in this work. The filled/empty symbols in the middle panel represents the points which are/are not affected by the new measured masses. The trend of the $d_{ZZ}[S_{2p}(N, Z)]$ for the iodine and cesium isotopes is smoother when calculated with the new masses presented in this work. Bottom panel) the resulted iodine chain ($Z = 53$) compared to the common mass models values (FRDM12 [41], UNEDF1 [43] and HFB24 [42]) shown by dashed lines. The HFB model seems to not reproduce the general constant trend of the observable, showing a progressive decrease from $N = 62$ to $N = 65$. The FRDM model shows a sudden change at $N = 63$. The UNEDF model describes best the general trend of the experimental data.

6.2.4 Partial half-life of α decaying iodine isotopes

The island of α -decaying nuclei in the medium-heavy neutron-deficient region comprises iodine ($Z = 53$) isotopes close to the proton drip line, with the lightest reported isotope to have an α -decay branch being ^{108}I [198]. The heaviest iodine isotope with a reported α -decay branch is ^{113}I , with a branching ratio of $3.31 \times 10^{-5} \%$ [199]. For the next iodine isotope (^{114}I), no α -decaying branch has been reported and only estimates have been made from the Q_α value obtained with the extrapolated masses from the droplet-model [199]. The $\pm 1 \sigma$ uncertainty of the Q_α value translates, in the Geiger-Nuttall law, into 3 orders of magnitude of uncertainty in the partial half-life of the ^{114}I α -decay. Thus the end of the island, where the alpha-emitters stop in iodine chain of isotopes, is unknown.

In this work, the first mass measurement with its high accuracy has been used to determine the Q_α of ^{114}I and thus a more precise calculation of the decay branching ratio of this nucleus is done based on the Geiger-Nuttall law (equation 1.9). The coefficients of the Geiger-Nuttall law for the iodine chain of isotopes were obtained from the existing data on α -decay, from ^{108}I to ^{113}I , obtaining a linear function with a slope of $A(z) = 76.67$ and an intercept value of $B(z) = -39.25$. The new Q_α value is used to determine the partial half-life $T_{1/2}$ and the branching ratio (BR) of the ^{114}I isotope for α -decay. The measured Q_α value with small uncertainty is tightly constraining the partial half-life, therefore, the branching ratio of the α -decay for this isotope (see figure 6.14). The α -decay branching ratio for ^{114}I is $7.7 \times 10^{-9} \%$ with a $\pm 1 \sigma$ uncertainty below one order of magnitude (from $4.9 \times 10^{-9} \%$ to $1.2 \times 10^{-8} \%$). With these values, one can predict the expected count rate of ^{114}I α -decay in future experiments to establish the end of the island of α -emitters in the medium-heavy range of neutron-deficient isotopes.

Figure 6.14: The logarithm of the partial half-lives vs. Q_α values for the iodine isotopes. The open squares show the known partial half-lives of the iodine chain reported in AME2016 [20]. These points were used to obtain the constants of the Geiger-Nuttall law [46, 47] represented with the (blue) line. The slope of the fitted linear function is $A(z) = 76.67$ with an intercept of $B(z) = -39.25$. The gray area indicates the influence of the $\pm 1\sigma$ uncertainty of Q_α value for ^{114}I on the partial half-life. The triangle and circle represent the values calculated from the Geiger-Nuttall law using the Q_α values which include the reported ^{114}I and ^{116}I masses presented in this work. The hatched green area indicates the influence of the experimentally-reduced uncertainty of Q_α value (see table 6.2) for partial half-lives with $\pm 1\sigma$ for ^{114}I .

6.3 Isotopes in the vicinity of $N = Z$ line

The isotopes in the vicinity of the $N = Z$ line are of great interest in the study of nuclear structure, decay properties and nucleon interactions in the isotopes with the same number of protons and neutrons [48–50]. The heaviest self-conjugate ($N = Z$) nucleus is the doubly-magic ^{100}Sn with several unique properties and nuclear structure effects [60]. The mass is one of the most fundamental properties to study for these nuclei. However, most of the heavy isotopes in the vicinity of the $N = Z$ line are known only with a poor mass accuracy or their mass has not been measured yet. Figure 6.15 is the chart of isotopes

showing the mass precision of the isotopes in the vicinity of the $N = Z$ line in the most neutron-deficient side of the chart far away from the valley of stability.

The production of these isotopes in the vicinity of the $N = Z$ line is challenging due to the very low production cross sections. For the production of the isotopes below ^{100}Sn in projectile fragmentation reactions, a 800 MeV/u ^{124}Xe ion beam is used at FRS with an intensity of 1.5×10^9 ions per spill and a typical spill length of 3 s with a repetition rate of every 4-5 s impinged on a beryllium target with thickness 8.045 mg/cm². The FRS magnets are adjusted to have ^{98}Cd at its center. The fragments are then stopped and thermalized in the cryogenic stopping cell of the FRS-IC operating at 85 K and 110 mbar corresponding to an areal gas density of 6.23 mg/cm², and with a mean ion extraction time of about 80 ms. The ions are then exported and transported to MR-TOF-MS for the high-precision mass measurements. The molecular background contamination from CSC was suppressed in the RFQ beam-line with the help of the IDI [167] method (see chapter 5).

Figure 6.15: The mass precision of the isotopes in the vicinity of the $N = Z$ line. The isotopes measured in this thesis are circled. The square boxes show the stable nuclei. The chart is exported and modified from Ref. [179].

6.3.1 Mass measurement in the vicinity of $N = Z$ line

Three measurements were done with different MR-TOF-MS settings in two turn numbers 800 and 850 IT. In total, twelve ground state's masses and two isomers were identified in these measurements.

Measurement for $A/q = 96$ (1/e) to $A/q = 98$ (1/e): the measurement was done with the number of turns of 800IT for the center mass of the analyzer. The MRS limited the mass range to the range of $m/q = 95.7$ (u/e) to $m/q = 98.2$ (u/e). The high-statistics molecule $^{12}\text{C}_2^{19}\text{F}_3^{16}\text{O}^+$ with 2450 counts was used for the TRC calibration over the measurement for 111 minutes. The ^{96}Pd isotope with 567 counts with a FWHM of 205 keV, corresponding to 404,000 resolving power, was used as the calibrant for the peak shape determination of the ions of interests during the mass evaluations. In this measurement, seven ground states of isotopes and two isomers are identified: ^{96}Ru , ^{96}Rh , ^{97}Pd , ^{97}Ag , ^{97m}Ag , ^{97}Rh , ^{97m}Rh , ^{98}Pd and ^{98}Cd . The ground state mass of ^{98}Cd is measured for the first time directly. The previous indirect measurements are from the β end-point energy measurement with $Q_{EC} = 5430 \pm 40$ keV [57] and $Q_{EC} = 5330 \pm 140$ keV [66]. The ground and isomeric states of ^{97}Rh were also measured for the first time in the direct mass measurement technique. The previous mass evaluation is from the β end-point energy $Q_{EC} = 3520 \pm 40$ keV. This value is a weighted average of two different measurements [200,201]. The ground and isomeric state of ^{97}Ag are in full agreement with the recent measurement at FRS-IC [202]. A very-low lying isomer ($E_{exc.}=51.98 \pm 0.09$ keV with 1.51 minutes half-life) of ^{96m}Rh , which is not resolved from the ground state, is reflected as an additional error contribution to the evaluation of the ground-state mass. The formulations are $M_0 = M_{exp.} - E_{exc.}/2$ with uncertainty of $\sigma_0^2 = \sigma_{exp.}^2 + (\sigma_{exc.}/2)^2 + (0.29E_{exc.})^2$ presented in AME16 Appendix B4 [20]. M_0 and $M_{exp.}$ are ground-state and experimentally-measured masses, respectively. $E_{exc.}$ is the excitation energy. σ_0 , $\sigma_{exp.}$ and $\sigma_{exc.}$ are the uncertainty for ground state, experimentally-measured value and the uncertainty of the excitation energy, respectively.

Measurement for $A/q = 99$ (1/e) to $A/q = 100$ (1/e): the measurement was done with the same number of turns (800IT) but MRS set from $m/q = 98.3$ (u/e) to $m/q = 100.4$ (u/e) range and collecting the ions for 26 minutes. The high-statistics molecule $^{12}\text{C}_2^{19}\text{F}_4^+$ with 5435 counts is used for the TRC calibration and also the peak shape determination during the analysis. A 189 keV FWHM was obtained for the calibrant ion corresponding to a resolving power of 461,000. Three nuclei are identified in this measurement: ^{99}Ag , ^{100}Cd and ^{100}Ag nuclei. The ^{100}Ag has a very-low lying isomer ($E_{exc.}=15.52 \pm 0.16$ keV with 2.24 minutes half-life) which is not resolved from the ground state and shows up as an extra error in the ground state mass evaluation using the standard procedure mentioned in the last paragraph. In the case of ^{99}Ag , only the

ground state has been identified with 54 counts. The isomeric state with an excitation energy of 506.1 ± 0.4 keV and 10.1 s half-life [203] is not observed.

Measurement for $A/q = 100$ (1/e) to $A/q = 101$ (1/e): the measurement was done with the number of turns of 850IT and MRS mass range cutting from $m/q = 99.3$ (u/e) to $m/q = 101.4$ (u/e) and an ion-collection time of 28 minutes. The high-statistics molecule $^{12}\text{C}_2^{19}\text{F}_4^+$ with 6899 counts with a FWHM of 171 keV, corresponding to 500,000 resolving power, was used for the TRC calibration and also the peak shape determination during the analysis. Three nuclei are identified in this measurement: ^{100}Cd , ^{100}Pd and ^{101}In . A weighted average is taken for the ^{100}Cd mass determined in the two measurements. The ground state mass measurement of ^{101}In is in full agreement with the recent measurement at FRS-IC [202]. However, only the ground state of ^{101}In has been identified in this measurement due to the low statistics (18 counts) and reported small isomer-to-ground-state ratio of 0.14 ± 0.03 in Ref. [202].

The mass evaluations for the isotopes with a low statistics are quite challenging. However, the overall high mass accuracy achieved for the known masses in these measurements together with the mass evaluation of the known isotopes with only 5-6 counts (^{97}Pd and ^{100}Pd) are used as a benchmark to pin down the mass value of the ^{98}Cd at low statistics (7 counts). Figure 6.16 shows the mass fitting of the ^{97}Pd and ^{100}Pd isotopes in full agreements with the well known literature values [20] and consistent with the previous measurement at the FRS-IC group for the case of ^{97}Pd with a higher-statistics evaluations reported in Ref. [204]. ^{98}Cd is then analyzed with the same technique as shown in figure 6.17 as the first direct mass measurement for this isotope so far. An average background of 1.9 ± 0.2 counts is measured over a wide range of masses and normalized to the area under the peak with a width of 0.00142 u/e (from 97.9259 u/e to 97.9273 u/e). The probability of having a random background peak in this range is estimated using the Poisson distribution to be 0.3% which confirms the identification of ^{98}Cd above the background. A mass excess value of -67649 ± 64 keV was determined for the ground state of ^{98}Cd (see table 6.5 for all details).

