Precision mass measurements of neutron-rich rare isotopes approaching the r-process path with the Canadian Penning Trap mass spectrometer

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DEDICATION

This thesis is dedicated to the four people who will read this.

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ABSTRACT

The masses of 15 neutron-rich nuclei were measured using the Canadian Penning Trap mass spectrometer (CPT) located at the Californium Rare Isotope Breeder Upgrade (CARIBU) facility at Argonne National Laboratory to an average mass precision of $\delta m/m \approx 10^{-7}$. This includes masses of five previously unmeasured ground-state nuclei and one of a newly resolved isomer. Generally good agreement is reached when comparing the data set in this thesis with previously established mass measurements. CARIBU provides neutron-rich radioactive beams in the vicinity of A = 105and A = 140, originating from the spontaneous fission of ²⁵²Cf. In this thesis, isotopes with fission branches as low as 3.3×10^{-4} products per 100 decays (¹⁵⁰Ba) and half-lifes as low as 222 ms (¹⁴²I) have been reached.

This thesis provides a thorough discussion of the precision mass measurement process, from ion production at CARIBU, to detection at the CPT where a time-of-flight-ion cyclotron resonance (ToF-ICR) technique is employed to determine the cyclotron frequencies of trapped ion species. Limitations of the measurement technique with respect to the current CPT system at CARIBU are discussed, and a new phase-imaging-ion cyclotron resonance (PI-ICR) procedure is introduced.

ABRÉGÉ

Les masses de 15 isotopes riches en neutrons ont été mesurées à une précision de $\delta m/m \approx 10^{-7}$ avec le "Canadian Penning Trap mass spectrometer" (CPT) qui est en opération à la source de faisceaux radioactifs "Californium Rare Isotope Breeder Upgrade" (CARIBU) située au laboratoire national d'Argonne près de Chicago. Ces mesures incluent cinq isotopes dont les masses n'avaient jamais été mesurées jusqu'a maintenant ainsi que la masse d'un nouvel isomère. Ces nouvelles données sont en bon accord général avec les mesures disponibles auparavant. CARIBU délivre des faisceaux radioactifs d'isotopes riches en neutrons des régions A= 105 et A= 140 produits par la fission du ²⁵²Cf. Dans cette thèse, des isotopes avec des embranchements de fission aussi faible que 3.3×10^{-4} par 100 fissions (¹⁵⁰Ba) et demi-vies aussi courte que 222 ms (¹⁴²I) ont pu être mesurés. Cette thèse présente une discussion détaillée du processus de mesure de masse, de la production à CARIBU jusqu'à la detection à la CPT avec la technique de mesure de résonance cyclotron par temps de vol (ToF-ICR) employée pour déterminer la masse des ions capturés dans le pièges à ion. Les limitations du systeme de mesure présentement en opération à la CPT sont aussi discutées et une nouvelle méthode basée sur la mesure de phase du mouvement cyclotron (PI-ICR) est introduite.

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CHAPTER 1

Introduction to precision mass measurements and physical motivations

Do not use dishonest standards when measuring length, weight or quantity. -Leviticus 19:35

1.1 Development of mass spectrometry

The birth of mass spectrometry can be traced back over 100 years to the work of JJ Thomson and student FW Aston in 1913 at Cambridge where they passed collimated beams through a region with perpendicular magnetic and electric fields and projected onto a photographic plate where they found more than one parabolic set of points were detected [1]. These parabolas are defined by the particular mass-to-charge ratios of the ion species present in the incident beam. Using this technique they were able to provide the first evidence of the existence of isotopes by identifying ²⁰Ne and ²²Ne [2]. From there Aston went on to build the first mass spectrograph in 1919 where by a series of electric and magnetic deflectors he was able to show a mass spectrum which was only dependent on m/q and not the velocity of the initial beam. Confirming the two isotopes of Ne as well as the existence of nearly 50 other nuclides, he was able to observe that the mass of the neutral atoms were less than the sum of the mass of the neutrons and protons within the nucleus [3]. He was also able to verify that along an isotopic chain the mass differences were not integer multiples of the neutron mass. This mass defect, known today as mass excess, was eventually identified as the binding energy of the nucleus. The breaking of this whole number rule along with the first measurement of a number of non-radioactive nuclides earned Aston the Nobel prize in chemistry in 1922.

Aston used his spectrograph to measure more than 200 nuclides to a relative mass accuracy of 10^{-4} [4]. From this point the tools developed for mass spectrometry exploded. The 1950s saw the development of the radio frequency (rf) quadrupole mass filter, a two-dimensional storage device, by Paul and colleagues[5]. Within a few years a research group at Cal Tech [6] and Paul's group in Germany had independently been adapting the mass filter device to store and confine charged particles in threedimensions. This device became known as the Paul trap and is commonly used today in ion beam cooling and preparation, as well as in ion trapping experiments where the open geometry of the trap allows for the insertion of an array of particle detectors [7].

The next movement in mass spectrometry was the confinement of charged particles using a combination of uniform magnetic fields and electrostatic fields produced by hyperboloid-shaped electrodes. This was described in detail by John R. Pierce in 1949 [8]. Hans Dehmelt coined the term *Penning* trap in 1967 [9] named after Frans M. Penning who improved ionization vacuum gauges (*Penning* gauges) by incorporating magnetic and electric fields with ion discharge to measure vacuum pressures to great accuracy[1]. For their work in developing ion traps, Dehmelt and Paul received a share of the Nobel prize for physics in 1989 [10]. Penning traps used for mass measurements today can achieve relative mass precisions of $\delta m/m \approx 10^{-8}$ for radioactive ions and $\delta m/m \approx 10^{-11}$ for stable ions.

1.2 Mass spectrometry of stable and radioactive ions using Penning traps

The first radioactive mass measurements were conducted using the ISOLTRAP Penning trap at CERN and reported in 1987 [11]. This publication included five isotopes of rubidium and one isotope of strontium measured with accuracy better than 10^{-6} . Following the success of ISOLTRAP a number of Penning trap experiments have sprung up all over the world. There are currently about 20 Penning trap experiments either operating or in the planning stages worldwide [4], including the Canadian Penning Trap (CPT) used to collect data in this thesis. Mass measurements are necessary for many fields including nuclear structure [12], nuclear astrophysics [13][14](see section 1.4), tests of the standard model [15], measurement of fundamental constants [16], improvement of mass models (see section 1.5), input data for the neutrino mass in the form of highly accurate measurements of Q-values for several double-beta decay processes [17], and more. Table 1–1, adapted from[4], outlines the relative mass precisions required for a number of different applications. The current scope of the research done with the CPT revolves around mass measurements made for astrophysical input, most recently [18][19] of exotic neutron-rich nuclides important to the rapid neutron-capture process (r-process). Motivation for these type of measurements will be discussed in the next couple of sections.

1.3 Synthesis of the elements

Of great importance to the understanding of our universe is the method by which elements are created. We know that hydrogen is by far the most abundant element found in nature and that fusion reactions in stars are responsible for the creation of the elements up to iron (Z = 26). The elemental abundances

Field	$\delta m/m$
General physics and chemistry	$\leq 10^{-5}$
Nuclear Structure	$\leq 10^{-6}$
Astrophysics	$\leq 10^{-7}$
Weak interaction studies	$\leq 10^{-8}$
Fundamental constants	$\leq 10^{-9}$
Tests of fundamental symmetries	$\leq 10^{-10}$
Tests of QED in highly-charged ions	$\leq 10^{-11}$
Neutrino physics	$\leq 10^{-11}$

Table 1–1: Required relative uncertainties $\delta m/m$ for a variety of different fields of physics.

relative to 10^6 silicon atoms derived from terrestrial, meteoritic, and solar data collected by Suess and Urey [20] are given in Figure 1–1 [21].



Figure 1–1: Atomic abundance data from Suess and Urey, illustrating a number of element-production processes

The shape of this curve has no trivial explanation. There are however, a few trends in this figure which are physically illuminating. A general exponential decrease in relative abundance out to mass number $A \sim 90$ suggests a very different production mechanism for masses on either side of this seemingly arbitrary border. This just means that the proportion of stars which live long enough to synthesize the heavier elements is small. Above mass 90, the abundance curve is approximately constant except for a series of *twin peaks* showing local maximas of slow (s) and rapid (r) neutron capture processes. Both of these processes start with a stable nucleus capturing a neutron. After capturing enough neutrons the nucleus becomes unstable and undergoes beta decay, wherein a neutron is transformed into a proton and a new element is thus created. As its name suggests, the s-process occurs when the time between neutron captures is much longer than the time scale for the resulting beta decay. Single n captures will lead to beta decay. This restricts the creation of elements to those close to the line of stability on a chart of nuclides. Due to the long lifetimes of isotopes involved in the s-process, many of nuclides have been well-studied in the lab and the process understood. The r-process is quite the opposite. The time between neutron captures is much smaller than the time scale at which beta decay occurs, so nuclides farther from the line of stability are produced. Many of these nuclides have short half-lifes and are thus difficult to study in the laboratory. This process will be discussed further in the next section.

The s- and r-processes are each responsible for roughly half of the isotopes in the range $70 \le A \le 209$ [21]. Figure 1–2 shows this mass number region of roughly constant production where we see r-process production peaks at $A \approx 80$, 130, and 190, while s-process maxima occur at $A \approx 90$, 140, and 210.



Figure 1–2: Measured solar system abundances resulting from the r-, and s-processes (black circles and lines respectively). Also shown is the contribution of the proton capture (p) process (open boxes) to the observed abundances, which in this region is orders of magnitude smaller than neutron-capture processes. Adapted from [22].

Maxima in this plot correspond to full neutron shells at N=50, 82, and 126. At these magic numbers the number of neutron captures is minimized so both n-capture processes come to a stop. Since the s-process nuclei generally undergo beta decay after each neutron capture and lie closer to the line of stability the neutron shells are filled at higher A values than the r-process peaks. Since the r-process path lies far from stability, properties of these neutron-rich nuclei must to be measured if we hope to understand the process one day.

1.4 Mass Measurements and the r-Process

The r-process requires a rich supply of neutrons. Starting with some existing nuclide ${}^{A}_{Z}X$ and a large flux of neutrons given some ideal temperature condition (on order of 1 GK) one of two reactions will occur before the nuclide has a chance to β -decay. Either neutron capture, ${}^{A}_{Z}X$ (n, γ) ${}^{A+1}_{Z}X$ or photodisintegration ${}^{A}_{Z}X$ (γ, n) ${}^{A-1}_{Z}X$ may occur. These two competing reactions will take place until an equilibrium is reached: $(n, \gamma) \rightleftharpoons (\gamma, n)$. Once this happens the r-process for this isotope chain is dead and eventually this new *waiting-point* isotope will β -decay back towards stability. After each β decay the same process can continue until another waiting-point nuclide is reached and again β -decay occurs. The relative abundances of isotopes in the waiting-point approximation is given by equation 1.1 [23],

$$\frac{Y(Z,A+1)}{Y(Z,A)} = n_n \frac{G(Z,A+1)}{2G(Z,A)} \left[\frac{A+1}{A} \frac{2\pi\hbar^2}{m_u kT}\right]^{3/2} \exp\left[\frac{S_n(Z,A+1)}{kT}\right]$$
(1.1)

where the ratio of isotopic abundances of two neighboring isotopes (Y(Z, A + 1) and Y(Z, A)) along a chain of single neutron captures depend linearly on the neutron number density n_n , on the ratios of the nuclear partition functions G(Z, A), and exponentially on the environmental temperature T and the value of the neutron separation energy S_n , which is simply given by:

$$S_n(A,Z) = M(A-1,Z) - M(A,Z) + m_n$$
(1.2)

where M(A, Z) is the mass of nuclide with mass number A and proton number Z, and m_n is the mass of the neutron. In equation 1.1 m_u is simply the atomic mass unit. Setting $Y(Z, A+1) \approx Y(Z, A)$ and ignoring the small differences in the nuclear partition functions we find that the neutron separation energy of the most abundant member of the isotopic chain is given by:

$$S_n \approx kT \ln\left[\frac{2}{n_n} \left(\frac{m_u kTA}{2\pi\hbar^2 (A+1)}\right)^{3/2}\right] \approx kT \ln\left[\frac{2}{n_n} \left(\frac{m_u kT}{2\pi\hbar^2}\right)^{3/2}\right]$$
(1.3)

where a second approximation of $A+1 \approx A$ was used to get the final result. This waiting-point nuclide neutron separation value is only a function of T and n_n . Given a temperature of 1.5 GK and neutron number density of 10^{24} cm⁻³ we find $S_n^0 \approx 3.0$. The determination of these waiting-point nuclides defines the r-process path along the chart of nuclides. If we plot the observed neutron separation energies as a function of neutron number, as in Figure 1–3, we clearly see that S_n is always highest for an even number of neutrons.



Figure 1–3: Neutron separation energy as a function of neutron number for a number of elements.

This pairing effect implies that the abundance maxima will occur for nuclides with an even number of neutrons and therefore it is more meaningful to determine the waiting-point nuclides by considering the two-neutron separation energy S_{2n} [24] which is defined analogous to equation 1.2. In terms of single neutron separation energies,

$$S_{2n}(A,Z) = S_n(A-1,Z) + S_n(A,Z)$$
(1.4)

which in our earlier approximation of $A + 1 \approx A$ tells us $S_{2n} \approx 2S_n$. Therefore we can approximate the r-process waiting-point nuclides and thus a potential r-process path under the temperature and neutron densities described above using $S_{2n} \approx 6.0$ MeV. Using the measured values in the 2012 Atomic Mass Evaluation [25] we can draw this path keeping nuclides with a S_{2n} between 5.7 and 6.4 MeV. The result is the red data points in Figure 1–4. This same path will be used in a few figures throughout this thesis. In the accurate determination of the neutron-separation energies is where the importance of precision mass measurements lies.

Figure 1–4 also shows relative mass uncertainties $\delta m/m$ for all measured mass values in the AME12. The extrapolated mass values from the mass evaluation have been omitted. The green and black nuclides in this plot are the isotopes measured to precisions of better than $\delta m/m = 10^{-8}$ and are



Figure 1–4: Chart of the nuclides showing the relative mass uncertainties $\delta m/m$ of all *measured* masses in the latest Atomic Mass Evaluation [25] along with a possible r-process path shown by the red data points.

found in in close proximity to the stable backbone of the chart. On the neutron rich side of stability above N = 90 there are few measurements available. The CPT is currently coupled to the Californium Rare Isotope Breeder Upgrade (CARIBU) facility (described further in chapter 3) which is capable of providing rare isotopes from this region for precise mass measurements and input into r-process calculations such as [26]. Complying with the general relative precisions listed in Table 1–1 the aim for mass measurements with the CPT is at least 10^{-7} .

1.5 Mass Models

Realistically many of the r-process waiting-point nuclides will never be produced in large enough quantities in the lab, or have half-lives long enough to be adequately studied. Since there is still a large gap for most of the chart of nuclides between isotopes whose masses have been measured to a precision required for astrophysical calculations and the waiting-point nuclides of the r-process, theoretical calculations have to be done to estimate these exotic masses. What we can do is provide mass measurements of isotopes as far away from stability as possible in order to improve the reliability and accuracy of these calculations. Figure 1–5 shows the binding energy of isotopes of barium calculated by popular mass models HFB26 [27], KTUY05 [28], ETFSI12 [29], DUZU [30], and WS32011 [31], as well as the latest compilation of measured masses AME12 [25], all relative to the FRDM95 [32]. The

most neutron-rich isotope of barium presented in the AME12 is ¹⁴⁸Ba but even before this isotope you can see the models begin to diverge. As you get to the extremely exotic isotopes of barium, which will never be measured in the laboratory, the models are diverging by tens of MeV.