Figure 6.16: The mass evaluation of the measured isotopes with low statistics: a) ^{97}Pd with an atomic mass excess of $\text{ME}_{\text{FRS-IC}} = -77830 \pm 69$ keV in agreement with the literature $\text{ME}_{\text{AME16}} = -77806 \pm 5$ keV and also consistent with another recent measurement at the FRS-IC group with $\text{ME}_{(\text{C.Hornung})} = -77798 \pm 37$ keV [202]; b) ^{100}Pd isotope with an atomic mass excess of $\text{ME}_{\text{FRS-IC}} = -85202 \pm 52$ keV in agreements with the literature value $\text{ME}_{\text{AME16}} = -85213 \pm 18$ keV (see table 6.5 for more details). The thin gray horizontal line shows the background level measured in the mass spectra.

Figure 6.17: The ^{98}Cd mass evaluation by fitting the wMLE using unbinned data shown in the lower section of the plot.

A separate background-measurement was done over two hours to monitor the background without the beam hitting CSC (figure 6.18). This measurement also confirms no background events close to ^{98}Cd mass while the same amount of calibrant ion ($^{12}\text{C}_2^{19}\text{F}_3^{16}\text{O}^+$) is observed.

Figure 6.18: The background measurements over two hours with beam off. MR-TOF-MS was set at 32IT. The gray band shows the area under the peak from 97.9259 u/e to 97.9273 u/e (0.00142 u/e) where ^{98}Cd would be expected to be observed.

The ground state of ^{97}Ag and the low-lying isomeric state ^{97m}Ag are fitted together with a so called double hyper-EMG [175] function. The mass excess of the ground state of $ME = -70940 \pm 19$ keV, the excitation energy of 608 ± 73 keV and the isomer-to-ground-state ratio of 0.079 ± 0.019 obtained from the measurement are in agreement with the recent measurement with FRS-IC setup reported in Ref. [204] with $ME = -70906 \pm 17$ keV, the excitation energy of 618 ± 38 keV and the isomer-to-ground-state ratio of 0.078 ± 0.005 .

In figure 6.19, the ground state of ^{97}Rh and the low-lying isomeric state ^{97m}Rh are fitted together considering a fixed distance between the ground state and the isomeric state used during the mass evaluations since the excitation energy of 258.76 ± 0.18 keV is well known from gamma spectroscopy [205]. This helps for a better determination of the ground state while the isomer is not fully resolved from the main peak. The mass of the ground state is directly measured for the first time. Figure 6.20 shows the results of the new direct mass measurements and the previously-reported indirect measurements for the ^{98}Cd and ^{97}Rh isotopes.

Figure 6.19: The ground state of ^{97}Rh and the low-lying isomeric state ^{97m}Rh . A fixed distance between the ground state and the isomeric state is used during the mass evaluations since the excitation energy of 258.76 ± 0.18 keV is well known from gamma spectroscopy [205].

Figure 6.20: The comparison of the atomic mass values from the FRS-IC direct mass measurements and the reported indirect measurements for ^{98}Cd (A. Plochocki et al. [66] and A. Stolz [57] [not a peer-reviewed publication]) and ^{97}Rh (B. Basu et al. [200] and V. L. Chikhladze et al. [201]) ground states.

Table 6.4 shows the different error components calculated for the new direct mass measurements of ^{98}Cd and ^{97}Rh .

Table 6.4: A list of error components of the mass uncertainty in the measurements for ^{98}Cd and ^{97}Rh nuclei.

Error [u]	^{98}Cd	^{97}Rh
Statistical	4.3E-5	1.3E-5
Calibrant	7.2E-6	7.1E-6
Peak shape	3.2E-5	4.0E-6
TRC	6.3E-6	6.2E-6
MRS	00	00
NPE	8.9E-7	8.8E-7
Contamination	1.4E-5	«1E-8
Δt_0	5.3E-9	3.3E-9
Δc	1.6E-5	8.2E-6
Total [u]	6.8E-5	1.9E-5

Table 6.5 represents a summary of the directly measured ground-state masses and the excitation energy of the isomers measured at FRS-IC. Figure 6.21 shows the difference between the measured atomic mass excess of all the nuclei investigated and the literature values.

Table 6.5: The results of the direct mass measurements with FRS-IC for the ground and isomeric states of the nuclei compared to the literature values from AME16 [20] and other literature data like those from recent measurements with FRS-IC [202]. Twelve ground-state masses and two isomers are identified in total. The ground states of ^{98}Cd and ^{97}Rh isotopes were measured directly for the first time. The production cross sections in the target are calculated by LISE++ for ^{124}Xe ion beam at 800 MeV/u on beryllium target.

Nuclei	Cross section (mb)	Half-life	Reference ion	ME _{FRS-IC} (keV)	ME Ref. [202] (keV)	ME _{AME16} (keV)	ME _{FRS-IC} - ME _{AME16} (keV)	Number of events
^{96}Ru	1.07e+1	stable	^{96}Pd	-86075 ± 28	-	-86080 ± 0.17	5 ± 28	15
^{96}Rh	2.48e0	9.9 min	^{96}Pd	-79655 ± 40	-	-79688 ± 10	33 ± 41	10
^{97}Pd	3.94e-1	3.1 min	^{96}Pd	-77830 ± 69	-77798 ± 37	-77806 ± 5	-24 ± 69	6
^{97}Ag	1.77e-3	25.5 s	^{96}Pd	-70940 ± 19	-70906 ± 17	-70830 ± 110	-110 ± 112	54
^{98}Pd	1.94e0	17.7 min	^{96}Pd	-81326 ± 21	-	-81321 ± 5	-5 ± 22	102
^{99}Ag	2.70e-1	2.07 min	$^{12}\text{C}_2$ $^{19}\text{F}_4$	-76709 ± 33	-	-76712 ± 6	3 ± 33	53
^{100}Ag	1.49e0	2.01 min	$^{12}\text{C}_2$ $^{19}\text{F}_4$	-78095 ± 31	-	-78138 ± 5	43 ± 32	12
^{100}Cd	2.74e-2	49.1 s	$^{12}\text{C}_2$ $^{19}\text{F}_4$	-74194 ± 12	-	-74195 ± 2	0.7 ± 12	74
^{100}Pd	1.07e+1	3.63 d	$^{12}\text{C}_2$ $^{19}\text{F}_4$	-85202 ± 52	-	-85213 ± 18	11 ± 55	5
^{101}In	5.00e-4	15.1 s	$^{12}\text{C}_2$ $^{19}\text{F}_4$	-68559 ± 25	-68535 ± 20	-68610 ± 200	51 ± 202	17
^{98}Cd	3.02e-5	9.2 s	^{96}Pd	-67649 ± 64	-	-67640 ± 50	-9 ± 81	7
^{97}Rh	6.54e0	30.7 s	^{96}Pd	-82553 ± 18	-	-82600 ± 40	47 ± 44	77
Isomer	Half-life	J^π	Exc. FRS-IC (keV)	Exc. Ref. [202] (keV)	Exc. AME16 (keV)	Isomer-to-ground- state ratio		
^{97m}Ag	100# ms	1/2 ⁻ #	608 ± 73	618 ± 38	400# ± 200#	0.079 ± 0.019		
^{97m}Rh	26.2 min	1/2 ⁻	fixed	-	258.76 ± 0.18	0.052 ± 0.038

Figure 6.21: The atomic mass-excess difference for the measured isotopes compared to the literature values at AME16 [20] or other labs. The green-colored error bars indicate the errors in the FRS-IC measurements and the gray band represents the literature error in mass excess. For the isotopes in the square boxes on the x axis, the new literature value from the recent measurements at FRS-IC is considered from Ref. [202]. The red isotopes in the right panel show the first direct mass measurements for ^{98}Cd , ^{97}Rh .

In order to confirm the accuracy of the measurements for the reported new masses, a histogram of the mass-excess deviation only for the measured isotopes with known masses (the nuclei in the left part of figure 6.21) are plotted in figure 6.22 resulting in a mean value of $\mu = -1.5 \pm 5.1 \text{ keV}$ and a 1 sigma standard deviation of $\sigma = 33 \text{ keV}$. This confirms the accuracy of the measurements and the reliability of the analysis method and the reported new masses for ^{98}Cd and ^{97}Rh isotopes.

Figure 6.22: Histogram of the difference between the mass excess and the AME16 values for the known masses (left part in figure 6.21) with a mean value of $\mu = -1.5 \pm 5.1$ keV and a 1 sigma standard deviation of $\sigma = 33$ keV.

6.3.2 Systematic studies of isotopes in the vicinity of $N = Z$ line

The separation energies and the decay properties of nuclei in the region of the $N = Z$ line can be studied using the new mass measurements. The measured masses show their impact in the two-neutron separation energies around the $N = 50$ shell closure (figure 6.23). The top panel shows the two-neutron separation energy for $Z = 44 - 49$ evaluated from AME16 data and AME16+(FRS-IC) measurements. The slope observed at before the shell-closure ($N = 49 - 50$) seems steeper for Cd than that of other neighboring nuclei. However, after the shell-closure ($N = 52 - 53$) not a significant slope-change is seen. The important nuclei here are ^{98}Cd , which is reported in this work, and ^{96}Cd with an extrapolated value with a large uncertainty (400# keV). The bottom panel compares the new measurements at FRS-IC (Cd $Z = 48$) with the common mass model values: FRDM12 [41], UNEDF [43] and HFB24 [42]. In the investigated region of $N = 52 - 53$ the UNEDF model describes the experimental values best, as the other models predict a larger slope. This model (UNEDF) also predicted a smoother slope at $N = 49 - 50$, resulting in Cd to have similar behavior as the other neighboring nuclei.

Figure 6.23: The top panel shows the two-neutron separation energies for $Z = 44 - 49$ from AME16 [Black] and AME16+(FRS-IC) [Red] measurements. The bottom panel compares the new measurements at FRS-IC with the common mass model values for Cd ($Z = 48$) nucleus (FRDM12 [41], UNEDF [43] and HFB24 [42]). The ## sign shows the extrapolated mass values used for both $M(Z, N)$ and $M(Z, N - 2)$ nuclei, and the # sign indicates that only one of the mass values is extrapolated. The filled red circles shows reported measurements of this work and non-filled red circles shows the AME values.

A new $Q_{EC} = 5421 \pm 71$ is calculated by using the directly measured mass of ^{98}Cd in this work. The new Q_{EC} value improved the uncertainty from the extrapolated value ($Q_{EC} = 5330 \pm 140$) reported in a peer-reviewed Ref. [66] from the (β^+ / EC) end-point energy measurements. Using the new Q_{EC} and the $\log(ft)$ values calculated from Ref. [206] together with the known decay scheme presented in Ref. [66], the summed Gamow-Teller strength ($B(\text{GT})$) is calculated (see equation 1.10) for the four observed transitions ($0^+ \rightarrow 1^+$) as $B(\text{GT}) = 2.9 \pm 0.2$ (see table 6.6). The new GT strength improved the uncertainty and it is still consistent with the previously reported value of $B(\text{GT}) = 3.5^{+0.8}_{-0.7}$ in Ref. [66]. The quenching of the GT strength is predicted and observed for the case of even-even nuclei at $N = 50$ close to doubly-magic ^{100}Sn ($N = Z = 50$) with the highest GT strength observed so far [61,64,66]. This was discussed in details in chapter 1.

Table 6.6: The $\log(ft)$ and individual Gamow-Teller strength $B(\text{GT})$ calculated for the four observed transitions ($0^+ \rightarrow 1^+$).

Energy [keV]	Branching ratio [%]	$\log(ft)$	$B(\text{GT})$
1691.1 ± 23	80%	3.3	1.95
1861.1 ± 5	6.5%	4.3	0.19
2164.9 ± 5	8.2%	3.9	0.49
2544.4 ± 8	2.8%	4.1	0.31

Chapter 7

Conclusions and outlook

The goal of this thesis was to develop new methods to study the nuclear structure for $A \sim 100$ neutron-deficient isotopes by means of half-life and mass measurements. The thesis is divided into three main sub-projects. First, the initial developments of the CISE setup for chemical isobaric separation of ions. Second, the developments in the gas-handling system of the Cryogenic Stopping Cell (CSC) of the FRS-IC setup. Third, half-life and mass measurements of medium-heavy and heavy nuclei by using MR-TOF-MS technique at the FRS-IC setup.

The CISE (Chemical Isobaric SEparation) setup is being developed at KVI-CART, the Netherlands. The technique will be used as an additional separation step for the low-yield and high-background isotope productions. CISE setup (shown in figure 4.2) consists of a gas catcher and an ion-guide that are coupled to a qToF mass spectrometer. The ion-optics simulations and the differential pumping calculations are presented in chapter 4. The technical design was developed for coupling of the gas catcher and ion-guide assembly to the qToF mass spectrometer and the construction has started.

The potential application of the setup will be for the separation of ^{100}Sn and ^{100}In from the other two isobars ^{100}Ag and ^{100}Cd that are produced in the appropriate fusion-evaporation reaction. Measurements have been performed by using an electrospray ion source attached to the qToF for the studies of the stable Ag, Cd, In and Sn ions. The chemical reactions have been investigated within the hexapole collision cell suggesting the proof-of-principle for chemical isobaric separation technique based on the different cluster formations. The results shown in figure 4.26 show a higher tendency of two isobars Ag and Cd to have cluster formations with the reactive gas contamination. On the other hand, In did not react with the reactive gas in the collision cell and was detected as atomic ions at qToF. Unfortunately, Sn could not be fully studied due

to a low production yields with the use of the electrospray ion source. In addition, the studies were limited due to the maximum allowed pressure in the hexapole collision cell limiting the amount of chemical reactions in it. The collision cells are usually used for CID (Collision Induced Dissociation) technique, operating at much lower pressures than CSC. However, the studies will serve as a guidance for future systematic studies after construction of the gas catcher for investigations at higher operating pressures and a better-controlled gas conditions.

The second part of the PhD project covered the developments and improvements in the gas handling system of the Cryogenic Stopping Cell (CSC) of the FRS-IC setup (presented in chapter 5). Operation of CSC at relatively high areal gas density (a factor of 10 higher than other operating cells, e.g. the one presented in Ref. [156]) makes FRS-IC setup much more sensitive to the gas impurities due to the higher number of collisions between ions and buffer gas atoms. Small amount of impurities can strongly influence the ion survival and extraction efficiency of the stopping cell. Therefore, the gas cleanliness of CSC must be improved and continuously monitored during the operations. To achieve this, the gas handling system of the FRS-IC setup was upgraded with some new gas purifiers. To investigate and validate the gas-cleanliness, measurements were performed using the new techniques developed for monitoring the different types of gas contaminations in CSC. Another challenge in gas cleanliness of CSC is the presence of noble gases in helium gas due to the history of gas bottles. Noble gases are not removed by other means and pose a problem for mass measurements; see Ref. [112]. To overcome this problem, the cold trap was constructed and tested successfully for the suppression of noble gases like Xe and Kr present in the He gas. A suppression factor of 6.5 and 1.7 was achieved for the Xe and Kr atoms, respectively (see figure 5.9 for the Xe suppression). The measurements were used to estimate the number of expected Xe^+ produced in the case of beam with much larger ionization in CSC compared to the offline sources (see table 5.2).

The third part of the PhD project entailed the new mass and half-life measurements of medium-heavy and heavy nuclei by using the MR-TOF-MS technique at the FRS-IC setup (presented in chapter 6). In the neutron-deficient region of chart of isotopes, the mass of ^{114}I has been measured for the first time together with the half-life of its ground state. Furthermore, the mass of ^{116}I was measured as the first direct mass measurement. The new measured masses were used to study nuclear structure and decay properties of the nuclei in this region. The two-neutron separation energies at $N = 61$ and 63 are, for the first time, determined directly and show a much smoother trend (figure 7.1 (a)) than expected before by extrapolated values. The effect of the new iodine masses are shown on the double difference of the two-proton separation energies in the Z direction improving the irregularities observed from the literature masses. The significantly improved uncertainty of Q_α value for α -decay of ^{114}I allows a

more accurate determination of the partial half-life and the branching ratio of $7.7 \times 10^{-9} \%$ with an uncertainty ranging from $4.9 \times 10^{-9} \%$ to $1.2 \times 10^{-8} \%$. This is an improvement by a factor of 9 (see figure 7.1 (b)). This allows to predict the expected count rate of ^{114}I α -decay in future experiments to establish the shore line of the island of α -emitters in the medium-heavy range of neutron-deficient isotopes.

Figure 7.1: a) The two-neutron separation energies of the iodine ($Z = 53$) isotopes. The comparison between AME 2016 [20] (black color) and the AME16 data plus new evaluations considering the new ^{114}I and ^{116}I masses (red color) are presented. b) The logarithm of the partial half-lives vs. Q_α values for the iodine isotopes. The gray area indicates the influence of the $\pm 1\sigma$ uncertainty of Q_α value from AME16 for ^{114}I on the partial half-life. The triangle and the circle represent the values calculated from the Geiger-Nuttall law using the Q_α values which include the reported ^{114}I and ^{116}I masses presented in this work. The hatched green area indicates the influence of the experimentally-reduced uncertainty of Q_α value (see table 6.2) for partial half-lives with $\pm 1\sigma$ for ^{114}I .

Furthermore, the masses of 12 ground states and 2 isomers are measured in the region of isotopes close to the $N = Z$ line below ^{100}Sn . The masses of ^{98}Cd and ^{97}Rh ground states are directly measured for the first time; together with the determination of the isomer-to-ground-state ratio in the case of ^{97}Rh isotope. A mass accuracy with a mean value of $\mu = -1.5 \pm 5.1$ keV with a 1σ standard deviation of 33 keV, showing an excellent agreement with the well-known literature masses. The results of the new mass measurements have an influence on two-neutron separation energy close to the $N = 50$ shell closure. They are also compared to the predictions of the mass models in this region. A new $Q_{EC} = 5421 \pm 71$ enables one to determine the Gamow-Teller Strength $B(\text{GT})$ more precisely. A $B(\text{GT})$ of 2.9 ± 0.2 is calculated from the new direct mass measurements on ^{98}Cd isotope in this work.

Figure 7.2 shows a summary of the mass excess difference for all measured masses in this thesis compared to the literature values. The comparison with the existing values in the left panel shows that our measurement system and analysis techniques are well understood and reliable. The masses of the nuclei in the right panel have been measured for the first time directly.

Figure 7.2: The atomic mass-excess difference for the measured isotopes compared to the literature values. The green-colored error bars indicate the FRS-IC measurements and the gray band represents the AME16 error in mass excess of the shown isotopes. For ^{97}Ag , ^{97m}Ag and ^{101}In isotopes the new literature value from the recent measurements at FRS-IC is considered from Ref. [202]. The red isotopes in the right panel show the first direct mass measurements for ^{98}Cd , ^{97}Rh and ^{116}I , together with the first mass measurement for ^{114}I . An estimation value is used for the literature value in the case of ^{114}I since there was no measurement before.

As an outlook to future experiments, the systematic studies on CISE project will be continued by full commissioning of the setup with the gas catcher and the ion-guide assembly attached to the qToF mass spectrometer. This will allow us to find the optimum chemistry condition for chemical isobaric separation technique and to extend the technique for the separation of exotic nuclei in accelerator-based experiments. This will be a potential method for measuring the doubly-magic ^{100}Sn for high-precision mass measurements.

The developments for the FRS-IC setup will serve as a major improvement for studying short-lived exotic nuclei. The different techniques that have been developed for gas-handling system of FRS-IC, will be implemented in the future gas recycling unit of the cryogenic stopping cell of the low-energy branch of the Super-FRS at FAIR. Furthermore, a completely new gas-line installed for trace gases is required for the experiments involving charge-state manipulations of ions. The trace gases with low ionization potentials like NO (IP of 9.25 eV) and CH_4 (IP of 12.70 eV) can be used, in future, for charge-state manipulation

of the extracted ions from CSC. This will solve the difficulties for extraction of expected highly-charged ions from CSC. All the efforts for the gas cleanliness and the charge-state manipulations will be important for the upcoming experiments at FRS@GSI for the measurements on $N = Z$ nuclei [207]. More precisely, the special interest in this region is the nuclear deformations of isotopes in the vicinity of ^{80}Zr which are refractory and difficult to produce in ISOL technique and they should be extracted as doubly-charged ions from the nitrogen dominated CSC.

All the developments and achievements in this field will push the campaign toward studying the more exotic isotopes. Extended mass measurements for the isotopes located at the more exotic side of the medium-heavy and neutron-deficient region of the chart of isotopes are required for understanding nuclear structure and decay properties of nuclei in this region. The results of the measurements would have a great impact on the astrophysical nuclear synthesis e.g. rp-process, and solve the puzzles for the isotopes around $N = Z$ line; toward catching the most special case of the doubly-magic ^{100}Sn with unique properties and mysteries in its shell structure.