Figure 1–5: Binding energies as calculated by a number of mass models in relation to the FRDM95 for isotopes of barium. Also included is the measured values taken from the 2012 atomic mass evaluation.

The root mean square errors between these mass models and the AME12 are 654 keV for FRDM95, 564 keV for HFB26, 1.02 MeV] for KTUY05, 1.04 MeV for ETFSI12, 286 keV for WS32011, and 394 keV for DUZU. Clearly more masses of neutron-rich nuclei are needed in order to identify which mass model is the most reliable when far from stability in different regimes of the chart of nuclides. In the next chapter we will begin to discuss the technology that allows for such measurements to be made.

CHAPTER 2 Ion confinement and manipulation

Laws of physics say them 9s weigh

more when they wet.

- Young Jeezy

In this chapter we will discuss trapping potentials in two- and three-dimensions and how we can use these potentials in two different types of traps: the radio-frequency quadrupole (RFQ) Paul trap, and Penning trap. I will go over what is required in order to confine ions with an RFQ, derive the eigenmotions of charged particles in a Penning trap, discuss both dipole and quadrupole excitations in a Penning trap, and finally touch upon one common technique used to make mass measurements with a Penning trap.

2.1 Trapping potentials in two- and three-dimensions: RFQ ion guides and traps

For a particle to be bound to some point in space it requires a restoring force proportional to the gradient of the confining potential. The general solution to Laplace's equation for infinitely long cyclindrical conductors is given by:

$$\Phi(r,\varphi) = (Ar^n + Br^{-n})(C\sin(n\varphi) + D\cos(n\varphi))$$
(2.1)

for n > 0 [33]. We can impose physically meaningful boundary conditions when we introduce a number of cylinders all distances r_0 from the origin, namely, zero potential at the origin $\Phi(0, \varphi) = 0$, and the potential at the surface of the cylinder being $\Phi(r_0, \varphi) = \Phi_0 \cos(n\varphi)$. These constraints give us:

$$\Phi(r,\varphi) = \Phi_0 \left(\frac{r}{r_0}\right)^n \cos(n\varphi) \tag{2.2}$$

where n now represents the symmetry of the trapping potential produced by 2n electrodes [34] and Φ_0 is some amplitude. The electric quadrupole field (n = 2) in Cartesian coordinates will therefore have the form [35]:

$$\Phi = \frac{V_0}{2r_0^2} (\alpha x^2 + \beta y^2 + \gamma z^2)$$
(2.3)

where V_0 is some potential difference between electrodes, r_0 is some characteristic distance between the electrodes, and α, β , and γ are constants. From Gauss' law where the charge density $\rho = 0$ and with this general potential we need to satisfy the Laplace equation $\nabla^2 \Phi = 0$. This is accomplished with $\alpha + \beta + \gamma = 0$. We achieve a two-dimensional trapping potential with $\gamma = 0$ and $\alpha = -\beta = 1$:

$$\Phi = \frac{V_0}{2r_0^2}(x^2 - y^2) \tag{2.4}$$

This potential is realized by four hyperbolically shaped rod-like electrodes as shown in Figure 2–1 [36]. When ions are injected into the center of these electrodes, equation 2.4 tells us that the ions will



Figure 2–1: Hyperbolic 4-rod electrode structure of RFQ ion guides and traps. The insert shows the equipotential lines.

eventually make contact with one of the electrodes, since the electric fields in the \hat{x} and \hat{y} directions have opposite signs. Instead, applying a periodic voltage of the form:

$$V_0 = U_0 + U_1 \cos(\omega t)$$
 (2.5)

with large enough rf, ω , will allow for containment and focusing of the ions within the four electrodes. This is the RFQ ion guide. Combining this with equation 2.4 leads to the following equations of motion:

$$\ddot{x} + \frac{q}{mr_0^2} (U_0 + U_1 \cos(\omega t)) x = 0$$

$$\ddot{y} - \frac{q}{mr_0^2} (U_0 + U_1 \cos(\omega t)) y = 0.$$
(2.6)

Upon making the following substitutions:

$$a = \frac{2qU_0}{mr_0^2\omega^2}, \qquad \tilde{q} = \frac{4qU_1}{mr_0^2\omega^2}, \qquad \eta = \frac{\omega t}{2},$$
 (2.7)

equations 2.6 become isomorphic to the Mathieu equation:

$$\frac{d^2x}{d\eta^2} + (a + \tilde{q}\cos(2\eta))x = 0$$

$$\frac{d^2y}{d\eta^2} - (a + \tilde{q}\cos(2\eta))y = 0$$
(2.8)

which is well studied. A general solution of the Mathieu equation can be worked out with the ansatz

$$x = \sum_{0}^{\infty} [A_k \cos(k\eta) + B_k \sin(k\eta)].$$
(2.9)

For a mathematically rigorous set of solutions see references [37] and [38]. Physically we care about the types of solutions (a and \tilde{q}) for which there are stable and unstable solutions [35]. In the stable region the ions are free to travel through the electrode structure in the \hat{z} direction while oscillating in the xy plane. The unstable regions result in the loss of ions by hitting the electrodes. A plot of the regions of stability in the $a - \tilde{q}$ phase space is shown in Figure 2–2.



Figure 2–2: {left}Shows the stability in the \hat{x} and \hat{y} directions in a two-dimensional quadrupole field as a function of the Mathieu parameters a and \tilde{q} . {right} We have zoomed in on the largest region of stability in both \hat{x} and \hat{y} directions. The max and min values of \tilde{q} for some constant value of a/\tilde{q} is shown. Figure adapted from [39].

These stability conditions constrain the values of U_0 , U_1 , r_0 , and ω for a given RFQ ion guide. To this point we have been able to trap ions in the xy plane while the ions travel in the \hat{z} direction. If we cut the rods into three sections (see Figure 2–3) we have essentially created three distinct RFQ ion guides where different values of U_0 can be applied to each section to create a harmonic potential which trap the ions along the \hat{z} direction.



Figure 2–3: Example of segmentation of RFQ electrodes to allow for trapping in three dimensions. Figure from [40]

This is done in both the RFQ buncher at CARIBU and the RFQ Paul trap used at the CPT which will both be discussed in the next chapter.

2.2 Ion Motion in a Penning Trap

The combination of magnetic and electric fields can also be used to trap charged particles. The magnetic field provides radial confinement of ions orbiting the field lines, and confinement in three dimensions is completed by imposing an electrostatic potential well along the axis of the magnetic field. The quadrupole electrode structure capable of supplying such an axial trapping potential is called a Penning trap. The basic structure consists of a hyperbolic-shaped *ring* electrode enclosed on the top and bottom by hyperbolic *endcap* electrodes as shown in Figure 2–4. See section 3.2 for more details on the structure of the CPT.



Figure 2–4: Cross section of the electrode structure implemented in a Penning trap to create the potential given by equation 2.11. The characteristic trap dimensions z_0 and r_0 are the orthogonal distances from the center of the trap to the endcap and ring electrodes respectively. The dashed lines are the asymptotic cones of the hyperbolas of revolution.

The circular motion of a charged particle in an external magnetic field is trivially derived, but it is important to establish the cyclotron frequency since it is the foundation for mass measurements in a Penning trap. The period of one revolution is given by $T = 2\pi r/v$ where r is the radius of ion's path and v is the ion's velocity. The radius can be determined by setting the centripetal force equal to the Lorentz force in the absence of an electric field. This gives us r = mv/(qB) where m/q is the mass to charge ratio of the ion, and B is the value of the magnetic field. Substituting r into the expression for the ion's period gives us a cyclotron frequency of:

$$\omega_c = \frac{qB}{m}.\tag{2.10}$$

This equation allows for the determination of the mass of a trapped charged particle from the measurement of this cyclotron frequency. Recalling equation 2.3, the Laplace condition is also satisfied if we choose $\alpha = \beta = -1$ and $\gamma = 2$. This gives us a three-dimensional trapping potential possible in a Penning trap:

$$\Phi(x, y, z) = \frac{V}{2z_0^2 + r_0^2} (2z^2 - x^2 - y^2)$$
(2.11)

where V is the potential difference between the endcaps and ring electrodes, and z_0 and r_0 are the characteristic trap dimensions of the Penning trap as shown in Figure 2–4.

A charged particle moving in magnetic and electric fields is subject to the usual Lorentz force

$$\mathbf{F} = -q\nabla\Phi + q(\dot{\mathbf{x}} \times \mathbf{B}) \tag{2.12}$$

In the center of the trap $\mathbf{B} = B_z \hat{z}$, so the z term in equation 2.12 comes only from the electrostatic potential and is given by

$$F_z = -q \frac{4zV}{2z_0^2 + r_o^2}$$

This result immediately gives us the axial frequency inside the Penning trap

$$\omega_z = \sqrt{\frac{4qV}{m(2z_0^2 + r_0^2)}} \tag{2.13}$$

Combining equations 2.10-2.13 with the Newtonian law of motion $\mathbf{F} = m\ddot{\mathbf{x}}$ we obtain, in terms of ω_c and ω_z :

$$\ddot{x} - \omega_c \dot{y} - \frac{\omega_z^2 x}{2} = 0 \tag{2.14}$$

$$\ddot{y} + \omega_c \dot{x} - \frac{\omega_z^2 y}{2} = 0 \tag{2.15}$$

$$\ddot{z} + \omega_z^2 z = 0. \tag{2.16}$$

Since equations 2.14, 2.15 show coupling of motion in the xy plane it is convenient to rewrite them both as one equation using the substitution u = x + iy [41]. Equations 2.14 and 2.15 then reduce to:

$$\ddot{u} + i\omega_c \dot{u} - \frac{\omega_z^2 u}{2} = 0.$$
(2.17)

Using the ansatz $u = e^{-i\omega t}$ we find the equality

$$\omega^2 = -\omega_c \omega + \frac{1}{2}\omega_z^2 \tag{2.18}$$

with solutions

$$\omega_{\pm} = \frac{1}{2} (\omega_c \pm \sqrt{\omega_c^2 - 2\omega_z^2}).$$
(2.19)

These two roots ω_+ and ω_- are known as the modified cyclotron frequency and magnetron frequency, respectively, and will be used throughout this thesis. Examination of equations 2.19 allows us to discover another essential formula

$$\omega_c = \omega_+ + \omega_-. \tag{2.20}$$

For typical Penning trap setups such as the CPT where $B \approx 6 \text{ T}$, $V \approx 10 \text{ V}$, $z_0 = 1.0 \text{ cm}$, and $r_0 = 1.16 \text{ cm}$ we find

$$\omega_+ >> \omega_z >> \omega_- \tag{2.21}$$

so $\omega_c \approx \omega_+$. Explicitly equation 2.19 gives us:

$$\omega_{-} = \frac{1}{2} \left(\omega_c - \omega_c \sqrt{1 - 2\frac{\omega_z^2}{\omega_c^2}} \right).$$

Given the relation in equation 2.21 this can be Taylor expanded to give the approximately mass independent magnetron frequency:

$$\omega_{-} \approx \frac{\omega_{z}^{2}}{2\omega_{c}} = \frac{2V}{B(2z_{0}^{2} + r_{0}^{2})}.$$
(2.22)

The three eigenmotions inside the Penning trap are nicely summarized in Figure 2–5.



Figure 2–5: Summary of the motion of charged particles in a Penning trap showing the axial oscillation (ω_z) and the two circular motions $(\omega_+ \text{ and } \omega_-)$. Adopted from [42].

Taking as a more general ansatz for equation 2.17:

$$u = \rho^{+} e^{-i\omega_{+}t} + \rho^{-} e^{-i\omega_{-}t}$$
(2.23)

where ρ^+ and ρ^- are the radii of the modified cyclotron motion and magnetron motion, respectively, we obtain the following parametrization of motion in a Penning trap:

$$x = \rho^{-} \cos(\omega_{-}t) + \rho^{+} \cos(\omega_{+}t)$$

$$y = -\rho^{-} \sin(\omega_{-}t) - \rho^{+} \sin(\omega_{+}t).$$
(2.24)

2.2.1 Dipole excitations in a Penning trap

Hitherto we have only considered the magnetic field in which the trap rests and the DC potential applied to the ring electrodes of the trap. Since the ion motion in a Penning trap is not simply characterized by the cyclotron frequency and is instead a superposition of the two circular motions along with the axial oscillation described above, we can first consider the motion in a Penning trap due to a dipole excitation of ω_{\pm} . If we consider a driving potential of $\Phi_d = V_d \cos(\omega t) x$ applied to the ring electrode we obtain an additional electric field term of

$$\mathbf{E}_x = -V_d \cos(\omega t) \hat{x} \tag{2.25}$$

and equation 2.17 now becomes:

$$\ddot{u} + i\omega_c \dot{u} - \frac{\omega_z^2 u}{2} = -\frac{qV_d}{m}\cos(\omega t).$$
(2.26)

With an ansatz similar to what we used before, but now with time dependent radii $\rho^{\pm}(t)$, with initial radii of $\rho^{\pm}(0)$, we find that when resonantly excited at ω_{\pm} the radius as a function of time is given

by [43]:

$$\rho^{\pm}(t) = \frac{1}{\omega_{+} - \omega_{-}} \sqrt{[(\omega_{+} - \omega_{-})\rho^{\pm}(0)]^{2} + \left(\frac{qV_{d}t}{2m}\right)^{2}}$$
(2.27)

Since ω_{-} is roughly mass-independent, equation 2.27 tells us how the radius of all ions in the trap will increase if the correct magnetron frequency is applied in a dipole excitation. However $\omega_{+} \approx \omega_{c}$ and is mass-dependent, so a resonant dipole excitation at ω_{+} will only increase the radius of those ions with ω_{+} equal to the one applied. Other ions will remain untouched.

2.2.2 Quadrupole excitations in a Penning trap

We can also consider a quadrupole rf driving potential of the form:

$$\Phi_q = -\frac{V_q x y}{2a^2} \cos(\omega_q t) \tag{2.28}$$

where V_q is the amplitude of the quadrupole rf pulse applied, a is the inner radius of the Penning trap, and ω_q is the applied frequency. Under the addition of this potential we still satisfy the Laplace equation. Accounting for this oscillating quadrupolar field applied to the four segments of the ring electrode during an excitation, we realize an additional force [44]:

$$F_x = qE_x = q\frac{V_q\cos(\omega_q t)}{2a^2}\hat{x}$$
(2.29)

$$F_{y} = qE_{y} = q\frac{V_{q}\cos(\omega_{q}t)}{2a^{2}}\hat{y}.$$
(2.30)

We could also consider the effect of damping on the target ions due to interaction between other ions in the trap or residual gas with the addition of a damping force:

$$\mathbf{F} = -\delta m \mathbf{v},\tag{2.31}$$

but the Penning trap sits in an area where we typically had a pressure of 10^{-10} Torr and for the majority of the measurements in this thesis the time spent in the Penning trap was kept to a minimum due to the short half-lifes of the ions of interest. A similar damping term is found in the derivation of the fitting function in Chapter 4, but analysis has shown that the damping term has little effect on the quality of fit used to determine the cyclotron frequency, so this damping term will be ignored. Just as we did in section 2.2.1 we can add these force terms to equations 2.14 and 2.15 and have a couple of differential equations that can be solved to give the radius of ions in the trap as a function of time and applied quadrupole frequency, ω_q . Assuming the motion in the trap is undamped ($\gamma = 0$),

in resonance when the applied quadrupole excitation frequency is equal to the cyclotron frequency of the species in the trap the amplitudes of magnetron and reduced cyclotron motion evolve as [44]:

$$\rho^{\pm}(t) = \rho^{\pm}(0) \cos\left(\frac{k_0 t}{2}\right) \mp \rho^{\mp}(0) e^{\pm i\Delta\phi} \sin\left(\frac{k_0 t}{2}\right)$$
(2.32)

where we have defined:

$$k_0 = \frac{qV_q}{2a^2m(\omega_+ - \omega_-)}.$$
(2.33)

A full oscillation from magnetron to modified cyclotron and back to magnetron motion requires a time of $2\pi/k_0$. So to convert from one motion to the other requires an excitation time of $t_{rf} = \pi/k_0$. This gives us a relation between excitation time and the applied amplitude of the quadrupole rf field:

$$V_q = 2a^2(\omega_+ - \omega_-)\pi \frac{m}{qt_{rf}} \quad \Rightarrow \quad 2a^2 B \frac{\pi}{t_{rf}} \tag{2.34}$$

where in the second part of equation 2.34 the approximation of $\omega_c \approx \omega_+ \gg \omega_-$ was made. A toy description of the conversion from purely magnetron motion to purely modified cyclotron frequency, where the ions are initially given a radius of 5 mm and allowed to transform as described by equation 2.32, is given in Figure 2–6. The figure is broken up into two images for simplicity. The image on the left shows how the motion changes between times t = 0 and $t = t_{rf}/2$, while the image on the right shows the final stage of conversion between times $t = t_{rf}/2$ to $t = t_{rf}$. Note that in this example of perfect conversion the radius of the modified cyclotron motion is equal to the initial radius of the magnetron motion.