Nederlandse samenvatting

De doelstelling van dit proefschrift was om nieuwe methoden te ontwikkelen en onderzoek te doen naar de kern structuur voor $A \sim 100$ neutron-deficiënte isotopen middels halfwaardetijd en massametingen. Het proefschrift is onderverdeeld in drie belangrijke deelprojecten: allereerst, de initiële ontwikkelingen van de CISE opstelling voor de chemische isobarische scheiding van ionen; en in het tweede deel, de ontwikkelingen in het gasbehandelingssysteem van de Cryogenic Stopping Cell (CSC) van de FRS-IC opstelling. Tenslotte, halfwaardetijd en massametingen van een aantal middelzware en zware kernen middels MR-TOF-MS techniek bij de FRS-IC opstelling waren gemeten.

De CISE (Chemical Isobaric SEparation) opstelling wordt ontwikkeld bij KVI-CART in Nederland. De techniek zal worden gebruikt als een aanvullende scheidingsstap voor de producties van isotopen met lage opbrengst en hoge achtergrond. De CISE opstelling (weergegeven in figuur 4.2) is opgebouwd uit een gasvanger en een ionengeleider die gekoppeld zijn aan een qToF-massaspectrometer. In hoofdstuk 4 worden de ionenoptische simulaties en de differentiële berekeningen van de pomp behandeld. Voor de koppeling van de gasvanger en de ionengeleider aan de qToF-massaspectrometer is het technisch ontwerp ontwikkeld en is de constructie in gang gezet.

Deze opstelling kan worden toegepast voor de scheiding van ^{100}Sn en ^{100}In van de twee andere isobaren ^{100}Ag en ^{100}Cd die in dezelfde fusie-verdampingsreactie worden geproduceerd. Om de stabiele Ag, Cd, In en Sn ionen te onderzoeken, zijn de metingen uitgevoerd met behulp van een elektro spray ionenbron gekoppeld aan de qToF. Er is onderzoek gedaan naar de chemische reacties binnen de hexapool-botsingscel, hetgeen de proof of principle voor chemische isobarische scheidingstechniek suggereert op basis van de verschillende clusterformaties. Op grond van de resultaten in figuur 4.26 is er een hogere waarschijnlijkheid van clusterformaties door isobaren Ag en Cd met de reactieve gascontaminatie. Terwijl de andere isobaar (In) niet reageerde met het reactieve gas in de botsingscel en als atoomionen werden gedetecteerd bij qToF. Als gevolg van een lage productieopbrengst, met het gebruik van de elektro spray ionenbron, kon Sn helaas niet optimaal worden onderzocht. Tevens werden de onderzoeken

gelimiteerd door de maximaal toegestane druk in de hexapole botsingscel, hetgeen de hoeveelheid chemische reacties in de hexapole botsingscel beperkt. De botsingscellen worden doorgaans gebruikt voor CID (Collision Induced Dissociation) techniek, waarbij gewerkt wordt met een aanzienlijk lagere druk dan bij CSC. De onderzoeken zullen echter dienen als leidraad voor toekomstige systematische onderzoeken na de constructie van de gasvanger voor onderzoek bij hogere werkdrukken en beter gereguleerde gascondities.

In het tweede deel van het PhD project werden de ontwikkelingen en verbeteringen in het gasbehandelingssysteem van de Cryogenic Stopping Cell (CSC) in de FRS-IC opstelling (gepresenteerd in hoofdstuk 5) behandeld. De werking van CSC bij een relatief hoge dichtheid van het gas (een factor 10 hoger dan andere werkingscellen, bijvoorbeeld degene gepresenteerd in Ref. [156]) zorgt ervoor dat de FRS-IC opstelling aanzienlijk gevoeliger is voor de gasonzuiverheden door het verhoogde aantal botsingen tussen ionen en buffergasatomen. De ionenoverleving en de extractie-efficiëntie van de stopcel kunnen fors worden beïnvloed door een geringe hoeveelheid onzuiverheden. De gasreiniging van CSC moet derhalve tijdens de werkzaamheden worden verbeterd en voortdurend worden gecontroleerd. Om dit te verwezenlijken is het gasbehandelingssysteem van de FRS-IC opstelling voorzien van een aantal nieuwe gaszuiveraars. Om de gasreiniging te onderzoeken en te valideren zijn er metingen uitgevoerd met behulp van de nieuwe technieken die ontwikkeld zijn voor het monitoren van de diverse soorten gasverontreinigingen in CSC. Door de geschiedenis van de gasflessen is de aanwezigheid van edele gasen in heliumgas een bijkomende uitdaging op het gebied van gasreiniging van CSC. De edelgassen worden niet op andere wijze verwijderd en vormen een probleem voor de metingen van de massa; zie Ref. [112]. Om dit probleem te verhelpen werd een koude val geconstrueerd en daarnaast succesvol getest voor de onderdrukking van edelgassen zoals Xe en Kr die in het He-gas aanwezig zijn. Voor de Xe- en Kr-atomen werd, respectievelijk, een onderdrukkingsfactor van 6,5 en 1,7 gerealiseerd (zie figuur 5.9 voor de onderdrukking van Xe). Met behulp van de metingen werd een raming gemaakt van het te verwachten aantal geproduceerde Xe^+ bij een bundel met een aanzienlijk grotere ionisatie in CSC ten opzichte van de offline-bronnen (zie tabel 5.2).

In het derde deel van het PhD project werden metingen van de nieuwe massa en de halveringstijd van een aantal middelzware en zware kernen uitgevoerd met behulp van de MR-TOF-MS techniek in de FRS-IC opstelling (gepresenteerd in hoofdstuk 6). In het gebied met het neutronentekort van de kaart van isotopen is voor het eerst de massa van ^{114}I gemeten tezamen met de halveringstijd van de grondtoestand. Voorts werd de massa van ^{116}I gemeten als de eerste directe massameting. Aan de hand van de nieuw gemeten massa's werden de kern structuur en de relevante eigenschappen van de kernen in deze omgeving bestudeerd. De scheidingsenergieën van twee neutronen bij $N = 61$

en 63 worden, voor het eerst, rechtstreeks bepaald en vertonen een aanzienlijk vloeiender verloop (figuur 7.3 (a)) dan voorheen werd verwacht door middel van geëxtrapoleerde waarden. De invloed van de nieuwe jodiummassa's wordt getoond op het dubbele verschil van de twee-protonen scheidingsenergieën in de Z -richting, waardoor de waargenomen onregelmatigheden uit de literatuurmassa's worden verbeterd. Dankzij de aanzienlijk verbeterde onzekerheid van de Q_α waarde α -decay van ^{114}I kan de gedeeltelijke halfwaardetijd en de branching ratio van $7.7 \times 10^{-9} \%$ accurater worden bepaald, waarbij de onzekerheid varieert van $4.9 \times 10^{-9} \%$ tot $1.2 \times 10^{-8} \%$. Hieruit volgt een verbetering van een factor 9 (zie figuur 7.3 (b)). Dit maakt het mogelijk om in toekomstige experimenten de verwachte telsnelheid van ^{114}I α -verval te voorspellen voor het vaststellen van de kustlijn van het gebied van α -stralers in het middelzware bereik van neutron-deficiënte isotopen.

Figure 7.3: a) De twee-neutronen scheidingsenergieën van jodium ($Z = 53$) isotopen. De vergelijking tussen AME16 [20] (zwarte kleur) en de AME16 gegevens plus nieuwe evaluaties met betrekking tot de nieuwe ^{114}I en ^{116}I massa's (rode kleur) worden gepresenteerd. b) De logaritme van de partiële halfwaardetijden vs. Q_α waarden voor de jodiumisotopen. De grijze oppervlakte geeft de invloed aan van de $\pm 1\sigma$ onzekerheid van de Q_α waarde uit AME16 voor ^{114}I op de partiële halfwaardetijd. De driehoek en de cirkel geven de berekende waarden op basis van de Geiger Nuttall wet met behulp van de Q_α waarden die de gerapporteerde ^{114}I en ^{116}I massa's omvatten die in dit werk worden weergegeven. Het gearceerde groene gebied geeft de impact aan van de experimenteel verminderde onzekerheid van de Q_α waarde (zie tabel 6.2) op de gedeeltelijke halfwaardetijden met $\pm 1\sigma$ voor ^{114}I .

Tevens worden de massa's van 12 grondtoestanden en 2 isomeren gemeten in het gebied van isotopen die zich dicht bij de $N = Z$ lijn onder ^{100}Sn bevinden. Voor het eerst worden de massa's van ^{98}Cd en ^{97}Rh grondtoestanden rechtstreeks gemeten; tezamen met de bepaling van de isomeer/grondtoestand verhouding in het geval van ^{97}Rh isotoop. Er is een massaanauwkeurigheid met

een gemiddelde waarde van $\mu = -1.5 \pm 5.1$ keV met een 1σ standaarddeviatie van 33 keV, hetgeen een uitstekende overeenkomst met de reeds bekende literatuurmassa's toont. Bij de nieuwe massametingen zijn de resultaten van invloed op de twee-neutronen scheidingsenergie in het bereik van de $N = 50$ schil-sluiting. Bovendien worden deze vergeleken met de voorspellingen van de massamodellen in deze regio. Dankzij een nieuwe $Q_{EC} = 5421 \pm 71$ kan men de Gamow-Teller sterkte $B(GT)$ nauwkeuriger bepalen. Op basis van de nieuwe directe massametingen op ^{98}Cd isotoop wordt een $B(GT)$ van 2.9 ± 0.2 berekend in dit onderzoek.

Figuur 7.4 toont een samenvatting van het verschil in massaoverschot voor alle gemeten massa's in dit proefschrift ten opzichte van de literatuurwaarden. Uit de vergelijking met de bestaande waarden in het linker gedeelte blijkt dat ons meetsysteem en analysetechnieken goed begrepen en betrouwbaar zijn. De massa's van de kernen in het rechter gedeelte zijn voor het eerst rechtstreeks gemeten.

Figure 7.4: Het verschil in atoommassa-overschot voor de gemeten isotopen ten opzichte van de literatuurwaarden. De groen gekleurde foutbalken tonen de FRS-IC metingen en de grijze band vertegenwoordigt de AME16 fout in massaoverschot van de getoonde isotopen. Voor de isotopen ^{97}Ag , ^{97m}Ag en ^{101}In wordt de nieuwe literatuurwaarde uit de recente metingen bij FRS-IC beschouwd van Ref. [202]. In het rechterdeel worden de eerste directe massametingen voor ^{98}Cd , ^{97}Rh en ^{116}I weergegeven, tezamen met de eerste massameting voor ^{114}I . In het geval van ^{114}I wordt een schattingswaarde gebruikt voor de literatuurwaarde, omdat er voorheen geen meting heeft plaatsgevonden.