2.3 Time-of-flight ion-cyclotron-resonance

With all of these Penning trap motions established, we can create a scheme in which to measure the cyclotron frequencies of ions. The technique used at the CPT is called time-of-flight ion-cyclotron-resonance (ToF-ICR). The basic premise consists of trapping ions in the trap and bringing them to an initial radius ρ_{-} via dipole excitation at ω_{-} , and then applying a quadrupole rf excitation to the ring electrodes of the Penning trap at some frequency ω_q . Then eject the ions from the trap and measure their time of flight from the center of a homogeneous magnetic field to a detector outside of the field. Then repeat the process over a range of ω_q values recording the ToF at each one. If $\omega_q = \omega_c$, the conversion shown in Figure 2–6 will occur and the ions will gain maximal radial energy which, upon leaving the magnetic field, will convert into linear kinetic energy along the field axis and reach the detector the quickest. A ToF spectrum spanning a range of frequencies will allow us to determine the



Figure 2–6: Complete conversion from magnetron to modified cyclotron motion in the Penning trap under excitation at frequency $\omega_q = \omega_c$. The blue dashed line is the initial radius of the ω_{-} motion.

cyclotron frequency. The attainable frequency resolution with this method is approximately [44], [45]:

$$\Delta \nu \approx \frac{0.8}{t_{rf}}.$$
(2.35)

This relation is an important one in determining the excitation time for the measurement of a particular isotope. There are two isomer measurements given in this thesis: $^{134}I^m$, and $^{146}La^m$ which required excitation times of 1000 ms, and 4000 ms respectively in order to resolve both states of the isotope. For $^{134}I^m$ a series of 2000 ms excitations were also performed. The mass calculated in Chapter 4 will be the combined result of 1000 and 2000 ms measurements.

The CPT moved into the CARIBU facility in 2010 and since then approximately 80 fission fragment masses have been measured, including six isomeric states. Figure 2–7 illustrates all of these measurements in relation to the stable backbone of the chart of nuclides.

Nearly all of the measurements have been of the heavy fission peak thus far, with only a handful of the lighter peak being seriously studied. Table 2–1 gives the fission branch and half-life of all measurements given in this thesis. Direct mass measurements of ^{149,150}Ba, ¹⁶⁴Eu ¹, ¹⁶²Sm, ¹⁶⁵Gd,

¹ A β -endpoint energy was measured in 2007 [46] but the mass calculated required the systematic predictions from the AME03 [47]. See section 4.6.1 for more details.



Figure 2–7: Section of the chart of the nuclides showing the masses measured at CARIBU. Stable isotopes are shown in black and the orange and green isotopes are those which are given in this thesis – the green being first time measurements with a Penning trap, and the orange showing repeated CPT measurements. Once again a possible r-process path is drawn.

and the ground state of ¹⁴⁶La were done for the first time. Measurements of ¹⁰⁶Mo, ¹⁰⁶Tc, and ¹⁶²Eu were firsts for the CPT at CARIBU. A few nuclides were remeasured in order to check the consistency of the CPT and to perhaps improve precision. These include ⁹⁵Sr, ¹³⁴I^{m,g}, ¹⁴²I, ¹⁴⁶La^m and ¹⁴⁸Ba.

Nuclide	252 Cf fission branch [48]	$t_{1/2}$ [49]
95 Sr	0.767	$23.90(14)\mathrm{s}$
$^{106}\mathrm{Mo}$	3.47	$8.73(12){ m s}$
$^{106}\mathrm{Tc}$	2.19	$35.6(6){ m s}$
$^{134}\mathrm{I}^m$	0.583	$3.52(4){ m m}$
$^{134}\mathrm{I}^{g}$	0.331	$52.5(2){ m m}$
^{142}I	$3.75 imes 10^{-3}$	$0.222(12)\mathrm{s}$
$^{146}\mathrm{La}^m$		$10.0(1){ m s}$
$^{146}\mathrm{La}^{g}$	2.39	$6.27(10)\mathrm{s}$
148 Ba	4.8×10^{-2}	$0.612(17)\mathrm{s}$
149 Ba	4.04×10^{-3}	$0.344(7)\mathrm{s}$
150 Ba	3.27×10^{-4}	$0.3\mathrm{s}$
$^{162}\mathrm{Sm}$	4.57×10^{-3}	$2.4(5)\mathrm{s}$
$^{162}\mathrm{Eu}$	4.7×10^{-2}	$10.6(10) \mathrm{s}$
$^{164}\mathrm{Eu}$	3.52×10^{-3}	$4.2(2) \mathrm{s}$
$^{165}\mathrm{Gd}$	$9.96 imes 10^{-3}$	$10.3(16)\mathrm{s}$

Table 2–1: Yield per 100 fissions (if known) and half-lifes of nuclides measured at CARIBU in this thesis.

CHAPTER 3 The Canadian Penning Trap system

You can't just pick and choose which laws to follow. Sure I'd like to tape a baseball game without the express written consent of Major League Baseball, but that's just not the way it works. - Hank Hill

In this chapter I will discuss the measurement process carried out with the CPT at CARIBU, starting with a brief description of the major components of CARIBU and what the facility provides. Then I will describe the CPT apparatus and the path that the ions follow en route to the Penning trap. Finally I will provide a detailed description of ion transportation mechanisms which make the precise mass measurements in this thesis possible.

3.1 CARIBU: Californium Rare Isotope Breeder Upgrade

Californium-252 is a radioactive isotope first discovered from the aftermath of the *Ivy Mike* thermonuclear device test in 1952 on the Enewetak Atoll [50]. The isotope has a half-life of 2.635(8) years and decays via alpha decay with a probability of 96.9% to ²⁴⁸Cm, and it will undergo spontaneous fission to a variety of decay products 3.1% of the time [51]. Due to the high flux of neutrons per fission of ²⁵²Cf (see Figure 3–1) the isotope has found many practical applications including brachytherapy used to treat certain type of cancers, neutron radiography, and as a neutron source for the commissioning of nuclear reactors [50].

Figure 3–2 shows the portion of the chart of nuclides which are populated from the spontaneous fission of 252 Cf and the extent to which the nuclides are produced per 100 fission yields. The two major peaks around A = 105 and A = 140 will be referred to as the light peak and heavy peak respectively throughout the rest of this thesis. The location of the fission products in relation to the r-process path as discussed in section 1.4 along with the relatively short half-life makes 252 Cf along an ideal ion source for the study of neutron-rich nuclei for astrophysical applications. The CARIBU facility was designed and built at Argonne National Laboratory in order to accommodate the need



Figure 3–1: Average number of neutrons emitted per fission for several heavy-elements. Data from [52].

for experiments in these isotopic regimes.



Figure 3–2: Portion of chart of nuclides showing the yield per 100 fissions of ²⁵²Cf. The red data points show a possible r-process path. The magic numbers in this region are highlighted.

To exploit this unique ion source for any kind of measurement the fission products must be thermalized, constrained, and transported to an experimental area. In extreme oversimplification this is what CARIBU provides. The layout of CARIBU is given in Figure 3–3 where the major components, namely the gas catcher, high-voltage cage, isobar separator, and RFQ ion buncher are labelled. There are two possible destinations for heavy-ion beams extracted by CARIBU, either towards the low-energy experimental area where the CPT is housed or towards ATLAS for re-acceleration to other experiments. In the next few subsections I will briefly describe the components of CARIBU with emphasis on the beam preparation for low-energy mass measurements at the CPT. More detailed and technical information relating to CARIBU can be found in recent PhD. theses by Jon Van Schelt [53] and Dan Lascar [54].



Figure 3–3: Layout of the CARIBU facility [53]

3.1.1 Gas Catcher

The chief piece of technology that allowed for the construction of CARIBU is the gas-filled gas catcher which symbolically and necessarily sits at the head of the facility. The gas catcher system was first developed at Argonne in 1998 as a means of transporting radioactive ions into the CPT [55]. It consists of two major sections, a cylindrical body and conical portion tapering to a small aperture where the ions may escape. Three processes allow for the success of the gas catcher: it is filled with high-purity helium gas which slows and thermalizes whichever species enters the system; a DC gradient along the approximate 2m length to extract ions before significant decay can occur; and an rf confining field used to focus ions away from any walls. During the measurement campaigns discussed in this thesis a 0.3 Ci source was used. The source is seated on a stainless steel plate and inserted into the back of the gas catcher. A gold degrader foil is inserted between the source and entrance of the body section in order to decrease the energy of the fission fragments entering the gas

catcher. The rf frequencies and amplitudes are separately controlled for the cone and body sections. The cone rf power is often adjusted between measurements depending on the number of ions or size of molecules coming out of the gas catcher being observed at the CPT. If more rf power is applied to the cone electrodes the confinement is increased and we are likely to see more fission fragments reach the CPT. However if there are molecules being formed in the system prior to the cone which have a larger size than the fission fragment isotopes, these will also be focused and transported along with the wanted ion species. So for isotopes with low fission branches where the number of molecules (including hydrocarbons, or radioactive molecules formed from the combination of fission fragments with water molecules or OH groups) is similar to the wanted species, the rf power on the cone is reduced such that only the smallest particles will be focused by the rf field (applied to the cone electrodes) and extracted out of the cone's nozzle. This reduces the number of the wanted species to some degree, but also removes a large amount of the unwanted species. After exiting the gas catcher the ions enter an array of RFQ ion guides separated by nozzles such that differential pumping may be performed isolating the ions from the residual He gas. Finally there is a section of acceleration electrodes from which the ions leave with an energy of up to $50 \,\mathrm{keV/e}$. This potential energy comes from the high voltage platform housing the gas catcher and RFQ cooler sections. This platform is powered by a 50 kV power supply which is typically biased at 36 kV. At this stage in the beam preparation we have provided little mass selection and must send the beam of ions with charge states of 1+ and 2+ through the isobar separator. The charge state of the ions depends to a large degree on the ionization energies of the fission products. The first and second ionization energies of elements between Z=1 and Z=100 are plotted in Figure 3-4.

There are a couple things to take away from these plots. First is the large first ionization energy of He making it ideal as a buffer gas for the gas catcher, buncher, and later the Paul trap at the CPT. We also notice local minima of first ionization energies around both fission fragment peaks, at rubidium and cesium. These elements are also both local maxima of second ionization energies. This gives us a hint as to which charge state is ideal for measuring certain nuclides. A generally observed rule at CARIBU is that elements with $Z \ge 56$ come out at 2+, while those with $Z \le 55$ come out at 1+. We still do observe barium, lanthanum, and cerium at 1+ but typically the yields are much greater at 2+.



Figure 3–4: First and second ionization energies from Z = 1 to Z = 100.

3.1.2 Isobar Separator

The isobar separator consists of two 60° bending magnets and various electrostatic focusing elements. It was designed to be compact to fit on the CARIBU deck, have transmission efficiencies greater than 90%, and have a high resolving power of $m/\Delta m \ge 20000$ [56].



Figure 3–5: CARIBU isobar separator layout showing a number of quadrupole (Q) and sextuple (S) focusing/steering elements with an electrostatic multipole (M) sandwiched between the two magnets. Figure from [56]

At mass number A = 142 this resolution would allow us to separate masses as little as 7.1 mu apart, meaning that the CPT could distinguish between isotopes with cyclotron frequencies only 30 Hz apart. Under the current system settings this resolution has not been obtained. Typical resolving powers observed during mass measurements are closer to $m/\Delta m \approx 7000-10000$, but some recent experiments have seen resolving power approaching $m/\Delta m \approx 20000$. After the isobar separator the ions come to an electrostatic deflector which bends ions towards the low-energy experimental area.

3.1.3 RFQ Ion Buncher

The next major component of the CARIBU system is the RFQ ion buncher. It is a gas filled linear RFQ ion guide and trap consisting of 49 electrode segments, the last three of which form the trap where the continuous beam is *bunched* [53]. Typically the trap is opened to accumulate ions for periods of 100 ms for ejection towards the CPT (see section 3.3). The buncher is inside a high voltage cage powered by the same 50 kV power supply used for the gas catcher platform so the ions still have energies near 36 keV/e that they left the gas catcher with. This is much too high to send to the low-energy experiments so an *elevator* segment was incorporated into the beamline, designed to bring the beam energy down to a manipulable level. After ejection from the trap the ions encounter an electrically isolated elevator. This section consists of a drift tube which is pulsed from the bias on the gas catcher platform down to approximately 2 kV while the bunches of ions are inside it. The ion bunches now leave CARIBU's jurisdiction and enter the low-energy beamline where they have drift potentials on the order of 2 keV/e.

3.2 The Canadian Penning Trap System

The CPT is housed in the bore of a 5.7 T superconducting magnet located on top of a 4 m tall tower. The layout of the tower is shown in Figure 3–6. In this section I will briefly discuss a number of important tower components before introducing the Penning trap itself.

3.2.1 Offline ion source

Just outside of Figure 3–6 is a cross where a stable ion source (SIS) is located. The electrically grounded SIS consists of cesium salt on top of a heating element, a number of accelerating electrodes, and a 90° deflector to inject the $^{133}Cs^+$ ions into the CPT system. Stable cesium is one of the most precisely measured masses mostly for the precise determination of the fine-structure constant and molar Planck constant values [57]. Its stability and precisely known mass make it a ideal candidate for calibration of other cyclotron frequencies measured in a Penning trap. The SIS is also used to tune a number of components of the system discussed throughout this chapter.



Figure 3–6: Schematic of the CPT tower showing the 90° deflector (deflector #3), RFQ Paul trap, Penning trap, ToF line, channeltron detector, various Einzel lenses and steerers, as well as diagnostic MCP detectors.