In het kader van toekomstige experimenten zullen de systematische studies van het CISE-project worden voortgezet door de volledige ingebruikname van

de opstelling met de gasvanger en de ionengeleider gekoppeld aan de qToF-massaspectrometer. Op deze manier kunnen we de optimale chemische conditie voor de chemische isobarische scheidingstechniek vaststellen en de techniek voor de scheiding van exotische kernen in experimenten op basis van versnellers uitbreiden. Dit zal een potentiële methode zijn voor het vangen van de dubbel magische ^{100}Sn voor zeer nauwkeurige massametingen.

Voor het bestuderen van kortlevende exotische kernen zullen de ontwikkelingen voor de FRS-IC-opstelling fungeren als een belangrijke verbetering. De verschillende technieken die ontwikkeld zijn voor het gasbehandelingssysteem van FRS-IC, zullen worden geïmplementeerd in de toekomstige gasrecycle-eenheid van de cryogene stopcel in de lage-energie tak van de Super-FRS bij FAIR. Tevens is een volledig nieuwe gasleiding voor spoorgassen vereist voor de experimenten met ladingstaat manipulaties van ionen. In de toekomst kunnen de spoorgassen met lage ionisatiepotentialen zoals NO (IP van 9,25 eV) en CH_4 (IP van 12,70 eV) worden gebruikt voor ladingstaat manipulatie van de geëxtraheerde ionen uit CSC. Hiermee worden de knelpunten voor de winning van de verwachte hoog geladen ionen uit CSC opgelost. Alle inspanningen voor de gasreiniging en de ladingstaat manipulaties zullen belangrijk zijn voor de komende experimenten op FRS@GSI voor de metingen op $N = Z$ kernen [207]. Om precies te zijn, het bijzondere belang in deze regio is de kern vervorming van isotopen nabij ^{80}Zr die refractair en lastig te produceren zijn met behulp van de ISOL-techniek en die als dubbel geladen ionen uit de door stikstof overheerste CSC zouden moeten worden geëxtraheerd.

Dankzij alle ontwikkelingen en prestaties op dit gebied zal de campagne zich richten op de bestudering van de meer exotische isotopen. Voor het begrijpen van de kern structuur en het verval van de kernen in dit gebied zijn uitgebreide massametingen nodig voor de isotopen die zich aan de meer exotische kant van het middelzware en neutron deficiënte gebied van de isotopenkaart bevinden. Met behulp van de resultaten van de metingen zou de astrofysische kernsynthese, bijvoorbeeld het rp-proces, sterk worden beïnvloed en zouden de puzzels voor de isotopen rondom de $N = Z$ lijn worden opgelost; om zodoende de meest bijzonder exemplaar van de dubbel magische ^{100}Sn met unieke eigenschappen en mysteries in de schilstructuur te kunnen vangen.

List of Abbreviations

CID	C ollision I nduced D issociation
CISE setup	C hemical I sobaric S eparator setup
CSC	C ryogenic S topping C ell
DC	D irect C urrent
ESR	E lectromagnetic S torage R ing
FAIR	F acility for A nti-proton and I on R esearch
FRS	F Ragment S eparator
FRS-IC	FRS Ion C ather
FT-ICR	F ourier T ransform I on C yclotron R esonance
FWHM	F ull W idth H alf M aximum
GS	G round S tate
Hyper-EMG	H yper E xponentially M odified G aussian
IDI	I solation D issociation I solation
IMS	I sochronous M ass S pectrometry
IS	I someric S tate
ISOL	I sotope S eparation O n- L ine
IT	I sochronous T urn
KS-test	K olmogorov S mirnov t est
KVI	K ernfysisch V ersneller I nstituut
KVI-CART	KVI C enter for A dvanced R adiation T echnology
LDM	L iquid D rop M odel
LEB	L ow E nergy B ranch
LMCO	L ow M ass C ut O ff
MR-TOF-MS	M ulti R eflection T ime O f F light M ass S pectrometer
MRS	M ass R ange S elector
MUSIC	M ultiple S ampling I onization C hamber
NPI	N on P erfect E ejection
NPI	N on P erfect I njection
NSM	N uclear S hell M odel
PI-ICR	P hase I maging I on C yclotron R esonance
PID	P article I Dentification
r-process	r apid neutron-capture process
RF	R adio F requency
RGA	R esidual G as A nalyzer

rp-process	rapid proton-capture process
s-process	slow neutron-capture process
SCI	SC Intillator
SMS	S chottky M ass S pectrometry
TOF-ICR	T ime O f F light I on C yclotron R esonance
TPC	T ime P rojectile C hamber
TRC	T ime R esolved C alibration
UNILAC	U Niversal L inear A Celerator
wMLE	w eighted M aximum L ikelihood E stimation

List of Figures

1.1	The mass uncertainties for more than 3000 nuclei measured at various laboratories [17, 18].	4
1.2	The evolution of the shell closure by plotting the two neutron and two-proton separation energies indicating the closed shells.	5
1.3	The deviations between the theoretical nuclear binding energies evaluated by LDM and the experimental values.	8
1.4	The predictive power of the mass models from Rh ($Z = 45$) to Cs Rh ($Z = 55$).	8
1.5	The logarithms of partial half-lives for the even-even Yb-Ra nuclei as a function of $Q_{\alpha}^{-1/2}$ described by Geiger-Nuttall law.	10
2.1	ISOLDE target before irradiation at ISOL facility of CERN [70, 71].	15
2.2	ISOLDE yields over the chart of isotopes taken from reference [72] based on the ISOLDE yield database.	15
2.3	The in-flight method at FRS facility [73] for the production and the separation of the ^{78}Ni nuclei as an example [73].	16
2.4	The predicted isotope yield for the future Super-FRS facility utilizing the in-flight technique (adopted from Ref. [72]).	17
2.5	The schematic view of the most common reaction mechanisms for the production of the new isotopes [86].	18
2.6	The cross cut of a penning trap working at TITAN, TRIUMF [92] and the motion of ions in the trap [93].	20
2.7	The Electromagnetic Storage Ring (ESR) at GSI facility, Darmstadt, Germany.	21
2.8	The Schottky Mass Spectrometry and Isochronous Mass Spectrometry methods for the mass measurements at ESR, GSI.	23
3.1	The effective forces applied to ions in a gas cell.	26
3.2	The FRS cryogenic stopping cell at GSI, Darmstadt, Germany.	27
3.3	The RF carpet and RF funnel structures.	28
3.4	The decay chain of the ^{223}Ra radioactive ion source.	30
3.5	The decay chain of the ^{228}Th radioactive ion source.	31
3.6	The fission products of the ^{252}Cf source.	32
3.7	Schematic view of the laser ablation ion-production technique.	33

3.8	The structure of a discharge ion source.	33
3.9	A cross cut of RF multiples in (x,y) plane.	34
3.10	The potential shapes for quadrupole, hexapole and octupole.	35
3.11	A quadrupole geometry.	38
3.12	The stability diagrams of x and y coordinates of a quadrupole.	40
3.13	The overlap of the stability diagrams in x and y coordinate.	40
3.14	The stability diagram of a quadrupole.	41
3.15	The location of the three masses $m_3 > m_2 > m_1$ in the stability region.	42
3.16	The different resolving-power lines $R_1 > R_2 > R_3$ in the stability regions.	43
3.17	Three general techniques for the ToF mass spectrometry for low- and high-precision mass spectrometry.	46
3.18	The definition of mass resolving power based on the 50% intensity level of a single Gaussian peak.	48
3.19	The Van der Waals radii of ions and buffer gas atoms in an elastic collision.	51
4.1	Nuclei produced in fusion-evaporation reaction $^{50}\text{Cr}+^{58}\text{Ni}$ at 5.1 MeV/u projectile energy, evaluated by using the statistical model PACE4 with the LISE++ software.	55
4.2	Schematic of the CISE setup which consists of a gas catcher and an ion-guide that are coupled to a commercial qToF.	59
4.3	The DC and RF forces applied to the ions inside the gas catcher.	60
4.4	Ion trajectories in the vicinity of the exit hole of the RF carpet.	61
4.5	Coupling ion-guide assembly including hexapole 1 and hexapole 2 and three electrostatic lenses in between.	62
4.6	The schematic view of the differential pumping system of the CISE setup.	63
4.7	The technical drawing of hexapole 1 in the left and a cut of the RF potential simulated by COMSOL in the right.	65
4.8	The phase space of the extracted ions from the gas catcher at a distance of 2 mm behind the RF carpet.	65
4.9	The energy spectrum of the extracted ions from the gas catcher at a distance of 2 mm behind the RF carpet.	66
4.10	Capturing the diverging ion beam extracted from the RF carpet.	66
4.11	Collision cooling of the ions in hexapole 1 at a pressure of $\sim 3 \times 10^{-3}$ mbar.	67
4.12	The evolution of the phase space of Ag^+ ions guided by hexapole 1.	68
4.13	The evolution of the phase space of AgCH_4^+ ions in hexapole1.	69
4.14	The energy spectrum of atomic ions Ag^+ (blue) and ion clusters AgCH_4^+ (purple) at the end of hexapole 1.	70

4.15	The number of collisions between Ag^+ ions and the buffer gas atoms (left panel) and between AgCH_4^+ ions and the buffer gas atoms (right panel) through hexapole 1.	71
4.16	The radial distribution of Ag^+ ions at the end of hexapole 1.	71
4.17	The radial distribution of AgCH_4^+ ions at the end of hexapole 1.	72
4.18	Hexapole 1 (125 mm in length), three electrostatic lenses (with diameters 6, 5 and 3 mm) and hexapole 2 (550 mm in length) in the ion-guide assembly.	72
4.19	Ion-guide assembly with the overall transmission efficiency above 90% for both atomic and ion cluster.	73
4.20	Energy spectrum of the ions when they reach the end of hexapole 2 with a mean energy of 14 eV for both ions.	73
4.21	Phase space of the ions when they reach the end of hexapole 2.	73
4.22	The separation of the Sn^+ , In^+ from AgCH_4^+ , CdCH_4^+ in a quadrupole mass filter.	74
4.23	The technical design of the gas catcher and the coupling ion-guide in the CISE setup.	76
4.24	The qToF mass spectrometer with the electrospray (z-spray) ion source in the beginning of the setup to replace the gas catcher for the production of Ag, In, Cd and Sn ions.	77
4.25	Electrospray ion source attached to the qToF for the production of Ag, Cd, In and Sn ions.	78
4.26	The proof-of-principle measurements with qToF setup for Ag, Cd, In and Sn ions.	80
5.1	The GSI Helmholtz Center for Heavy Ion Research located at Darmstadt, Germany.	86
5.2	The high-energy beam-lines of the GSI facility.	87
5.3	The FRagment separator (FRS) [73] at GSI.	88
5.4	The FRS ion-catcher setup at final focal plane of the fragment separator FRS at GSI for the high-precision mass measurements and isobaric separation [152].	89
5.5	The Multiple-Reflection Time-Of-Flight Mass Spectrometer MR-TOF-MS at FRS Ion Cathcer setup [108,155].	90
5.6	The upgraded gas-handling system of the FRS Ion Catcher setup.	92
5.7	The cold trap (CT) gas purifier cooled with liquid nitrogen.	93
5.8	The vapor pressure curves of different gases [160].	94
5.9	The Xe^+ count rates coming from the CSC filled without (top plot) and with (bottom plot) the cold trap in the gas line.	96
5.10	Electron-current measurement on entrance flange produced by deposited energy from stopping of the high-energy ions.	97
5.11	The logarithmic mass spectra of ions with $A/q = 132$ and 134 for the fission-fragment measurements over 10 hours.	100

5.12	The ions rates for ^{132}Xe and ^{134}Xe coming from the impurities of the gas without using the cold trap in the gas line.	101
5.13	The Xe^+ contamination identified in MR-TOF-MS over four days of continuous operation of CSC operating at 165 mbar.	102
5.14	a) The helium gas temperature, b) the carpet temperature, c) the remaining gas pressure at helium gas bundle, and d) the LN_2 level of the cold trap over 4 days of continuous operation of CSC operating at 165 mbar.	103
5.15	The RGA installed in the extraction-RFQ section after CSC.	104
5.16	The RGA scans for three different gas purification lines filling the Cryogenic Stopping Cell.	106
5.17	The extraction-RFQ scans corresponding to the gas conditions a, b and c presented in figure 5.16.	107
5.18	The specifications of the SAES gas purifiers.	108
5.19	The extraction-RFQ scan for CSC filled at 75 mbar with the gas purifying from passive and active getter lines.	108
5.20	The subtracted RGA scan shown to demonstrate the difference between passive and active getters in the gas line.	109
5.21	The overall gas cleanliness condition for extraction of the products from ^{228}Th offline source.	110
5.22	The classical model for the charge-exchange mechanism at low-energy collisions.	111
5.23	The expected and experimentally identified charge state of the element at the FRS-IC setup.	112
5.24	The reduced mobility of the main possible charge carriers in the He gas [171].	114
5.25	The effect of charge-exchange reactions in the beamline and MR-TOF-MS	116
5.26	text shown in list of figures here	117
6.1	The data evaluation algorithm for the MR-TOF-MS mass and uncertainty evaluations [155].	120
6.2	The primary decay modes in the chart of isotopes and the island of the α emitters in the medium-heavy neutron-deficient region.	126
6.3	The mass spectrum with and without using MRS	128
6.4	The Time-Resolved Calibration (TRC) for improving the peak broadening in the measurement.	129
6.5	The LS fit on the calibrant ion $^{86}\text{Kr}^{14}\text{N}_2^+$ to obtain the peak shape parameters and the precision calibration factor R	130
6.6	The wMLE fit on the unbinned data for $^{116}\text{I}^+$	130
6.7	The comparison of the direct mass measurement in this experiment compared to the indirect measurements of Beck et al. [185] and Gowdy et al. [186].	131

6.8	Measured mass-to-charge ratio spectrum including the calibrant $^{86}\text{Kr}^{14}\text{N}_2^+$ ($A = 114$) and the ion of interest $^{114}\text{I}^+$	133
6.9	The synthetic data generated with the same resolving power, peak shape and total count rate as in the data obtained for ^{114}I and a fixed excitation energy known in AME16 [20].	134
6.10	The estimated mass deviation from the pure ground state (GS) peak for the different contributions of GS and the Isomeric State.	134
6.11	The half-life measurements of the ^{114}I by storing the ions in the RFQ beamline.	136
6.12	The two-neutron separation energies of the iodine ($Z = 53$) isotopes.	138
6.13	The double difference of the two-proton separation energy in the Z direction for different isotopic chains.	140
6.14	The logarithm of the partial half-lives vs. Q_α values for the iodine isotopes.	142
6.15	The mass precision of the isotopes in the vicinity of the $N = Z$ line.	143
6.16	The mass evaluation of the measured isotopes with low statistics (^{97}Pd and ^{100}Pd).	146
6.17	The ^{98}Cd mass evaluation by fitting the wMLE using unbinned data shown in the lower section of the plot.	146
6.18	The background measurements over two hours with beam off.	147
6.19	The ground state of ^{97}Rh and the low-lying isomeric state ^{97m}Rh	148
6.20	The comparison of the atomic mass values from the FRS-IC direct mass measurements and the reported indirect measurements for ^{98}Cd and ^{97}Rh	148
6.21	The atomic mass-excess difference for the measured isotopes compared to the literature values at AME16 [20] or other labs.	151
6.22	Histogram of the difference between the mass excess and the AME16 values for the known masses.	152
6.23	The two-neutron separation energies for $Z = 44 - 49$ from AME16 and AME16+(FRS-IC) measurements and comparison with the common mass models.	153
7.1	a) The two-neutron separation energies of the iodine ($Z = 53$) isotopes. b) The logarithm of the partial half-lives vs. Q_α values for the iodine isotopes.	157
7.2	The atomic mass-excess difference for the measured isotopes compared to the literature values.	158
7.3	a) De twee-neutronen scheidingsenergieën van jodium ($Z = 53$) isotopen. b) De logaritme van de partiële halfwaardetijden vs. Q_α waarden voor de jodiumisotopen.	163
7.4	Het verschil in atoommassa-overschot voor de gemeten isotopen ten opzichte van de literatuurwaarden.	164

List of Tables

1.1	The generally required mass-precision for probing different fields [1].	6
3.1	The decay properties of the ^{223}Ra radioactive ion source	30
3.2	The decay properties of the ^{228}Th radioactive ion source	31
3.3	Comparison between the main characteristics of the multiple ion-guides	37
4.1	Experimental cross sections and expected production rates of ^{100}Sn , ^{100}Cd and ^{100}Ag and ^{100}In entering the gas catcher at SHIPTRAP.	56
4.2	The reaction rate coefficients reported in Ref. [144] for the reaction of Ag, Cd, In and Sn with reactive gas CH_4 in a room temperature helium bath.	57
4.3	The reaction rate coefficients reported in Ref. [145] for the reaction of Ag, Cd, In and Sn with reactive gas H_2O in a room temperature helium bath.	57
4.4	Sample solution preparation with different concentrations.	78
4.5	The natural abundance of the Ag, In, Cd and Sn elements on earth.	79
4.6	The clusters formed by Ag^+ ions and the buffer gas atoms in the hexapole collision cell.	81
4.7	The clusters formed by Cd^+ ions and buffer gas in hexapole collision cell.	82
4.8	The final results show the reaction rate of Ag, In, Cd ions chemically reacting with the buffer gas at the hexapole collision cell.	84
5.1	The measured Xe contamination levels from two random helium gas bottles used for FRS-IC.	95
5.2	The measurements for Xe suppression with using the cold trap in the gas line.	98
5.3	The Kr^+ count rate identified on MR-TOF-MS with and without the cold trap in the gas line	99
5.4	The ionization potential of He and different possible contaminations in the gas cell.	113

5.5	The atomic ionization potentials of the ^{228}Th products [168, 169] and the identified charge state at FRS-IC gas cell.	113
5.6	The usage of a fresh gas purifier at RFQ beamline resulting in a reduction of the amount of charge-exchange reactions taking place at the beamline before the RFQ mass filter.	118
6.1	Three measurements performed for the ^{114}I isotope and the resulting weighted average of the independent measurements. . . .	132
6.2	A summary of the resulting mass and half-life measurements for the ^{114}I and ^{116}I nuclei together with the new evaluated Q_α value calculated from the new direct mass measurements.	136
6.3	A list of various components of error to the mass uncertainty of the iodine mass measurements.	137
6.4	A list of error components of the mass uncertainty in the measurements for ^{98}Cd and ^{97}Rh nuclei.	149
6.5	The results of the direct mass measurements with FRS-IC for the ground and isomeric states of the nuclei compared to the literature values.	150
6.6	The $\log(ft)$ and individual Gamow-Teller strength $B(\text{GT})$ calculated for the four observed transitions ($0^+ \rightarrow 1^+$).	154

Bibliography

- [1] K. BLAUM, *Physics Reports* **425**, 1 (2006).
- [2] M. BLOCK, *Nuclear Instruments and Methods in Physics Research Section B* **376**, 265 (2016).
- [3] J. J. THOMSON, *Rays of Positive Electricity and Their Application to Chemical Analysis*, Longmans, Green & Co., London 1913.
- [4] F. W. ASTON, *Mass Spectra and Isotopes*, 1st and 2nd eds., Longmans, London 1933, 1941.
- [5] J. THOMSON, *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science* **13**, 561 (1907).
- [6] A. J. DEMPSTER, *Physical Review* **20**, 631 (1922).
- [7] S. BAUER, *Journal of the American Society for Mass Spectrometry* **12**, 975 (2001).
- [8] J. MATTAUCH, *R. Z. Physik* **89**, 786 (1934).
- [9] A. O. NIER, *Physical Review* **52**, 933 (1937).
- [10] ANONYMOUS, *Physical Review* **69**, 674 (1946).
- [11] W. C. WILEY and I. H. MCLAREN, *Review of Scientific Instruments* **26**, 1150 (1955).
- [12] H. S. W. PAUL, *Zeitschrift für Naturforschung A* **8**, 448 (1953).
- [13] P. VON F.M., *Physica* **3**, 563 (1936).
- [14] J. WOUTERS et al., *Nuclear Instruments and Methods in Physics Research Section A* **240**, 77 (1985).
- [15] J. WOUTERS et al., *Nuclear Instruments and Methods in Physics Research Section B* **26**, 286 (1987).
- [16] T. ERONEN et al., *Progress in Particle and Nuclear Physics* **91**, 259 (2016).
- [17] Nucleus-Win v. 2.1., CSNSM-Orsay (In2p3/CNRS).
- [18] G. AUDI et al., *Chinese Physics C* **41**, 030001 (2017).