3.2.2 Lower section of the tower

I will describe the elements below the gate valve labelled V6 in Figure 3–6 as the lower section. Immediately downstream of the SIS cross is our first diagnostic feedthrough. The feedthrough consists of a silicon surface barrier detector and Microchannel plate detector and is known as Si/MCP 0. This diagnostic is used to determine transmission efficiency through the low-energy beamline. When ions from CARIBU approach the tower they possess energies of roughly 2keV/e. To bring them down to ground potential an electrostatic elevator is used which is similar to the one at CARIBU. This CPT elevator is set to a drift tube potential of -1490 V when using the SIS since the stable ¹³³Cs ions begin at the same ground as the rest of the tower. Next the ions enter the ion drift chamber containing the 90° deflector and a quadrupole steering section. The deflector can also be biased at drift tube potential allowing ions to travel straight through this chamber onto another diagnostic Si detector, known as Si 1/2. This detector serves to locate the path of the ions from the exit of the buncher into the center of the ion chamber. When tuning any beam we need to be careful to avoid steering directly into a detector since its position once inside the beamline is not precisely controlled.
The exact orientation of a diagnostic detector with respect to the alignment of the beamline may differ over time, so maximizing rates on a few nearby detectors is the optimal method. Now going up the tower the ions encounter an array of steerers and lenses before entering the Paul trap section. Details of RFQ traps were discussed in section 2.1. The electrode structure of our Paul trap is given in Figure 3–7.



Figure 3–7: Electrode layout of the cryogenically cooled gas-filled linear RFQ Paul trap used at the CPT. In this image beam travels from left to right.

The biases of the electrodes during capture, trapping, and ejection are given in Table 3–1. In order to further thermalize and efficiently capture ions before injection into the CPT, the trap is filled with high-purity He gas. The operating pressure of the trap is approximately 10^{-5} Torr. The trap is also cryogenically cooled to near liquid nitrogen temperatures to further aid in ion confinement in the trap.

Electrode	Capture (V)	Trapped (V)	Ejection (V)
Deceleration	10.3	19.3	19.3
S1	-0.8	6.2	26.2
S2	-6.9	-6.9	-6.9
S3	6.2	6.2	-53.8
Top endcap	20.7	20.7	-39.3

Table 3–1: RFQ Paul trap bias voltages during capture, trapping, and ejection.

After ejection from the Paul trap we have a set of steerers and lenses before another diagnostic feedthrough containing Si/MCP 3. This is the most commonly used diagnostic as it allows us to tune both the depth of the trap and trap timing pulses to maximize the transmission of cooled and bunched ions through the lower section of the tower. On a good day the efficiency between the exit of the buncher and Si 3 will be approximately 70%. After this diagnostic cross there is another set of steerers and lenses before V6.

3.2.3 Upper section of the tower

From V6 up to the channeltron detector is what I will refer to as the upper section of the tower. Directly after V6 is our last set of quadrupole steerer and lenses before the ions enter the Penning trap. Next there is a cross containing the last diagnostic, MCP 4. There is also a cryopump attached directly to this cross allowing us to obtain pressure of approximately 3 nTorr. The ion bunches then enter a drift tube leading towards the Penning trap.

The CPT has a seven electrode configuration shown in Figure 3–8.



Figure 3-8: The seven electrode configuration of the CPT showing the aperture size and two characteristic trap dimensions z_0 and r_0 .

The ring electrode –which is segmented into four quadrants such that quadrupolar and dipolar excitations are possible– and top and bottom endcaps are of hyperbolic shape in order to apply the required trapping potential discussed in Section 2.2. An aperture of diameter 0.5 cm in each of the endcap electrodes ruins this ideal trapping potential. To compensate, an electrode is added above and below each aperture. These electrodes are then tuned to their values given in Table 3–2 to the

	Bias Voltages (V)				
Electrode	Capture	Trapped	Ejection		
Bottom correction tube	-4.4	0.60	0.6		
Bottom endcap	-7.5	-3.50	-3.50		
Bottom correction ring	-9.17	-9.17	-9.17		
Ring	-13.55	-13.55	-13.55		
Top correction ring	-9.17	-9.17	-9.17		
Top endcap	-3.5	-3.50	-13.50		
top correction tube	0.6	0.6	-14.4		

Table 3–2: CPT trapping electrode biases

point where the trapping efficiency is maximized while not inducing any electronics timing-dependent

shifts in measured frequencies. For example, when tuning the correction tube electrodes we wish to determine the bias voltage where the observed modified cyclotron frequency for a particular isotope is independent of the start of the Penning trap capture pulse.

Once ejected from the Penning trap, the ion bunches travel through a ToF line of electrodes leading from the magnetic field center of 5.7 T to the channeltron detector where the magnetic field is approximately 0.01 T. The electrode structure in this line is shown in Figure 3–9.



Figure 3–9: TOF drift tube electrode assembly leading from the CPT to the channeltron etector

Table 3–3: Biases of the electrodes along the ToF line defining the ion optics leading from the Penning trap to the channeltron detector.

ToF electrode:	А	В	С	D	Е	F	G	Η	Ι	H/I stress
Bias (V) :	-16	-100	-250	-500	-400	-800	-140	-800	-800	-800

ToF A is the longest electrode in this assembly and is where the ions see the largest shift in magnetic field. By the end of this section the ion motion has largely been converted from purely radial to purely linear. The biases along this ToF line are also given in Table 3–3. After ToF A the remaining electrodes serve mainly as ion optics to direct the ions through the aperture leading to the detector without inducing any mass-dependent kicks that would affect the ToF measured.

The current detector used at the CPT is a DeTech model 402A-H channel electron multiplier (channeltron). It consists of a dynode plate, horn, and anode. Ions strike the dynode plate of the detector which is biased at -4000 V and release electrons which travel through a semi-conductor coated horn biased at 2900 V which causes a cascade of electrons every time an electron strikes the walls of the horn. This charge then accumulates on the anode of the channeltron and a signal is generated. The channeltron has a timing resolution of approximately 25 ns [58].

3.3 Measurement Procedure

In this section I will describe the electronic signals used to transport bunches of ions from the CARIBU buncher to the Penning trap and subsequently recorded to file. Figure 3–10 is a summary of what will be described here. The starting point of a measurement cycle is in the top left hand corner of this figure, labelled with a **1**.



Figure 3–10: A simplified diagram showing the precise flow of timing pulses required to transfer fission products from CARIBU to the CPT using the ToF-ICR technique for determining cyclotron frequencies. Numbers 1-6 are referenced in the text to aid the reader.

From CARIBU buncher to linear Paul trap

The signal that starts the whole process is a 1 kHz clock which outputs a sinusoidal wave with a period of 1 ms. This output triggers a rate divider module where the user can set a number of counts before an output signal is sent. This rate divider dictates the time the buncher accumulates ions. Typically this value was set at 100 ms so it would count 100 periods from the clock and then trigger a coincidence module (labelled with a 2). The other signal that this module waits for is the one which indicated that the linear Paul trap is empty, which will be true at the start of the measurement. Once both of the signals are realized, there are four output signals which are sent. One goes back to the buncher telling it that it is ready to eject. Two high precision delay generators from Data Design Corporation (DG11A), with timing resolutions of 10 ns [59], are triggered at the same time. Each of these modules has four independent outputs where delays of up to 167.7 ms can be created. One of these modules is responsible for triggering the CARIBU elevator and the CPT elevator. The CARIBU elevator (discussed briefly in section 3.1) is triggered on the order of $10 \,\mu s$ –exact times depend on the mass-to-charge ratio of the ion beam – after the eject pulse is sent. The CPT elevator is similar in design to the CARIBU elevator and functions to bring the ions, now with energy of roughly 2 keV/e, down to ground potential in order for the ions to be captured by the low voltage Paul and Penning traps. The elevator begins at ground and once triggered by the DG11A, roughly $100\,\mu s$ after the buncher eject, the potential is dropped to a negative potential depending on the energy of the ion beam. The second DG11A sends the trigger signals for the deceleration and capture pulses required for the Paul trap. Approximately $10\,\mu s$ after the CPT elevator is fired, the signals to begin these pulses are sent. The deceleration electrode is the endcap prior to section 1 (S1) of the Paul trap, and is dropped from 19.3 V to 10.3 V. At the same time S1 is dropped from 6.2 V to -0.8 V. This creates a DC gradient for the ions to be injected into the trap. After another $5 \mu s$ the DG11A sends another signal to restore the deceleration electrode. One final signal from this module is sent after another 8-10 μs ending the capture pulse and restoring the harmonic potential in the trap. The fourth signal from the 2-input coincidence module triggers another rate divider, where the number of ejected bunches from the buncher allowed to be captured by the Paul trap is set. For each bunch of ions released from the CARIBU buncher the rate divider count will go up by one. Once the set number of bunches captured is reached, a logic signal is sent to a flip-flop box saving that the trap is full. At this point the same signal is sent to another 2-input coincidence module (labelled by 3) that

will only allow for the trapped ions to be ejected once the Penning trap is empty. This module serves to prevent the Paul trap from ejecting until the Penning trap contents have been ejected.

Paul trap to Penning trap

If the "Penning trap empty" signal and "Paul trap full" signal both reach the 2-input coincidence module, an output triggers another two DG11A delay generators. The first one sets the timing for the Paul trap ejection and Penning trap deceleration pulses. After the final capture a delay of 30 ms is inserted to allow the last bunch of ions to become sufficiently cooled from interactions with the He buffer gas. Then the Paul trap ejection is triggered where the S1 potential is increased by 20 V and section 3 (S3) and the top endcap electrodes are dropped by $60 \,\mathrm{V}$. This provides a kick to the ions exiting the trap in such a way as to prepare them for capture in the Penning trap. Once the Paul trap is empty a set signal is sent back to the 2-input coincidence module (2) allowing for the buncher to start sending ions to the Paul trap again. Simultaneously the start of the Penning trap deceleration pulse is triggered. The deceleration electrode directly before the Penning trap is pulsed from 4.1 V down to $-146 \,\mathrm{V}$. The second DG11A module sets the delays for the Penning trap capture pulse, as well as the trap raising pulse and evaporation pulses (discussed is section 3.3.1). Roughly $50 \,\mu s$ after this DG11A is triggered, the Penning trap capture pulse is activated where the bottom endcap and correction tube are dropped for approximately $10 \,\mu s$ and is then closed to its original setting over $1 \mu s$. Once this capture pulse is complete the trap raising pulse brings the ring electrode from -13.55 V to -6 V over the course of approximately 2 ms whereupon the evaporation pulse is turned on by decreasing the top correction tube potential for 0.5 ms. The top correction tube and ring electrodes are then adiabatically returned to their original biases. At this point ions have been ejected from the Paul trap, captured in the Penning trap, and the high energy ions that were initially captured have been removed.

Eigenmotion excitation

After approximately 7 ms has passed since the final capture in the Paul trap, the last DG11A module triggers a Jorway model 221 delay generator (labelled by 4) which sets the delays for all of the *slow* pulses used in the Penning trap. This controls the triggers and durations of the dipole and quadrupole pulses applied to the four quadrants of the ring electrode. The length of these pulses are on the order of 10 ms so the less expensive Jorway 221 module with timing resolution of $1 \mu s$ [60] is sufficient. The Jorway sends three triggers to the *frequency selector* (labelled as 5) which define the duration of the ω_+, ω_- , and ω_c excitations. These windows are coupled to the frequencies originating from three function generators. The ω_{-} and ω_{c} frequencies are applied by separate Stanford Research Systems 30 MHz function generators (DS345), while the ω_{\pm} cleaning frequencies (see section 3.3.1) are applied by a Tabor waveform generator (model WW1071). The output of this module is three sequential pulses: the ω_+ pulse, ranging from 50 ms to 500 ms at frequencies on the order of 1 MHz; the $\omega_$ pulse with a fixed duration of 10 ms at a frequency of ≈ 1550 Hz; and a ω_c at the trapped species' approximate cyclotron frequency with a duration between 50 ms and 4000 ms depending on half-life or precision requirements. This output is given to a *rf splitter* module where the signal is copied and shifted 180° out of phase. These two opposite-phased pulse sequences are sent to a phase selector module where they are met by four trigger signals from the Jorway. This module has four outputs which send the required signal to each of four ring electrodes, labelled as north (N), south (S), east (E), and west (W). If a dipole pulse is requested by the user (i.e. ω_{-} , and ω_{+} excitations) the phase selector gives a pair of adjacent ring electrodes, say N and W, one phase of the rf pulse and the opposite electrodes, say E and S, receive the 180° out-of-phase rf pulse. When it comes time for the ω_c quadrupole pulse to be applied, the four quadrants of the ring are again split into pairs, but this time opposite electrodes are given the same phase. So the N and S electrodes would be at one phase while the E and W electrodes are at the opposite phase. Once the quadrupole pulse has come to an end, a trigger is sent from the Jorway telling the Penning trap to eject. Once this trigger is read, the top endcap and top correction tube potentials are dropped for approximately 2 ms before returning to their original settings. This ejection is not as dramatic as the Paul trap or CARIBU buncher eject since we do not want to impart any extra energy to the ions as they travel towards the detector.

Data acquisition

Once the ions have been ejected from the trap, the Jorway sends a trigger to a LeCroy 3521a multichannel scaler (MCS) to start counting. The MCS (labelled as 6) has 256 channels which can be converted into channels in the time domain by the experimenter. An external advance input to the MCS allows one to dictate the amount of time between each MCS channel. A 10 MHz clock is connected to a rate divider set to the number of steps in one MCS channel. For all data in this thesis a time step of 1 channel = $1 \mu s$ was used, so the rate divider was set to take 10 counts from the clock and then tell the MCS to increase its channel number by one. While it is scanning from channels 1 to 256, it is reading ion pulse signals from our channeltron detector. If a *hit* is recorded,

the MCS tags which channel it was in when the channeltron received the signal, and records it to file. Once the 256 channels have been scanned, a signal is sent back to the 2-input coincidence (3)saying that the Penning trap is empty. Once the Paul trap is full again both inputs will be satisfied and a signal is sent telling the flip-flop box that the Paul trap is empty. The output of the flip-flop then goes back to the first 2-input coincidence module (2) controlling the ejection rate from the CARIBU buncher allowing it to keep sending bunches. In order for continuous ejection rates out of the CARIBU buncher, which is necessary in order to maintain constant deck voltage [53], the number of bunches accumulated in the Paul trap must be sufficient to allow for the Penning trap cycle to be carried out. For example, if a total ion manipulation time (see next section) of 1000 ms is required before ejection from the Penning trap, the number of shots accumulated in the Paul trap must be at least 10. If less than 10 are requested there will be a delay before the 2-input coincidence (3) is triggered by the end of measurement signal, and thus a delay between ejections from the buncher leading to unstable beam delivery. This is referred to as *skipping shots*. If this is avoided and seamless ejection and capture between the buncher and Paul trap is achieved, the entire process described up to this point, is repeated with the only difference being that the quadrupole pulse is applied to the ring electrode of the Penning trap at a different frequency. The MCS now counts signals from the channeltron and stores this data in a new column. Once the quadrupole pulse function generator has cycled through the user defined range of frequencies, a *scan* is complete. The data file is now a table with 256 rows and N columns where N is the number of frequencies in the scan.