- [19] K. HEYDE and M. WAROQUIER, *Nuclear Physics A* **167**, 545 (1971).
- [20] W. HUANG et al., *Chinese Physics C* **41**, 030002 (2017).
- [21] C. F. V. WEIZSÄCKER, *Zeitschrift für Physik* **96**, 431 (1935).
- [22] H. A. BETHE and R. F. BACHER, *Review of Modern Physics* **8**, 82 (1936).
- [23] K. HEYDE, *The Nuclear Shell Model*, Springer-Verlag Berlin Heidelberg, 1994.
- [24] J. JÄNECKE and P. MASSON, *Atomic Data and Nuclear Data Tables* **39**, 265 (1988).
- [25] T. TACHIBANA et al., *Atomic Data and Nuclear Data Tables* **39**, 251 (1988).
- [26] P. MOLLER et al., *Atomic Data and Nuclear Data Tables* **59**, 185 (1995).
- [27] J. DUFLO and A. ZUKER, *Physical Review C* **52**, R23 (1995).
- [28] S. LIRAN and N. ZELDES, *Atomic Data and Nuclear Data Tables* **17**, 431 (1976).
- [29] P. E. HAUSTEIN, *Atomic Data and Nuclear Data Tables* **39**, 185 (1988).
- [30] L. SPANIER and S. JOHANSSON, *Atomic Data and Nuclear Data Tables* **39**, 259 (1988).
- [31] P. MASSON and J. JÄNECKE, *Atomic Data and Nuclear Data Tables* **39**, 273 (1988).
- [32] Y. ABOUSSIR et al., *Nuclear Physics A* **549**, 155 (1992).
- [33] J. DUFLO, *Nuclear Physics A* **576**, 29 (1994).
- [34] W. MYERS and W. SWIATECKI, *Nuclear Physics A* **601**, 141 (1996).
- [35] A. ARCONES et al., *Progress in Particle and Nuclear Physics* **94**, 1 (2017).
- [36] S. E. WOOSLEY et al., *Review of Modern Physics* **74**, 1015 (2002).
- [37] J. J. COWAN et al., *Physics Reports* **208**, 267 (1991).
- [38] M. PIGNATARI et al., *The Astrophysical Journal* **710**, 1557 (2010).
- [39] H. SCHATZ et al., *Physical Review Letters* **86**, 3471 (2001).
- [40] A. SOBICZEWSKI and Y. A. LITVINOV, *Physical Review C* **89**, 024311 (2014).
- [41] P. MÖLLER et al., *Atomic Data and Nuclear Data Tables* **109**, 1 (2016).
- [42] S. GORIELY et al., *Physical Review C* **88**, 024308 (2013).
- [43] M. KORTELAJINEN et al., *Physical Review C* **82**, 024313 (2010).
- [44] K. SANTHOSH et al., *Nuclear Physics A* **825**, 159 (2009).

- [45] J. FAN and C. XU, *Nuclear Physics A* **989**, 1 (2019).
- [46] H. G. PH.D. and J. N. B.SC., *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science* **22**, 613 (1911).
- [47] C. QI et al., *Physics Letters B* **734**, 203 (2014).
- [48] J. DOBACZEWSKI and I. HAMAMOTO, *Physics Letters B* **345**, 181 (1995).
- [49] M. OINONEN, *Nuclear Physics A* **682**, 12 (2001).
- [50] P. BACZYK et al., *Physics Letters B* **778**, 178 (2018).
- [51] V. ISACKER et al., *Phys. Rev. Lett.* **74**, 4607 (1995).
- [52] J. ENGEL et al., *Physics Letters B* **389**, 211 (1996).
- [53] S. G. FRAUENDORF and J. A. SHEIKH, *Nuclear Physics A* **645**, 509 (1999).
- [54] Y. SHIMBARA et al., *Modern Physics Letters A* **25**, 1976 (2010).
- [55] I. MARDOR et al., *arXiv:2011.13288* (2020).
- [56] I. BENTLEY and S. FRAUENDORF, *Physical Review C* **88**, 014322 (2013).
- [57] A. STOLZ et al., *GSI Scientific Reports* **1**, 7 (2001).
- [58] D. LUBOS, , et al., *Physical Review Letters* **122**, 222502 (2019).
- [59] F. C. PORTER, *Progress in Particle and Nuclear Physics* **91**, 101 (2016).
- [60] T. FAESTERMANN et al., *Progress in Particle and Nuclear Physics* **69**, 85 (2013).
- [61] C. B. HINKE et al., *Nature* **486**, 341 (2012).
- [62] J. DOBACZEWSKI et al., *Zeitschrift für Physik A Atomic Nuclei* **329**, 267 (1988).
- [63] B. A. BROWN and K. RYKACZEWSKI, *Physical Review C* **50**, R2270 (1994).
- [64] K. RYKACZEWSKI et al., *Zeitschrift für Physik A Atomic Nuclei* **322**, 263 (1985).
- [65] P. GRAF et al., *Acta* **20**, 140 (1987).
- [66] A. PŁOCHOCKI et al., *Zeitschrift für Physik A Hadrons and Nuclei* **342**, 43 (1992).
- [67] K.-H. SCHMIDT et al., *Nuclear Physics A* **701**, 115 (2002).
- [68] P. BRICAULT et al., *Nuclear Physics A* **701**, 49 (2002).
- [69] E. KUGLER, *Hyperfine Interactions* **129**, 23 (2000).
- [70] R. CATHERALL et al., *Nuclear Instruments and Methods in Physics Research Section B* **204**, 235 (2003).

- [71] J. AL-KHALILI and E. ROECKL, *The Euroschool Lectures on Physics With Exotic Beams*, Number v. 2 in Lecture Notes in Physics, Springer Berlin Heidelberg, 2006.
- [72] M. P. REITER, *Pilot experiments with relativistic uranium projectile and fission fragments thermalized in a cryogenic gas-filled stopping cell*, PhD thesis, University of Giessen, Germany, 2015.
- [73] H. GEISSEL et al., *Nuclear Instruments and Methods in Physics Research Section B* **70**, 286 (1992).
- [74] T. AUMANN, *Progress in Particle and Nuclear Physics* **59**, 3 (2007).
- [75] W. R. PLASS et al., *International Journal of Mass Spectrometry* **349-350**, 134 (2013).
- [76] Y. YANO, *Nuclear Instruments and Methods in Physics Research Section B* **261**, 1009 (2007).
- [77] T. KUBO, *Nuclear Instruments and Methods in Physics Research Section B* **204**, 97 (2003).
- [78] M. HAUSMANN et al., *Nuclear Instruments and Methods in Physics Research Section B* **317**, 349 (2013), XVIth International Conference on ElectroMagnetic Isotope Separators and Techniques Related to their Applications, December 2–7, 2012 at Matsue, Japan.
- [79] M. WINKLER et al., *Nuclear Instruments and Methods in Physics Research Section B* **266**, 4183 (2008).
- [80] H. GEISSEL et al., *Nuclear Instruments and Methods in Physics Research Section B* **204**, 71 (2003).
- [81] D. J. MORRISSEY and B. M. SHERRILL, *In-Flight Separation of Projectile Fragments*, pp. 113–135, Springer Berlin Heidelberg, Berlin, Heidelberg, 2004.
- [82] T. OHNISHI et al., *Journal of the Physical Society of Japan* **79**, 073201 (2010).
- [83] M. LA COMMARA et al., *Nuclear Physics A* **669**, 43 (2000).
- [84] W. KURCEWICZ et al., *Zeitschrift für Physik A Atoms and Nuclei* **308**, 21 (1982).
- [85] V. I. ZAGREBAEV et al., *Physical Review C* **85**, 014608 (2012).
- [86] H. GEISSEL, GSI, Private communications, (2018).
- [87] M. BLOCK et al., *European Physical Journal A* **25**, 49 (2005).
- [88] J. DILLING et al., *Nuclear Instruments and Methods in Physics Research Section B* **204**, 492 (2003).

- [89] G. BOLLEN et al., *Nuclear Instruments and Methods in Physics Research Section A* **532**, 203 (2004).
- [90] V. KOLHINEN et al., *Nuclear Instruments and Methods in Physics Research Section A* **528**, 776 (2004).
- [91] G. BOLLEN et al., *Nuclear Instruments and Methods in Physics Research Section A* **368**, 675 (1996).
- [92] A. CHAUDHURI et al., *Applied Physics B* **114**, 99 (2014).
- [93] G. BOLLEN, *The Euroschool Lectures on Physics With Exotic Beams*, Number v. 1 in *Lecture Notes in Physics*, Springer Berlin Heidelberg, 2006.
- [94] E. M. RAMIREZ et al., *Nuclear Instruments and Methods in Physics Research Section B* **317, Part B**, 501 (2013).
- [95] M. MUKHERJEE et al., *European physical Journal A* **35**, 1 (2008).
- [96] M. SMITH et al., *Physical Review Letters* **101**, 202501 (2008).
- [97] M. B. COMISAROW et al., *Chemical Physics Letters* **25**, 282 (1974).
- [98] M. B. COMISAROW and A. G. MARSHALL, *Chemical Physics Letters* **25**, 282 (1974).
- [99] B. FRANZKE, *Nuclear Instruments and Methods in Physics Research Section A* **B24/25**, 18 (1987).
- [100] V. HANNEN et al., *Journal of Instrumentation* **8**, P09018 (2013).
- [101] B. SCHLITT et al., *Hyperfine Interactions* **99**, 117 (1996).
- [102] F. BOSCH, *Measurement of Mass and Beta-Lifetime of Stored Exotic Nuclei*, pp. 137–168, Springer Berlin Heidelberg, Berlin, Heidelberg, 2004.
- [103] M. HAUSMANN et al., *Nuclear Instruments and Methods in Physics Research Section A* **446**, 569 (2000).
- [104] R. WOLF et al., *Nuclear Instruments and Methods in Physics Research Section B* **376**, 275 (2016).
- [105] P. SCHURY et al., *International Journal of Mass Spectrometry* **433**, 40 (2018).
- [106] M. ROSENBUSCH et al., *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* **463**, 184 (2020).
- [107] T. DICKEL et al., *Hyperfine Interactions* **240** (2019).
- [108] T. DICKEL et al., *Nuclear Instruments and Methods in Physics Research Section A* **777**, 172 (2015).
- [109] M. RANJAN, *Design and characterization of a cryogenic stopping cell for radioactive ions*, PhD thesis, University of Groningen, 2012.