3.3.1 In-trap manipulation

Removal of high energy ions

The removal of higher-energy ions in the trap begins with an adiabatic increase in the potential of the ring electrodes to a value of 7.5 V above the starting potential, then the potential applied to the top correction tube electrode is quickly dropped, "evaporating" the higher-energy ions out of the trap. The ring electrodes are then adiabatically brought back to their starting potentials and the low-energy ions remain trapped. These pulses are done every cycle and are called the trap raising pulse (TRP) and evaporation pulse, respectively. The calculation of an ideal TRP was completed by former CPT student Shane Caldwell and is reproduced below. Recall from section 2.2 that the axial frequency is given by:

$$\omega_z = \sqrt{\frac{4qV}{m(2z_0^2 + r_0^2)}} = \sqrt{\alpha(V_{ec} - V_r)}$$
(3.1)

where we have explicitly wrote the potential difference $V = V_{ec} - V_r$ with V_{ec} being the voltage applied to the top and bottom endcap electrodes and V_r being the voltage initially applied to the ring electrodes. We also defined a parameter $\alpha = 4q/(m(2z_0^2 + r_0^2))$ which includes the characteristic trap dimensions and m/q value for the ion species in the trap. For this calculation α has no time dependence. Since we are applying the TRP to the ring electrode we consider the time varying potential $V_r(t)$ and thus the axial frequency will change with time. We wish to create a small perturbation to $\omega_z(t)$ and calculate $V_r(t)$ under such perturbation.

$$\frac{d\omega_z}{dt} = \frac{-\alpha}{2\sqrt{\alpha(V_{ec} - V_r(t))}} \frac{dV_r}{dt}$$
(3.2)

We define the change in ω_z over one period as,

$$\delta_{\omega_z} = \frac{d\omega_z}{dt} \frac{2\pi}{\omega_z} \tag{3.3}$$

And set this deviation from the initial ω_z equal to a constant,

$$\frac{\delta_{\omega_z}}{\omega_z} = \xi \tag{3.4}$$

we have

$$\frac{-\pi\alpha}{[\alpha(V_{ec}-V_r)]^{3/2}}\frac{dV_r}{dt} = \xi \tag{3.5}$$

Now integrating both sides from times t = 0 to t = t

$$\xi t = \frac{2\pi}{\sqrt{\alpha}} \left(\frac{1}{\sqrt{V_{ec} - V_r(0)}} - \frac{1}{\sqrt{V_{ec} - V_r(t)}} \right)$$
(3.6)

Rearranging gives us a formula for the voltage applied to the ring electrodes as a function of time:

$$V_r(t) = V_{ec} - \left(\frac{2\pi\sqrt{V_{ec} - V_r(0)}}{2\pi - \xi t \sqrt{\alpha(V_{ec} - V_r(0))}}\right)^2$$
(3.7)

Equation 3.7 doesn't explicitly give us the most efficient trap raising pulse, but it does give us its form. It allows you to set an increase in the ring voltage over a specified length of time for which you

can solve for the constant ξ and then determine the remainder of the trap raising pulse curve. The amplitude and duration of the TRP are tuned alongside the evaporation pulse by taking cyclotron frequency measurements of ¹³³Cs and trying to maximize the depth of the ToF spectrum while keeping as many ions as possible. The TRP used for most of the measurements in this thesis kept roughly 60% of the ions in the trap. The pulse chosen was given an amplitude of 7.5 V over a duration of 2 ms, with a plateau for 200 μs where the evaporation pulse was applied.

Cleaning of nearby contaminants

Once the ring electrode is adiabatically lowered to its starting potential, we should have eliminated the higher energy ions from the trap and are ready to begin the measurement cycle. This begins with a dipole excitation at the modified cyclotron frequency of the species that we are trying to remove. The mass-dependence of the ω_+ motion allows us to increase the orbital radius of selected ions in the Penning trap to the point where they will collide with the endcap electrode upon ejection and not make it to the detector. This process is referred to as *cleaning* of contaminants. We have to be careful to avoid cleaning at frequencies too close to the wanted species ω_+ . If we clean too close we will give some initial energy to the wanted species prior to quadrupole excitation, leading to lower ToFs off of cyclotron resonance and possibly shifting the frequency at which the ions are most resonantly excited. This is dangerous and requires careful tuning. Using the SIS we make ToF measurements of ¹³³Cs while applying a dipole excitation at the ω_+ of ¹³³Cs for a length of 50 ms at some amplitude, AV. The value of A is chosen when no ions make it to the detector. Then the applied ω_+ is shifted by a number of Hz away from ¹³³Cs until the applied excitation has zero effect on the cyclotron resonance. This process is then repeated with a dipole pulse lasting 100 ms, and 200 ms at amplitudes of A/2, and A/4 respectively in order to determine what durations of time were needed to clean contaminants at various proximities to the wanted species without disturbing it. We found that a 50 ms dipole excitation at ω_+ was able to be used on contaminants with cyclotron frequencies 40 Hz or more away from the desired ion species. We saw effective scaling up to 400 ms where contaminants 5 Hz away could be removed from the trap. To find contaminants in a beam from CARIBU, a wide scan of possible cyclotron frequencies (see the next section) is carried out with no ω_{\pm} pulse applied. A ToF spectrum is recorded showing resonant cyclotron peaks of all species in the trap. The cyclotron frequencies are measured to a precision of roughly 0.1 Hz and the corresponding modified cyclotron frequencies are calculated and the experimenter chooses the appropriate duration

and amplitude required to remove all contaminants. The closest contaminant dictates the length of the cleaning pulse in the current system. If there are two contaminants found, say, 12 Hz and 45 Hz away from the desired nuclide, a cleaning of 200 ms is chosen for both contaminants. If this cleaning process is well configured, the desired ions will remain at the original trapping radius while the contaminants will be orbiting at significantly larger radii.

Increasing of radius by magnetron excitation

Recall from equation 2.22 that the magnetron motion is mass-independent and the frequency is a product of the characteristic trap dimensions, magnetic field, and potential difference between the ring and endcap electrodes. Immediately after the dipole ω_+ excitation has ended, another dipole excitation at ω_{-} is carried out where the radius of all remaining trapped ions are increased. The duration of this pulse is 10 ms. An increase in the magnetron motion radius can reduce the potential energy of the ions by approximately $5 \,\mathrm{eV}$ with a typical Penning trap setup [61]. Increasing the radius of the modified cyclotron motion has the opposite effect, the larger the radius of ω_{+} motion, the more radial kinetic energy the ions possess. Recall from section 2.2.2 that under complete conversion the resultant radius of the modified cyclotron motion is equal to the initial radius of the magnetron motion. Prior to ejection from the Penning trap we want the resonantly excited ions to have much more kinetic energy than the non-excited ions, such that the difference in ToF from the trap to the detector between the two cases is maximal. The largest possible magnetron radius gives us the largest possible modified cyclotron radius, providing maximized radial kinetic energy, which is transformed into linear kinetic energy once the ions leave the magnetic field giving the largest ToF difference between resonantly and non-resonantly excited ions. This allows for the most precise measurement of the cyclotron frequency. Too large a radius, however, and we run the risk of losing ions from contact with the Penning trap electrodes themselves. The dipole magnetron excitation also forces all of the trapped ions into the same radial plane, such that they all are exposed to the same magnetic field.

Quadrupole excitation

Finally a quadrupole excitation at a range of frequencies near the desired nuclide's cyclotron frequency are scanned through, one frequency per bunch of ions captured in the trap. If the applied frequency, $\omega_q = \omega_c$ then the ions will undergo conversion from magnetron to modified-cyclotron motion as described in Figure 2–6, gaining maximal radial energy and therefore reaching the detector with the shortest ToF. At other frequencies this conversion will not be complete resulting in a longer ToF. Durations of this pulse ranged from 50 ms to 4000 ms in this thesis. Part of the tuning procedure was determining the amplitude of the quadrupole pulse that would result in the complete conversion between eigenmotions. Equation 2.34 serves as a starting point for determining the amplitude required, but does not take into account the response of the electronics at the high frequencies we are applying. If double the conversion amplitude is applied at $\omega_q = \omega_c$, the motion of the ions will be converted from magnetron to modified cyclotron and back to magnetron frequencies. This means that on resonance the ions will be ejected with the same energies as ions far away from resonance. Again we use the SIS and vary the applied rf amplitude of the quadrupole excitation until we observe a ToF spectrum showing no resonance at ω_c . Half of this amplitude is therefore the one that will result in complete conversion. Since $V_{rf} \propto t_{rf}^{-1}$, longer excitation times will require smaller conversion amplitudes. This tuning process is usually repeated for a couple of excitation times to ensure that the chosen conversion amplitude scales with excitation time correctly.

This concludes the measurement process currently employed at the CPT. A nice way to summarize the journey of the ions from the buncher exit to detection is a series of pulse timing diagrams shown in Figures 3–11, 3–12. Starting with Figure 3–11 we show the pulses used to transfer ions from the buncher exit to capture in the Penning trap. The information flow in this diagram represents only a single bunch of ions captured in the linear trap. For the case of ¹⁵⁰Ba two shots were captured in the linear trap so the first four steps (CARIBU elevator through Paul trap capture) in this figure would be repeated before the delayed ejection occurs. Pulse lengths in this diagram are to scale except for the delay between the last capture in the linear trap to it's ejection which is 30 ms.



Figure 3–11: Transfer of ions from CARIBU to capture in the CPT. These specific time were used for the measurement of 150 Ba in this thesis. Note the change of time scale after the linear trap capture pulse.

The in-trap manipulation pulse scheme is shown in Figure 3–12. All pulse times are with respect to the CPT capture trigger.



Figure 3–12: Penning trap measurement cycle of 150 Ba with 80 ms cleaning, and 70 ms quadrupole excitation.

CHAPTER 4 Data analysis and mass results

With four parameters I can fit an elephant, and with five I can make him wiggle his trunk. [62] - John Von Neumann

With the ion transfer and fission fragment mass measurement process established we can discuss how an array of time-of-flights is used to establish an isotopes cyclotron frequency and mass. This chapter will first describe the fitting function used to determine the cyclotron frequency of a given ion species before discussing the mass measurement campaigns at the CPT conducted during this work. An emphasis on the calibration process will be made before finally discussing our results with respect to previous measurements.

4.1 Precision

Determining the precision for a Penning trap measurement depends most strongly on the number of ions detected N, and the excitation time t_{rf} . A study of ISOLTRAP measurements [45] has found that the relation between these two parameters and precision using the ToF-ICR technique is given by:

$$\frac{\delta m}{m} = \frac{\delta \omega_c}{\omega_c} \propto \frac{m}{qB} \frac{1}{t_{rf}\sqrt{N}} \tag{4.1}$$

So precision can be increased by using longer excitation times, by charge-breeding the ions during transport to the trap to increase q, by having a strong magnetic field, or simply by acquiring more statistics. Half-lifes put a strict limit on the duration of a useful measurement; q is restricted because ions leave CARIBU at charge states of +1 or +2; the magnetic field is fixed at roughly 5.7T; so while using the maximum t_{rf} that half-life and measurement duration allow, improved precision comes from detecting more ions, which means measurements of the weaker produced neutron-rich nuclides from CARIBU can take several hours. Recall from section 1.4 that the minimum relative mass precision required for astrophysical input is $\delta m/m = 10^{-7}$. This precision is reached when the statistical uncertainty on the cyclotron frequency is approximately 0.1 Hz.

4.2 Fitting Function

Once the contents of the Penning trap is ejected, the ions travel through varying magnetic and electric fields. Ideally we could calculate the exact time each ion takes to travel the distance from the middle of the trap to the channeltron detector. We *simply* need to know the energy of each ion as a function of position (from trap to detector), the mass of the ion, and the distance traveled. However the total energy comes from not only the initial axial energy E_0 , but also the energy lost due to the changing potential $E_1 = qV(z)$ that the ions see as they pass through the drift tube assembly towards the detector. We also must consider the potential energy originating from the magnetic $E_2 = -\mu \cdot \mathbf{B}$, where $\mu = E_r/B_0$ is the magnetic moment of the ions with a radial energy of E_r in the center of the trap where the magnetic field is B_0 , and $\mathbf{B} = B(z)\hat{z}$ is the magnetic field gradient between the trap and detector. The radial energy will not be a constant but for now we will just say that it will depend on the quadrupole frequency applied to the ions while in the trap ω_q . We now have the total energy of the ions as they travel the length of the ToF line: $E_{tot} = E_0 - qV(z) + E_r(\omega_q)B(z)/B_0$, and we can find the total time of flight by integrating from trap center at $z = z_0$ to the detector located at $z = z_1$:

$$t(\omega_q) = \int_{z_0}^{z_1} \sqrt{\frac{m}{2\left(E_0 - qV(z) + \frac{E_r(\omega_q)B(z)}{B_0}\right)}} dz$$
(4.2)

Of course calculating this integral requires that we know B(z), V(z), and $E_r(\omega_q)$ precisely at all times. Continuous measurement of these inputs is not feasible so we must establish a fitting function that will consistently and accurately determine the cyclotron frequency.

From a publication in 2011 by George $et \ al.$ [63] the cyclotron energy induced by a square enveloped excitation like the one we employ is given by:

$$E_r = \frac{e^{-2\gamma t_{rf}} \cdot 4g^2}{\sqrt{(4g^2 + \delta^2 - \tilde{\gamma}_1^2)^2 + 4\tilde{\gamma}_1^2\delta^2}} \left[\sin^2\left(\frac{\tilde{\omega}_R t_{rf}}{2}\right) + \sinh^2\left(\frac{\tilde{\gamma}_R t_{rf}}{2}\right)\right]$$
(4.3)

where δ is the difference between the applied frequency and the cyclotron frequency of the ions in the trap, γ is a damping coefficient, g is a coupling parameter proportional to the amplitude of the rf pulse, t_{rf} is the duration of the applied quadrupole excitation, $\omega_R = \sqrt{4g^2 + \delta^2}$ is the Rabi frequency which describes the oscillation between the two eigenmotions ω_- and ω_+ described in section 2.2, and the following shorthands have been used:

$$\tilde{\gamma}_1 \approx 2\gamma \frac{\omega_c}{\sqrt{\omega_c^2 - 2\omega_z^2}} \tag{4.4}$$

$$\tilde{\omega}_R = \frac{1}{\sqrt{2}} \sqrt{\sqrt{(\omega_R^2 - \tilde{\gamma}_1^2)^2 + 4\tilde{\gamma}_1^2 \delta^2} + \omega_R^2 - \tilde{\gamma}_1^2}$$
(4.5)

$$\tilde{\gamma}_R = \frac{1}{\sqrt{2}} \sqrt{\sqrt{(\omega_R^2 - \tilde{\gamma}_1^2)^2 + 4\tilde{\gamma}_1^2 \delta^2}} - \omega_R^2 + \tilde{\gamma}_1^2.$$
(4.6)

Also described in section 2.2 was the trapping condition: $\omega_c \gg \omega_z$. Equation 4.4 can then be further simplified to $\tilde{\gamma}_1 \approx 2\gamma$. It will also be convenient to define $g = \pi h/2$, and in terms of frequencies $\delta = 2\pi(\nu_i - \nu_c)$, where ν_i is the set of applied frequencies and ν_c is cyclotron frequency. With all of these substitutions we can write down our representation of the cyclotron energy in terms of our various fitting parameters and independent variable ν_i as:

$$E_{r}(\gamma, t_{rf}, h, \nu_{i}, \nu_{c}) = \frac{e^{-2\gamma t_{rf}} \cdot \pi^{2}h^{2}}{\sqrt{(\pi^{2}h^{2} + 4\pi^{2}(\nu_{i} - \nu_{c})^{2} - 4\gamma^{2})^{2} + 64\gamma^{2}\pi^{2}(\nu_{i} - \nu_{c})^{2}}} \times \left[\sin^{2}\left(\frac{t_{rf}}{2\sqrt{2}}\sqrt{\sqrt{(\pi^{2}h^{2} + 4\pi^{2}(\nu_{i} - \nu_{c})^{2} - 4\gamma^{2})^{2} + 64\gamma^{2}\pi^{2}(\nu_{i} - \nu_{c})^{2}} + \pi^{2}h^{2} + 4\pi^{2}(\nu_{i} - \nu_{c})^{2} - 4\gamma^{2}}\right) + \sinh^{2}\left(\frac{t_{rf}}{2\sqrt{2}}\sqrt{\sqrt{(\pi^{2}h^{2} + 4\pi^{2}(\nu_{i} - \nu_{c})^{2} - 4\gamma^{2})^{2} + 64\gamma^{2}\pi^{2}(\nu_{i} - \nu_{c})^{2}} - \pi^{2}h^{2} - 4\pi^{2}(\nu_{i} - \nu_{c})^{2} + 4\gamma^{2}}\right)\right]$$

$$(4.7)$$

On resonance, when $\nu_i = \nu_c$, equation 4.7 simplifies to

$$E_{r,0}(\gamma, t_{rf}, h) = \frac{e^{-2\gamma t_{rf}} \cdot \pi^2 h^2}{\pi^2 h^2 - 4\gamma^2} \sin^2\left(\frac{t_{rf}}{2}\sqrt{\pi^2 h^2 - 4\gamma^2}\right)$$
(4.8)

Now that we have some approximation of radial energy imparted onto the ions during rf quadrupole excitation, we can begin to create a ToF approximation meant to compensate for all of the unknowns in equation 4.2. This derivation was initially completed by former CPT graduate students Shane Caldwell and Jon Van Schelt.

We start by breaking up the total energy of the ions after ejection into a *baseline* energy, E_b , which would describe the energy of the ions if no excitation were applied, and a radial energy term describing the energy given to the ions during excitation, E_r . It follows that the total time of flight, t_{tof} obeys the relation:

$$\frac{1}{t_{tof}^2} \propto E_b + E_r. \tag{4.9}$$

Simply rearranging 4.9 gives us:

$$t_{tof} \propto \frac{1}{\sqrt{E_b \left(1 + \frac{E_r}{E_b}\right)}} \tag{4.10}$$

When no radial energy is induced we demand the time-of-flight be a certain baseline time, b. Enforcing this boundary condition leaves us with the equality:

$$t_{tof} = \frac{b}{\sqrt{1 + \frac{E_r}{E_b}}}.$$
(4.11)

Since we do not have any exact knowledge of the value of the baseline energy E_b we can rewrite it in terms of known or adjustable parameters. When the applied quadrupole frequency is equal to the cyclotron frequency, the ions will have maximal energy and will therefore reach the detector in the shortest amount of time. So at $E_r = E_{r0}$ the time of flight is at a minimum, $t_{tof} = b - d$ where d is the *depth* of the spectrum.

Subbing these two constraints into equation 4.10:

$$b - d = \frac{b}{\sqrt{1 + \frac{E_{r,0}}{E_b}}}.$$
(4.12)

Rearranging gives us a relation for the baseline energy in terms of physical parameters b and a which we can fit

$$\frac{1}{E_b} = \frac{1}{E_{r,0}} \left[\left(\frac{b}{b-d} \right)^2 - 1 \right]$$
(4.13)

Substituting this into equation 4.10 gives,

$$t_{tof} = \frac{b}{\sqrt{1 + \frac{E_r}{E_{r,0}} \left[\left(\frac{b}{b-d}\right)^2 - 1 \right]}}$$
(4.14)

The resultant equation gives the *true* time of flight, and not the time that is recorded in file. There is a measurable delay that exists between the ejection of ions from the Penning trap and the initialization of the the MCS recording the time of flight to file. We incorporate this delay into the fitting function by inserting a parameter s with units of time. We will denote the parameters recorded in file using primed coordinates: t'_{tof} , b'. The *true* baseline and total ToF in terms of the primed coordinates is then b = b' + s, and $t_{tof} = t'_{tof} + s$ respectively. The depth d, which is just given by the baseline minus the minimum in ToF value at the centroid of the fit, remains the same in both the *true* and recorded data sets since we are adding a constant s to both the baseline and the total ToF:

$$t'_{tof} = \frac{b' + s}{\sqrt{1 + \frac{E_r}{E_{r,0}} \left[\left(\frac{b' + s}{b' + s - d} \right)^2 - 1 \right]}} - s$$
(4.15)

If exactly one species of ions is present in the trap, such is the case when using an offline stable ion source, this equation is sufficient. But when contaminant ions are present in the trap we need to excogitate what effect the non-excited ions will have on the ToF spectrum. Lets say that we have two species of ions in the trap, A and B, and we wish to measure A. When the applied quadrupole frequency on the ring electrodes is equal to the cyclotron frequency of A, ω_{c_A} , the ions A will receive a maximal increase in rotational energy while species B will either receive no increase or will see an increase not exceeding species A depending on the mass of A relative to B. Once ejected, A will travel to the detector and the difference in ToF between the baseline far from resonance and on resonance will be the same as if A was the only species in the trap. However B will also be ejected at the same time but will reach the detector with ToF similar to the non-excited ions of A. The value of ToF that will be recorded to file will be the average of these two ToFs. If the number of A ions is equal to the number of B ions, the apparent depth of the spectrum will be half of which we would expect for a pure cloud of ions in the trap. To account for this we would need to be able to tag ions of A and B and eliminate any B from the spectrum. One could imagine only selecting the first ions which hit the detector for the region of frequencies in close proximity to the cyclotron frequency which should be solely A; while keeping all other data, since the species A and B should have the same baseline energy away from resonance. When attempting this sort of analysis we find that it is difficult to make objective ToF cuts without incorporating bias into the data. Figure 4–1a shows a plot of the number of counts recorded at every frequency and value of ToF measured for ¹³³Cs where the shape of the resonance is clear. When examining ions from CARIBU the spectra quickly become more chaotic once there is more than one particular species in the trap. Figures 4–1b and 4–1c show the data collected for $^{165}\mathrm{Gd}$ and $^{162}\mathrm{Sm}.$

For the *clean* ¹³³Cs file one could imagine making subjective ToF cuts at different frequencies without losing any sleep over guilt from inducing bias into the fit. There are three distinct frequency groupings in Figure 4–1a: namely the two sidebands roughly defined by frequency channels 0-14, and 27-44; and the centroid zone from channels 15-26. It is reasonable to only include data on the sidebands that was recorded between, say, $125 \,\mu s$ and $200 \,\mu s$ and in the centroid area between $105 \,\mu s$ and $150 \,\mu s$



Figure 4–1: Comparison of ToF data collected between pure and contaminated trap inhabitants

without the loss of any information. And in fact since the vast majority of the data is included, this fit produces accurate results. Attempting this same procedure for the ¹⁶⁵Gd file still seems possible in that we could define our three zones by channels 0-42, 43-58, and 59-71. In this example in the centroid zone there is a clear gap between the ¹⁶⁵Gd ions that were resonantly excited and those that were not and came out with the baseline energy of the sidebands. One could make ToF cuts of $105-150 \,\mu s$ for each sideband and $65-105 \,\mu s$ for the centroid region and produce an accurate fit. However this same procedure becomes more subjective and quickly dissolves into "guess and check" until a visually pleasing fit is found for measurements such as ¹⁶²Sm as shown in Figure 4–1c. Until a more algorithmic approach to the separation of wanted and unwanted ions is established, the fitting function described in this section will continue to be used for averaged ToF data recorded to file. The reduction of the depth due to the averaging of ToFs in the centroid region when contamination is present can be characterized by hand-placing another parameter, n, into the ToF function which stands to represent the percentage of ions excited at resonance. This parameter will be allowed to vary between n = 0 and n = 1. The final ToF fitting function is given by equation 4.16:

$$t'_{tof} = (b'+s) \left(1 - n + \frac{n}{\sqrt{1 + \frac{E_r}{E_{r,0}} \left[\left(\frac{b'+s}{b'+s-d}\right)^2 - 1 \right]}} \right) - s$$
(4.16)

such that when n = 1 equation 4.15 is reproduced. The frequency and quadrupole excitation dependence are included in E_r and $E_{r,0}$, given by equations 4.7 and 4.8 respectively. Note that this function is only reliable when one resonant peak is produced. In cases where two or more masses are measured in the same window (e.g. when both isomer and ground states are measured) a trivial generalization of equation 4.16 is used. This function is explicitly shown in Appendix A.

Now that a fitting function is established with parameters ν_c , γ , b', s, d, t, h, and n ready to be fit we may move on to the measurements made in this thesis.

4.3 Measurement campaigns

4.3.1 Prerequisite measurements

The only physical parameter we measure directly in the ToF-ICR technique is the time of flight from trap to detector of ions over a range of applied quadrupole frequencies. To transform these ToF's into a mass we need to do two things: we must fit the ToF spectra to determine the cyclotron frequency; and we must convert these cyclotron frequencies into a mass. Each of these steps requires a different calibration procedure during offline analysis. For masses in this thesis there were two mass-to-charge ratio regimes studied: $A/q \approx 75$ and $A/q \approx 133$ corresponding to the heavy peak 2+ ions, and 1+ ions respectively. Due to the difference in cyclotron frequencies between these two regimes different measurement parameters are used. Specifically, the TRP and evaporation pulses were different as was the amplitude of applied quadrupole excitation required to obtain full conversion between magnetron and modified cyclotron motions. The mass difference results in ToF spectra with different baselines, and ToF depths. In order to accurately measure the cyclotron frequency using the ToF function given in equation 4.16, we must fix a number of parameters in the fitting function by repeatedly taking precise measurements of some reference ion using one of the two sets of measurement parameters. For 1+ ions with $\nu_c \approx 600 \,\mathrm{kHz}$, we use ¹³³Cs⁺, and for the heavy fission peak 2+ ions with $\nu_c \approx 1 \,\mathrm{MHz}$, we typically use a hydrocarbon originating from CARIBU such as $C_6H_4^+$. Unfortunately, in this work we were unable to definitively isolate $C_6H_4^+$. Instead we conducted repeatable measurements of some molecule which has yet to be identified in the vicinity of $C_6H_4^+$. I will denote this ion as ⁷⁶X for the remainder of this thesis. Either $^{133}Cs^+$ or ^{76}X will be used to establish fitting parameters to determine all cyclotron frequencies given in this chapter.

The next necessity is to convert the cyclotron frequency into mass. Recall the cyclotron frequency is given by:

$$\nu_c = \frac{qB}{2\pi m} \tag{4.17}$$

where m is the mass of the ion with charge state q. If we knew the magnetic field to the precision we wish to find m, we could just apply this equation as it is. We can eliminate the need for knowing Bif we use ratios of cyclotron frequencies of the unknown mass (m_a) and a well-known mass (m_b) :

$$m_a = \frac{q_a m_b \nu_b}{q_b \nu_a} + q_a m_{e^-} \tag{4.18}$$

where $m_{e^-} = 548.579909067(14) \,\mu u$ [16] is the electron mass. The statistical mass uncertainty can then be found in the usual way as:

$$\delta_{m_a} = \sqrt{\left(\frac{q_a \nu_b}{q_b \nu_a}\right)^2 \delta_{m_b}^2 + \left(\frac{q_a m_b}{q_b \nu_a}\right)^2 \delta_{\nu_b}^2 + \left(\frac{q_a m_b \nu_b}{q_b \nu_a^2}\right)^2 \delta_{\nu_a}^2 + q_a^2 \delta_{m_{e^-}}^2}$$
(4.19)

The $\delta_{m_{e^-}}$ term in equation 4.19 is negligible but is left for completeness. Since the ion ⁷⁶X has not been explicitly identified we cannot use it as m_b in equation 4.18. Instead ¹³³Cs⁺ is used to determine the mass of all nuclides in this thesis. This may lead to systematic uncertainties in the mass determination which is further discussed in section 4.5.1. To eliminate any excitation duration influence on the mass calculation, measurements with similar values of t_{rf} are compared. Determination of the mass of ¹⁵⁰Ba for instance, which was measured using a 70 ms excitation, was completed using a 70 ms excitation of ¹³³Cs. There is one exception in this work in which the mass of a 4000 ms excitation of ¹⁴⁶La^{g,m} was carried out using a 500 ms excitation of ¹³³Cs. This systematic uncertainty will also be discussed.

4.3.2 List of experiments

To minimize the effect of fluctuations in magnetic field at the trap center (see Section 4.5.3) measurements made at CARIBU were quickly followed by measurements of a calibration source to determine a set of fitting parameters. These calibration measurements were done with the same steering, timing, and frequency settings as to reduce the systematic uncertainties as much as possible. For masses presented in this thesis four short measurement-calibration experimental runs were carried out.

Experiment I: Starting in the fall of 2013 from September 5-16 successful measurements of ${}^{134}I^{m,g}$, ${}^{142}I$ were carried out; followed by a set of calibration data from our stable ion source of ${}^{133}Cs^+$ from September 19-22.

We then carried out two successive measurements of 2+ ions.

Experiment II: On September 23 and 24 148,149,150 Ba were measured, followed by a measurement of 76 X on September 24.

Experiment III: From September 25-28 measurements of ¹⁶⁵Gd, ^{162,164}Eu, and ¹⁶²Sm were made,

calibrating with another measurement of 76 X on September 28 and 29.

Experiment IV During October 2-4 we attempted to measure some of the light peak fission fragments. This was just the second attempt at mass measurements from the light peak at CARIBU, the goal being to test the efficiency of transport of these lighter ions and to see which isotopes were delivered at charge states of 1+ and 2+. At the time, the CARIBU gas catcher was not completely optimized to transport these light ions, and measurements of light peak neutron-rich nuclides far from stability proved difficult. Nevertheless, measurements of 95 Sr, 106 Mo, and 106 Tc were made. These had all been measured previously at different experiments but we took the opportunity to compare ourselves with these measurements with 133 Cs used as a calibration over the next three days. Finally a measurement of 146 La^{g,m} was made on November 15 with a measurement of 127 I·CH₃ the next day as a mass determination calibrant.

4.4 Choice of fitting parameters

In section 4.2 I have established the fitting function and introduced all of the parameters used to determine the cyclotron frequency and thus mass of a specific isotope. I also briefly introduced the problem of determining which data to keep when creating ToF spectra. In this section I will attempt to clarify and justify all steps on the path to determining the cyclotron frequency from the ToF-ICR technique, as well as show an example where the calibration files are used to establish fitting parameters for measurements made at CARIBU. Our data files consist of averaged t'_{tof} values at each frequency step, with corresponding uncertainties given by the standard error. All fits will be made by χ^2 minimization using the Levenberg-Marquardt algorithm.

4.4.1 Time-of-flight cuts

Nuclides studied in this thesis have mass number-to-charge ratios ranging from 74 to 146, and all data taken during this experimental period was completed with the same MCS scaling factor of 1 channel equal to $1 \mu s$. This allows us to objectively determine time-of-flight cuts for all data files. Looking at the number of counts recorded at each MCS channel for nuclides where we have a good understanding of all species in the trap we can come up with a relation between upper and lower TOF cuts and A/q ratios. In Figure 4–2a we see the *entire ToF spectrum*, a histogram for ¹³³Cs showing the number of counts recorded for each μs . Between the red dashed lines is the data that will be used to make a spectrum of the ToF as a function of applied quadrupole frequency as shown in Figure 4–2b that is used to determine the cyclotron frequency.



Figure 4–2: ToF cut for a high statistics measurement of the cyclotron frequency of $^{133}Cs^+$ and the resulting ToF spectrum.