- [110] J. NEUMAYR et al., *Nuclear Instruments and Methods in Physics Research Section B* **244**, 489 (2006).
- [111] S. PURUSHOTHAMAN, *Superfluid helium and cryogenic noble gases as stopping media for ion catchers*, PhD thesis, University of Groningen, 2008.
- [112] I. MISKUN, *A Novel Method for the Measurement of Half-Lives and Decay Branching Ratios of Exotic Nuclei with the FRS Ion Catcher*, PhD thesis, University of Giessen, Germany, 2019.
- [113] I. MARDOR et al., *EPJ Web of Conferences* **239** (2020).
- [114] G. STANIC, *Stopping efficiency of spontaneous fission fragments in the cryogenic stopping cell of the FRS ion catcher*, Summer school at GSI Helmholtz Institute, 2018.
- [115] D. DAVIES et al., *Nuclear Instruments and Methods in Physics Research Section A* **569**, 883 (2006).
- [116] C. IZZO et al., *Nuclear Instruments and Methods in Physics Research Section B* **376**, 60 (2016).
- [117] E. HAETTNER et al., *Nuclear Instruments and Methods in Physics Research Section A* **880**, 138 (2018).
- [118] D. J. DOUGLAS et al., *Mass Spectrometry Reviews* **24**, 1 (2005).
- [119] A. V. TOLMACHEV et al., *Analytical Chemistry* **72**, 970 (2000).
- [120] V. R. RAO and A. BHUTANI, *International Journal of Mass Spectrometry* **202**, 31 (2000).
- [121] R. E. MARCH and J. F. TODD, *International Journal of Mass Spectrometry* **377**, 316 (2015).
- [122] P. H. DAWSON, *Quadrupole mass Spectrometry and its applications*, ELSEVIER SCIENTIFIC PUBLISHING COMPANY, 1976.
- [123] M. SUDAKOV et al., *International Journal of Mass Spectrometry* **408** (2016).
- [124] D. GERLICH, *Inhomogeneous RF Fields: A Versatile Tool for the Study of Processes with Slow Ions*, chapter 1, pp. 1–176, John Wiley, Ltd, 2007.
- [125] R. WESTER, *Journal of Physics B: Atomic, Molecular and Optical Physics* **42**, 154001 (2009).
- [126] T. MAJIMA et al., *Physical Review A* **85**, 053414 (2012).
- [127] W. C. WILEY and I. H. MCLAREN, *Review of Scientific Instruments* **26**, 1150 (1955).
- [128] S. J. SCHOWALTER et al., *Review of Scientific Instruments* **83**, 043103 (2012).
- [129] A. KOSIERB et al., *Vacuum* **83**, 137 (2009).

- [130] M. GUILHAUS et al., *Mass Spectrometry Reviews* **19**, 65 (2000).
- [131] X. YUAN et al., *International Journal of Mass Spectrometry* **434**, 52 (2018).
- [132] Y. HASHIMOTO et al., *Journal of the American Society for Mass Spectrometry* **17**, 1669 (2006).
- [133] T. DICKEL et al., *International Journal of Mass Spectrometry* **412**, 1 (2017).
- [134] P. SCHURY et al., *Nuclear Instruments and Methods in Physics Research Section B* **317**, 537 (2013).
- [135] Y. ITO et al., *Physical Review C* **88**, 011306 (2013).
- [136] SIMION v. 8.0/8.1, Idaho national laboratory, United States.
- [137] COMSOL Multiphysics v. 5.2., COMSOL AB, Stockholm, Sweden.
- [138] A. A. KWIATKOWSKI et al., *Physal Reviews C* **80**, 051302 (2009).
- [139] T. D. MORRIS et al., *Physical Review Letters* **120**, 152503 (2018).
- [140] P. SCHURY et al., *Physical Review C* **75**, 055801 (2007).
- [141] M. CHARTIER et al., *Physical Review Letters* **77**, 2400 (1996).
- [142] G. MÜNZENBERG et al., *Nuclear Instruments and Methods in Physics Research Section B* **161**, 65 (1979).
- [143] Y. KUDRYAVTSEV et al., *Nuclear Instruments and Methods in Physics Research Section B* **179**, 412 (2001).
- [144] A. SHAYESTEH et al., *The Journal of Physical Chemistry A* **113**, 5602 (2009).
- [145] P. CHENG et al., *The Journal of Physical Chemistry A* **111**, 8561 (2007).
- [146] B. ANDJELIC, *in preparation*, PhD thesis, University of Groningen, 2021.
- [147] A. MOLLAEBRAHIMI, B. ANĐELIĆ, et al., *Nuclear Instruments and Methods in Physics Research Section B* **463**, 508 (2020).
- [148] J. NEUMAYR, *The buffer-gas cell and the extraction RFQ for SHIPTRAP*, PhD thesis, Ludwig-Maximilians-Universität München, 2004.
- [149] N. ANGERT and C. SCHMELZER, *Kerntechn.* **11**, 690 (1969).
- [150] K. BLASCHE and B. FRAN CZAK, The Heavy ion synchrotron SIS, in *3rd European Particle Accelerator Conference (EPAC 92)*, pp. 9–13, 1992.
- [151] H. WEICK et al., *Nuclear Instruments and Methods in Physics Research Section B* **164-165**, 168 (2000).
- [152] W. PLASS et al., *Nuclear Instruments and Methods in Physics Research Section B* **317**, 457 (2013).

- [153] H. GEISSEL et al., *Nuclear Instruments and Methods in Physics Research Section B* **204**, 71 (2003).
- [154] T. DICKEL et al., *Nuclear Instruments and Methods in Physics Research Section B* **376**, 216 (2016).
- [155] S. A. S. ANDRÉS et al., *Physical Review C* **99**, 064313 (2019).
- [156] C. DROESE et al., *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* **338**, 126 (2014).
- [157] I. MISKUN et al., *International Journal of Mass Spectrometry* **459**, 116450 (2020).
- [158] T. SONODA et al., *Review of Scientific Instruments* **87**, 065104 (2016).
- [159] K. MUNAKATA et al., *Journal of Nuclear Science and Technology* **36**, 818 (1999).
- [160] W. WAGNER, *Cryogenics* **13**, 470 (1973).
- [161] I. POHJALAINEN, *Gas-phase chemistry, recoil source characterization and in-gas-cell resonance laser ionization of actinides at IGISOL*, PhD thesis, University of Jyväskylä, 2018.
- [162] D. NICHITA, *in preparation*, PhD thesis, IFIN-HH/ELI-NP, Bucharest Magurele, Romania, 2021.
- [163] M. P. REITER, *Internal Reports for Module Specialization*, GSI, Germany.
- [164] SAES Pure Gas (www.saespuregas.com), USA.
- [165] K. STEPHAN et al., *The Journal of Chemical Physics* **80**, 3185 (1984).
- [166] R. K. CURRAN, *The Journal of Chemical Physics* **38**, 2974 (1963).
- [167] F. GREINER et al., *Nuclear Instruments and Methods in Physics Research Section B* **463**, 324 (2020).
- [168] R. D. LEVIN and S. G. LIAS, *National Bureau of Standards* **71** (1982).
- [169] F. W. McLAFFERTY, *Organic Mass Spectrometry* **3**, 1225 (1970).
- [170] S. M. BORGHESANI A.F., *Electron Mobility and Localization in High-Density Helium Gas in an Extended Temperature Range*, Springer, Boston, MA, 1998.
- [171] H. ELLIS et al., *Atomic Data and Nuclear Data Tables* **17**, 177 (1976).
- [172] S. A. S. ANDRÉS, *Developements for Multi-Reflection Time-Of-Flight Mass Spectrometer and their Applications to high-Resolution Accuracy Mass Measurements of Short-lived Exotic Nuclei*, PhD thesis, University of Giessen, 2018.
- [173] C. WILL, *Achieving one million mass resolving power with a multiple-reflection time-of-flight mass spectrometer*, Master Thesis, 2019.

- [174] J. BERGMANN, Entwicklung und Anwendung einer integrierten Systemsteuerung und Datenaufnahme für Flugzeitmassenspektrometer, Master Thesis, 2015.
- [175] S. PURUSHOTHAMAN et al., *International Journal of Mass Spectrometry* **421**, 245 (2017).
- [176] M. KARSON, *Journal of the American Statistical Association* **63**, 1047 (1968).
- [177] A. RINK, *Mass and Life-time Measurement of the 1.7 ms 215-Po Isotope-A Crucial Test of the Novel Concept of the Cryogenic Ion Catcher for the Super-FRS at GSI-FAIR*, PhD thesis, University of Giessen, Germany, 2017.
- [178] T. DICKEL et al., *Physics Letters B* **744**, 137 (2015).
- [179] Colorful Nuclide Chart, Web: www.people.physics.anu.edu.au.
- [180] V. V. ELOMAA et al., *Physical Review Letters* **102** (2009).
- [181] A. MARTIN et al., *European Physical Journal A* **34**, 341 (2007).
- [182] D. SCHARDT et al., *Nuclear Physics A* **368**, 153 (1981).
- [183] C. MAZZOCCHI et al., *Physical Review Letters* **98**, 212501 (2007).
- [184] R. D. PAGE et al., *Zeitschrift für Physik A Hadrons and Nuclei* **338**, 295 (1991).
- [185] E. BECK, *Proceedings International Conference on the Properties of Nuclei Far From the Region of Beta-Stability*. **CERN 70-30 1**, 353 (1970).
- [186] G. M. GOWDY et al., *Physical Review C* **13**, 1601 (1976).
- [187] K. SÜMMERER and B. BLANK, *Nuclear Physics A* **701**, 161 (2002), 5th International Conference on Radioactive Nuclear Beams.
- [188] D. FREEDMAN and P. DIACONIS, *Zeitschrift für Wahrscheinlichkeitstheorie und Verwandte Gebiete* **57**, 453 (1981).
- [189] B. ZIMMERMANN, *Private Communication* (1995).
- [190] A. K. JAIN et al., *Nuclear Data Sheets* **128**, 1 (2015).
- [191] I. MISKUN et al., *European Physical Journal A* **55**, 148 (2019).
- [192] A. BOHR and B. MOTTELSON, *World Scientific Singapore* (1998).
- [193] E. LEISTENSCHNEIDER et al., *Physical Review Letters* **120**, 062503 (2018).
- [194] B. S. ISHKHANOV et al., *Chinese Physics C* **43**, 014104 (2019).
- [195] Y. LITVINOV et al., *Nuclear Physics A* **756**, 3 (2005).
- [196] J. MORAGUES et al., *Nuclear Physics A* **99**, 652 (1967).

- [197] H. DANIEL et al., *Zeitschrift für Physik A Hadrons and Nuclei* **172**, 202 (1963).
- [198] R. D. PAGE et al., *Zeitschrift für Physik A Hadrons and Nuclei* **338**, 295 (1991).
- [199] D. SCHARDT et al., *Nuclear Physics A* **368**, 153 (1981).
- [200] B. BASU and A. PATRO, *Nuclear Physics* **33**, 347 (1962).
- [201] V. L. CHIKHLADZE et al., *Theoretical Physics* **43**, 453 (1962).
- [202] C. HORNUNG et al., *Physics Letters B* **802**, 135200 (2020).
- [203] A. KALSHOVEN et al., *Nuclear Physics A* **337**, 120 (1980).
- [204] C. HORNUNG, *High-Resolution Experiments with the Multi-Reflection Time-Of-Flight Mass Spectrometer at the Fragment Separator FRS*, PhD thesis, University of Giessen, Germany, 2018.
- [205] W. PLUECKEBAUM, *Zeitschrift für Physik A Hadrons and Nuclei* **273**, 393 (1975).
- [206] lof(ft) calculator (<https://www.nndc.bnl.gov/logft/>), nndc.
- [207] W. R. PLASS, T. DICKEL, et al., *Hyperfine Interactions* **240**, 73 (2019).

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