The ToF spectra for ¹³³Cs has been the cleanest spectra attainable at the CPT. Compare this to a particularly ugly ToF histogram for the short-lived ¹⁵⁰Ba in Figure 4–3a. In order to observe ¹⁵⁰Ba -with a half-life of 300 ms and a fission branch of 3.27×10^{-4} a number of nearby more abundant contaminants had to be cleaned out using appropriate ω_{\pm} dipole excitations (as discussed in section 3.3.1) including ¹⁵⁰La, ¹⁵⁰Ce, ¹⁵⁰Nd, ¹⁵⁰Pr, as well as four other unknown contaminants with mass 150. The noise in this spectrum is difficult to explicitly identify but a few sources are possible. Due to the short half-life of ¹⁵⁰Ba, the cleaning cycle could only be run for 80 ms. With this short an excitation, it is possible that some of these contaminants were not being completely eliminated from the trap and were ejected with more energy than the sought after barium and thus being detected at short times. This would create a peak on the ToF spectrum at smaller times, possibly around the $t \approx 20 \,\mu s$ or $t \approx 45 \,\mu s$ peaks. We also must deal with β^- decay of the short-lived trapped species, in this case ${}^{150}\text{Ba} \rightarrow {}^{150}\text{La} + e^-$; the lanthanum could be given a kick and come out faster than any remaining ¹⁵⁰Ba, adding to the short ToF peaks. The point is that looking at ToF spectra similar to that of Figure 4–3a make it impossible to objectively pick ToF cuts containing the wanted species. Ideal candidates for the ToF cut determination will be those with *clean* ToF spectra. This means minimal cleaning to avoid an excess of low ToF counts, long-lived ions to avoid any β^- decay, and large fission branch yields in order to increase the signal-to-noise ratio in this spectrum. Besides



Figure 4–3: The effect of ToF cuts as described in this section when applied to the neutronrich short-lived ¹⁵⁰Ba²⁺ ion. The result of no ToF cut and the scaled ToF cut are shown as reflected by the ToF as a function of applied ω_q spectra.

the obvious candidate of ¹³³Cs –which is stable and comes from an offline source, so no cleaning is required– the radioactive nuclides ¹⁴⁴Cs, ¹⁰⁶Mo, and ⁹³Rb from CARIBU were chosen. These ToF cuts are shown in Figure 4–4. The linear relationships are given by: $ToF_{low} = 0.77A/q + 7.86$ and $ToF_{high} = 0.87A/q + 84.97$. These dictate the ToF cuts used for all measurements in this thesis.



Figure 4–4: Fit to upper and lower ToF bounds for well-measured masses. This allows us to objectively determine ToF cuts for all measured species with mass-to-charge ratio of A/q.

An example of the importance of using this method to choose ToF cuts is given in Figure 4–3. If we include the entire ToF histogram in Figure 4–3a we create the ToF spectrum in Figure 4–3b which does not show any sign of resonance at the expected value of ω_c of ¹⁵⁰Ba. Applying the ToF cuts and keeping only the blue data in Figure 4–3a we achieve the spectrum in Figure 4–3c.

4.4.2 Portion of ions excited n

The only case where we are certain of the identification of all the ions in the trap is when we take measurements of 133 Cs from our offline stable ion source. For this isotope only, the value of n is set equal to 1.0. This allows us to determine an absolute depth given a pure set of ions. For all radioactive isotopes from CARIBU n was allowed to vary between zero and one. A difficulty arose during the analysis of the 2+ ions from CARIBU where we generally use the hydrocarbon $C_6H_4^+$ as a calibrant since it has a similar A/q value to the ions from the heavy fission peak, and therefore a similar ω_c , and has an extremely precisely known mass. To make high precision measurements of $C_6H_4^+$, a number of nearby contaminants had to be cleaned so it is difficult to assess whether a value of n=1 is appropriate for these sets of calibration data. In fact a low statistics activity scan at A=146and q = 2+ was done with no cleaning where ¹⁴⁶Ba, ¹⁴⁶La, and ¹⁴⁶Ce were simultaneously measured. The sum of the depths of the three spectra was greater than the depth of the $C_6H_4^+$ spectra implying that our calibrant hydrocarbon was not strictly the only species in the trap during the measurement. The solution to this is fixing n at a few values close to one, then finding the value of d, s, and h to be fixed for other data from CARIBU. We can then let n vary freely for the 2+ ions while fixing the scaled values of d, s, and h. We know that we have found a satisfactory value of n for the calibration files when the value of n from the least-squares fit for unknown species is less than 1.0.

4.4.3 Excitation time, t_{rf}

When first fitting the ToF spectra of ¹³³Cs all parameters are allowed to vary. The uncertainty in the applied duration of quadrupole excitation time is well under the standard error of other parameters in the fitting function since the duration is set by the Jorway 221 (discussed briefly in section 3.3) which has timing resolution better than $1 \mu s$. It was evident for excitation times less than 250 ms that the value of t_{rf} that best described the data was not exactly the length of time that the ring electrodes applied the quadrupole excitation for. An example is shown in Figure 4–5 for a 50 ms excitation of ¹³³Cs where the data is fit using equation 4.16 with fixed values of $t_{rf} = 50 ms$ in Figure 4–5a and $t_{rf} = 46 ms$ in Figure 4–5b.

Notice the difference in the precision of the fitted centroid frequency and the value of the reduced χ^2 between these two figures. All available 50 ms files showed this same ostensible difference in expected t_{rf} . Because of this dramatic improvement of the fit to the data, $t_{rf} = 46 \text{ ms}$ was taken to be fact for



(a) ToF spectrum fit with a fixed value of t_{rf} = 50 ms
(b) ToF spectrum fit with a fixed value of t_{rf} = 46 ms
Figure 4–5: A look at the difference in the quality of the fit between fixed t_{rf} values of 50 ms and 46 ms.

all other 50 ms files in this thesis. Similar behaviour was seen at excitation times of 70 ms, 100 ms, and 200 ms where the *actual* value of t_{rf} was fixed at 66 ms, 97 ms, and 197 ms respectively.

4.4.4 Depth of spectra, d

As mentioned previously, the depth of spectra is an important parameter which gives us information about the quality of a measurement. It allows us to judge the effectiveness of cleaning nearby contaminants while the measurement is taking place, and it allows us to estimate the number of ions of a particular isotope reaching the detector giving us a sense of the overall transportation efficiency. During the initial tuning process, one of the goals is to maximize the depth using ¹³³Cs. Larger depth values gives us more precise measurements in a shorter amount of time. We have observed consistently through previous measurements at the CPT [54], [53] as well as in this work, that the depth of the spectra is not independent of t_{rf} . It follows a linear relationship out to at least $t_{rf} = 4000 \, ms$. It is possible that at longer excitation times the ions lose energy through interaction with other ions in the trap and thus when ejected take longer to reach the detector. The necessity to not *skip shots*, as discussed in section 3.3, requires that large numbers of shots be captured in the Paul trap when t_{rf} is large, meaning that there is potential for a large number of ions to be in the Penning trap at once. We attempt to avoid this by either steering away some of the ions well before the Paul trap such that each shot accumulates only a few ions, or by decreasing the rf voltage applied to the cone of the gas catcher. But a 4s excitation still requires that all of the ions spend 4s in the trap giving the ions more time to interact with each other. The determination of d for experiment I is shown in Figure 4–6. For experiment I we find $d = -2.7t_{rf} + 47.9$ where t_{rf} is in units of seconds, while the depth is given in units of μ s. A similar procedure was followed for experiments II, III, and IV, and the results are given in Table 4–2. Experiment II showed no significant correlation between depth and excitation time, rather remained constant within uncertainty across all three calibration measurements.



Figure 4–6: The depth of ToF spectra as a function of the duration of the quadrupole excitation, t_{rf} , for ¹³³Cs⁺ ions. This was the calibration data taken during experiment I.

4.4.5 Degree of conversion factor, h

From George *et al* [63], we know the time to convert between ω_{-} and ω_{+} is given by:

$$t_{conv} = \frac{2}{\sqrt{4g^2 - \tilde{\gamma}_1^2}} \operatorname{arccot}\left(\frac{2\gamma}{\sqrt{4g^2 - \tilde{\gamma}_1^2}}\right)$$

where γ is the damping constant, $\tilde{\gamma_1} \approx 2\gamma \omega_c / \sqrt{\omega_c^2 - 2\omega_z^2}$, and g is a coupling parameter proportional to the applied rf amplitude. If we take the undamped case we find $t_{conv} = \pi/2g \equiv 1/h$. If we are not applying the quadrupole excitation with the ideal amplitude V_{rf} (recall section 2.2.2), we do not find $t_{conv} = t_{rf}$. However, since for any given experiment we use the same scaled amplitudes we are able to plot ht_{rf} as a function of t_{rf} and obtain a number which gives us a sense of the quality of our conversion. This will allow us to fix h for the rest of the measurements carried out during the experiment. Figure 4–7 shows the result of h determination during experiment I. Where more than one measurement was taken for a given t_{rf} the weighted average is used. The uncertainty on t_{rf} is much smaller than the data points represented here.



Figure 4–7: Determination of the excitation time dependence of h. The red band shows the weighted average and uncertainty of ht_{rf} .

For experiment I, $ht_{rf} = 0.83(1)$. Since ht_{rf} is significantly less than 1.0 we know that for future experiments we should take more time in tuning the conversion between magnetron and modified cyclotron motions. Experiments II and III showed very good conversion between the two motions, while experiment IV showed similar results as experiment I.

4.4.6 MCS delay parameter s

As discussed in section 4.2 the hand-placed parameter s represents a read-out delay that exists between the Penning trap ejection signal and the trigger signal to the MCS. A peculiar facet of the fitting function is that when allowing s to vary, the best fit is always achieved when s < 0. A typical value for singly charged ions is $s \approx -75 \,\mu s$ which suggests that the MCS is triggered 75 μ s before the ions are ejected from the trap. If this were accurate, and it was simply a problem with the pulse timing in our system, we would expect to see exactly zero ions hit the detector before 75 μ s since they are still trapped in the Penning trap. This is not the case for many measurements. The unphysical nature of s is likely due to the relative physical simplicity of our fitting function. Distinct measurements also elicit different values of s, which should at least remain a constant for a particular nuclide. Instead, a strong correlation with excitation time t_{rf} is observed. Experiments I and IV included measurements over a wide range of excitation times. The variation in s over the broad range of times examined in experiment I is given in Figure 4–8.

With the typical uncertainties on s, there is no clear trend when measuring with excitation times less than 1000 ms. Experiments II and III all consist of fast cycles due to half-life limitations, so a



Figure 4–8: For experiment I, the value of s is plotted against excitation time for a number of different ${}^{133}Cs^+$ calibration files.

constant value of s was discerned from the limited number of data points. For these two experiments –which involved the cyclotron frequencies on the order of 1 MHz– study of our unknown calibrant ⁷⁶X yielded values of $s = -35.2 \,\mu$ s, and $s = -45.0 \,\mu$ s respectively.

4.5 Systematic uncertainties

Complete understanding of the measurement device should always be of equal importance to understanding the physics ingrained in any scientific data. In order to report masses with any confidence we must consider any quirks and biases in the CPT system which might have had some effect on the data collected.

4.5.1 Influence of calibrant on ω_c determination

Masses in this thesis were calculated by using the known mass and measured cyclotron frequency of 133 Cs. The heavy doubly charged nuclides measured have much different A/q ratios than our calibrant, so the possibility of the cyclotron frequency at different A/q regimes being shifted is a systematic effect which we must consider. Table 4–1 summarizes the differences between the measured cyclotron frequencies of four accurately-known masses, and the expected cyclotron frequencies scaled from the measured frequency of 133 Cs.

One of the most prominent contaminants in the system is a stable molecule made up of 127 I and CH₃. Further proof of the presence of 127 I in the system was the measurement of 127 I·H. While these molecules have not been explicitly measured in previous experiments, their constituents have very precisely known masses. A measurement of 93 Rb was made at ISOLTRAP in 2002 [64], and 146 Ba²⁺

Ion	Mass from AME12 (μu)							
$^{133}Cs^+$	$132 \ 904903.381(9)$							
	Mass from AME12 (μu)	Measured ω_c (Hz)	Expected ω_c (Hz)	$\Delta\omega_c \ ({\rm Hz})$				
127 I·CH ₃ ⁺	$141 \ 927398(4)$	620981.47(2)	620981.46(2)	0.02(2)				
127 I·H ⁺	$127 \ 912297(4)$	689024.11(4)	689024.14(2)	-0.04(4)				
$^{93}\mathrm{Rb}^+$	$92 \ 922039(8)$	948481.04(4)	948481.20(8)	-0.17(9)				
$^{146}Ba^{2+}$	$145 \ 929186(22)$	1207904.56(4)	1207904.81(9)	-0.25(9)				

Table 4–1: Data used to determine the adjusted cyclotron frequency due to the mass difference between the measured nuclides and 133 Cs.

was measured with the CPT in 2006 [65]. When the $\Delta \omega_c$ discrepancies of these four ions are plotted as a function of A/q we observe a linear trend. Figure 4–9 shows the result of fitting these data points to a line with the requirement that at A/q = 133, $\Delta \omega_c = 0$. The fitted slope was a = 0.0038(5) Hz/u.



Figure 4–9: Adjusted ω_c from well-known masses and ¹³³Cs calibrations.

We find a mass-dependent shift in the cyclotron frequency given by:

$$\omega_{c_{adj}} = \omega_{c_{meas}} - 0.0038(A/q - 133) \tag{4.20}$$

where $\omega_{c_{meas}}$ is the cyclotron frequency found from fitting the ToF spectrum for each nuclide and $\omega_{c_{adj}}$ is the adjusted cyclotron frequency that will be used to determine the mass of the nuclide.

Such an adjustment leads to the addition of a systematic uncertainty originating from the quality of the fit in Figure 4–9:

$$\delta\omega_{c_{adj}} = \sqrt{\delta\omega_{c_{meas}}^2 + (A/q - 133)^2 \delta a^2} \tag{4.21}$$

where δa is the uncertainty in the adjustment factor a.

4.5.2 Influence of reference mass t_{rf} on mass calculation

As mentioned earlier, the lack of a $t_{rf} = 4000 \,\mathrm{ms}$ calibration of ¹³³Cs during experiment IV forced the use of a $t_{rf} = 500 \,\mathrm{ms}$ cyclotron frequency to determine the mass of ¹⁴⁶La^{m,g}. Since for all other nuclides in this work the mass was determined using the same excitation time for both the reference and unknown measurements, this possible systematic effect should be considered. Using experiment I values of ω_c for ¹³³Cs across a number of excitation times, we can calculate the mass of the ground and excited states of ¹³⁴I outlined later in this chapter. This is shown in figures 4–10a and 4–10b. Although the calculated masses seem to converge as t_{rf} increases, the values determined using a 500 ms excitation and a 4000 ms one are equal within statistical uncertainty. More precisely, differences of 0.8(2.2) amu and 0.8(6.5) amu were found for excited and ground states respectively.



Figure 4–10: Weighted average of the measured neutral masses of 134 I^{m,g} calculated using 133 Cs cyclotron frequencies found at several different excitation times during experiment I.

This systematic effect can thus be ignored.

4.5.3 Magnetic field drift

In order to characterize the stability of the magnetic field which the trap lies in, we can look for any temporal shifts in the cyclotron frequency of ¹³³Cs from our offline stable ion source. Measurements over the course of three months are shown in Figure 4–11. The jumps in frequencies seen at 30 days and again at 70 days are due to a combination of changing the steering of ions into the trap and re-tuning of biases applied to the correction tubes of the Penning trap. We typically observed these shifts in frequency domains between calibration data sets since when we are taking beam from CARIBU, subtle tuning adjustments are often required in order to maximize transport and trapping

efficiency. Then the settings used for CARIBU beam are always kept for the following calibration run to minimize systematic biases.



Figure 4–11: Values of ν_c for ¹³³Cs over the course of about three months for a few different excitation times

The stability of ν_c measurements under the same set of parameters over the course of 30 days is shown in Figrue 4–12a. We observe an average frequency increase 0.23(5) mHz per day, which equates to a small magnetic field change of 3×10^{-10} T per day. These measurements were made about a month before we started taking beam from CARIBU. Immediately following experiment I, a large number of calibration measurements were taken to again characterize any magnetic field shift. Figure 4–12b shows the cyclotron frequency measurements over about 100 hours. The average hourly increase was $34(45) \mu$ Hz, which is slightly more variation than was observed over the 30 day period prior to any measurements at CARIBU. The combination of the hourly increase being smaller than the uncertainty in the fit and the long term magnetic field drift of less than 1 ppb allow us to largely ignore the magnetic field uncertainty in the cyclotron frequency determination. The statistical and mass-dependent cyclotron frequency shift uncertainties dominate all measurements.

4.6 Results

A summary of the fitting parameters used to determine the cyclotron frequency for each nuclide in a particular experiment is given in Table 4–2.



(b) Short term stability during experiment 1

Figure 4–12: Measured values of the cyclotron frequency of 133 Cs over time for two different periods. Any drift is due to small changes in the magnetic field in the center of the trap.

Table 4–2: Summary of calibration fitting parameters for each measurement campaign undertaken in this thesis. In this table t_{rf} is in units of s.

Experiment	Calibrant	$d(t_{rf})$ (µs)	$ht_{rf} \ (\mu s)$	$s(t_{rf})$ (µs)	n	Measured Nuclides
I II III IV a	$^{133}Cs^+$ $^{76}X^+$ $^{76}X^+$ $^{133}Cs^+$	$\begin{array}{r} -2.7t_{rf}+47.9\\ 28.0\\ -10.1t_{rf}+28.9\\ -1.5t_{rf}+34.4\end{array}$	$\begin{array}{c} 0.83 \\ 0.983 \\ 1.02 \\ 0.83 \end{array}$	$-3.8t_{rf} - 67.5 \\ -35.2 \\ -45.0 \\ -72.7$	$1.0 \\ 0.8 \\ 0.8 \\ 1.0$	${}^{134}I^{m,g}, {}^{142}I$ ${}^{148,149,150}Ba$ ${}^{162,164}Eu, {}^{162}Sm, {}^{165}Gd$ ${}^{95}Sr, {}^{106}Mo,$ ${}^{106}Tc, {}^{146}La^{g,m}$

^a Due to large A/q difference between calibrant and measured nuclides, d and h were allowed to vary for light peak nuclides

Experiment IV has a caveat in terms of the parameters used to find the cyclotron frequencies of ⁹⁵Sr, ¹⁰⁶Mo, and ¹⁰⁶Tc. These measurements were completed using the same conversion amplitude as was used for ¹³³Cs. Due to mass differences of 27 and 38, we cannot assume the same degree of conversion between the calibrant data and measured nuclides. In fact we have to assume smaller values of ht_{rf} . Similarly the spectrum depth is representative of completely converted mass A = 133 ions which cannot be identical to the depths of mass A = 95,106 ions. Because of a lack of suitable calibrant for the light fission peak nuclides at this moment, the d and h parameters were allowed to vary when determining the cyclotron frequencies for these three ions. For the measurement of $^{146}La^{m,g}$, however, the parameters were applicable due to the relatively small mass difference of 13. For the three light peak ions, the values given in Table 4–2 were used as maximum allowed values when performing the fit. The effect on the fitted cyclotron frequency for 95 Sr when allowing the parameters d and h to vary is shown in Figure 4–13.



Figure 4–13: Systematic uncertainty in finding the cyclotron frequency, resulting from the lack of suitable calibrant to determine the value of d and h fitting parameters for the measurement of 95 Sr in experiment IV.

Both figures show a linear correlation between the fixed value of d, h, and the resultant cyclotron frequency. However, both procedures give a systematic uncertainty on ν_c of approximately 0.0003 Hz, much smaller than the statistical uncertainty of 0.013 Hz and the uncertainty due to the mass difference between 95 Sr and 133 Cs of 0.019 Hz. So any mass-influencing effect relating to the variance of d and h in experiment IV can be easily neglected. This is possible for the three measurements of light fission peak nuclides given in this thesis since they all had high enough fission branches and long enough lifetimes in order for *clean* measurements to be made with the CPT. More exotic light peak nuclides measured at the CPT in the future will require a calibrant ion with mass-to-charge ratio in the vicinity of A = 100.

With the fitting parameters in Table 4–2 we can now fit the ToF spectra and determine the cyclotron frequencies. Using the adjusted frequency given by equation 4.20, and the mass and appropriate cyclotron frequency of 133 Cs, we can determine the mass of our targeted isotopes. There were many cases where more than one measurement of a specific isotope was taken. For nuclides such as 142 I and 164 Eu where ω_c was found multiple times using the same excitation duration, a weighted average of the cyclotron frequency was calculated and used to determine the mass. In cases such as 162 Sm and

¹⁶²Eu where ω_c was found using multiple excitation durations a mass was found for each file using the a calibration measurement with the corresponding value of t_{rf} . A weighted average of these distinct mass measurements was then taken to determine the final mass.

A summary of determined isotopic masses in the form of atomic mass units (u) and mass excess in keV, are given in Table 4–3 as well as a comparison to the masses listed in the latest atomic mass evaluation in 2012. The half-life of each isotope measured is also given as an indicator into the difficulty of the measurement using the ToF-ICR technique.

Nuclide	$t_{1/2}$	Mass (μu)	Mass excess (keV)	$\Delta m_{cpt-AME12} \ (keV)^a$
$^{95}\mathrm{Sr}$	$23.90(14)\mathrm{s}$	$94 \ 919354.8(3.9)$	-75120.5(3.6)	1.5(7.0)
$^{106}\mathrm{Mo}$	$8.73(12){ m s}$	$105 \ 918265(14)$	-76130(10)	11 (13)
$^{106}\mathrm{Tc}$	$35.6(6){ m s}$	$105 \ 914442(21)$	-79696(19)	79(22)
$^{134}\mathrm{I}^m$	$3.52(4){ m m}$	$133 \ 910121.11 \ (0.89)$	-83721.65(0.83)	21(6)
$^{134}\mathrm{I}^{g}$	$52.5(2){ m m}$	$133 \ 909792.2 \ (4.9)$	-84028.1(4.6)	31(8)
^{142}I	$0.222(12)\mathrm{s}$	$141 \ 939411(45)$	-56438(42)	-1668(370)
$^{146}\mathrm{La}^m$	$10.0(1){ m s}$	$145 \ 925846.6(8.6)$	-69073.4(8.0)	-154(130)
$^{146}\mathrm{La}^{g}$	$6.27(10){ m s}$	$145 \ 925690(11)$	-69219(11)	-169(32)
^{148}Ba	$0.612(17)\mathrm{s}$	$147 \ 938177.5(4.4)$	-57587.3(4.1)	2.7(60)
^{149}Ba	$0.344(7){ m s}$	$148 \ 943218.9(7.7)$	-52891.2(7.2)	129(200#)
^{150}Ba	$0.3\mathrm{s}$	$149\ 946377(98)$	-49948(91)	302(310#)
$^{162}\mathrm{Sm}$	$2.4(5){ m s}$	$161 \ 941568.1(6.4)$	-54428.9(6.0)	101(200#)
$^{162}\mathrm{Eu}$	$10.6(1){ m s}$	161 936980 (38)	-58703(35)	-13(69)
$^{164}\mathrm{Eu}$	4.2(2) s	$163\ 942423.9(6.3)$	-53631.8(5.9)	-301(210#)
$^{165}\mathrm{Gd}^{b}$	$10.3(1.6)\mathrm{s}$	$164 \ 938967.8(6.5)$	-56851.1(6.0)	-361 (300#)

Table 4–3: Masses measured using the Canadian Penning Trap in this thesis

 a # denotes uncertainty on extrapolated mass excess values from AME12

^b Unable to definitively resolve from nearby contaminant molecule

4.6.1 Mass results discussion

Of the 15 masses presented in this thesis five are new measurements, and the other 10 were found to better precision than those in the atomic mass evaluation. At first glance it is concerning that of the 10 re-studied masses, only four agree with the mass evaluation value within 1σ , while just five are within 2σ . It may be more illuminating to compare our mass results with recent measurements from the past decade. Table 4–4 shows mass excesses found and the experiments where the measurements took place, as well as the mass excess differences between previous results and our values in Table 4–3.

Nuclide	Experiment/Type	Reference	Mass excess (keV)	$\Delta m_{cpt-other}$ (keV)
	of measurement			
95 Sr	ISOLTRAP	[64]	-75109(9)	-11.5(9.7)
$^{106}\mathrm{Mo}$	JYFLTRAP	[66]	-76139(10)	9(14)
$^{106}\mathrm{Tc}$	JYFLTRAP	[67]	$-79736 (5)^{a}$	40(20)
$^{134}\mathrm{I}^m$	CPT	[53]	-83722.7(6.9)	1.1(6.9)
$^{134}\mathrm{I}^{g}$	CPT	[19]	-84040.8(6.4)	12.7(7.9)
^{142}I	Storage ring	[68]	-54770(250)	-1668 (250)
146 La	CPT	[65]	$-69100 \ (29)^{b}$	-119(31)
^{148}Ba	β - endpoint	[69]	-57590(60) ^c	2.7(60)
$^{162}\mathrm{Eu}$	β - endpoint	[46]	-58700 (60)	-3(69)
$^{164}\mathrm{Eu}$	β - endpoint	[46]	-53320 (410) ^d	-312(410)

Table 4–4: Recent mass excess results from other experiments for the nuclides measured in this thesis.

^a Unknown impurities in trap during measurement

^b Could not distinguish between ground state and excited state

 c Calculated using AME12 mass of $^{148}\mathrm{La}$

 d Used extrapolated mass value from AME03 to obtain this mass excess

We agree within 2σ for seven of these nine measurements.

Previously measured masses

⁹⁵Sr: This isotope of strontium was measured previously at ISOLTRAP [64]. We differ from their value by 1.2σ . They used a simple Gaussian function to determine the cyclotron resonance. Perhaps our more physically meaningful fitting function produced a more accurate determination of ν_c . ⁹⁵Sr is much closer to the line of stability on the chart of nuclides than the heavy fission peak nuclides found in this thesis, having only seven more neutrons than the most abundant stable isotope of strontium. As a result of its accessibility, a number of β -endpoint energy measurements of ⁹⁵Sr have been carried out, and are listed in the mass evaluation. The combined value of these Q_{β} and direct measurements agree with our value presented in Table 4–3.

¹⁰⁶**Mo**: A previous measurement of ¹⁰⁶Mo was made at JYFLTRAP in 2006 [66]. We agree with both the atomic mass evaluation adjusted mass and the Penning trap result within 1σ .
¹⁰⁶**Tc**: This isotope of technetium was studied at JYFLTRAP in 2007 [67]. Their value disagrees with the adapted value in the mass evaluation by 3σ while the two Penning trap mass excesses differ by 2σ . A current lack of calibrant ion in the A \approx 100 mass range may be responsible for the discrepancy in accuracy, although a similar calculation of ¹⁰⁶Mo yields a mass excess that is in agreement with the JYFLTRAP value. There seems to be systematic uncertainties unaccounted for in the JYFLTRAP measurement as they state that they had problems with unknown "trap impurities" during the measurement of this isotope, yet the mass uncertainty is not significantly larger than other *clean* measurements in the same publication. Nevertheless this isotope will be revisited in the near future with the CPT.

¹³⁴I^{g,m}: Both states were measured using the CPT in 2012 and a 3σ disagreement was found between the measured value of ¹³⁴I^g and the 2003 atomic mass evaluation value [53],[19]. For this reason we decided to re-measure the two states. The mass of the isomeric state found using the CPT in 2013 agrees with the value from 2012, while the ground state is well within 2σ . Yet when we compare to the newest mass evaluation from 2012 we see differences of 3.5σ and 3.9σ for the metastable and ground states of the isotope, respectively. The two dominant inputs into the final mass quoted by the AME12 are β -endpoint measurements ¹³⁴Te(β^{-})¹³⁴I and ¹³⁴I(β^{-})¹³⁴Xe. In the next mass evaluation the discrepancy between the masses found using indirect and direct methods will likely favour the Penning trap measurements as it has between successive publications of mass evaluations in the past [47][25].

¹⁴²I: The only measurement that shows a stark disagreement with the mass evaluation is that of ¹⁴²I. The only previous measurement was done as part of a PhD thesis [68] using the storage ring at GSI in Darmstadt in 2004. Many of the masses presented in this thesis agree with a later publication from the same experimental group [70], and with a few isotopes measured with the CPT [53]. With a half-life of approximately 200 ms, this is a difficult isotope to measure using the ToF-ICR technique at CARIBU where we are subject to a wide array of contaminants in the form of stable and radioactive molecules. The result found in this thesis was not a single measurement but a weighted average of four separate measurements over two days. While these measurements were self-consistent the larger

than usual mass difference between Penning trap and storage ring results, warrants a re-measurement using the CPT in the near future.

¹⁴⁶La^{g,m}: The ¹⁴⁶La mass published by Savard *et al* and then later adopted by the AME12 actually turns out to be the metastable state ¹⁴⁶La^m. This value agrees with the one measured for this thesis.

¹⁴⁸**Ba**: The only previous measurement of ¹⁴⁸Ba was a Q_{β} measurement from 1990 [69]. Typically the β -endpoint measurements are not trusted too far from stability[25], but for ¹⁴⁸Ba (ten neutrons from the most common stable isotope) the mass excess calculated using the Q_{β} obtained in 1990, and the ¹⁴⁸La mass from the AME12, agrees with our measurement.

First-time measured masses

For the five nuclides in this thesis where the mass has been evaluated for the first time, extra care must be taken in order to confirm the identity of the nuclide being measured. We are able to determine the approximate cyclotron frequencies expected for each unknown mass, but when coming from extrapolated mass values of the 2012 atomic mass evaluation we are left with relatively large ranges of frequencies which could match the mass evaluation data. We should also consider that the extrapolated values may simply be incorrect.

Such a determination is made by considering the number of expected ions of a certain nuclide given the transmission efficiencies throughout the CPT system, the number of ions observed of a positively identified isotope from CARIBU (e.g. ¹⁴⁴Ba which has a well known mass, and therefore cyclotron frequency; and happens to belong to a mass number that is contaminant free from CARIBU), the fission branch from ²⁵²Cf in comparison to the well-known isotope, and half-life consideration. For example if an isotope has a half-life of 100 ms and we observe a cyclotron frequency using a 150 ms cycle time, we may want to re-measure the same isotope using a 500 ms cycle time. During a cycle the incident beam of ions should have decayed through multiple half-lives leaving fewer ions detected and often a shallower ToF spectrum depth since the ratio of wanted ions to contaminant ions in the trap would have decreased. If however, both of the cyclotron frequency measurements yield similar ion numbers and depths then we can conclude that the contents of the trap are not the desired isotope. ^{149,150}**Ba**: At Z=56, the isotopes of barium have been historically simple measurements at CARIBU. Because of the large difference between the second ionization energies of cesium (Z=55) and barium. we observe Cs at charge states of 1+ and Ba at charge states of 2+. This is beneficial as there is typically no contaminant on the smaller cyclotron frequency of the barium isotopes. This is as opposed to many other elements such as isotopes of lanthanum which have the heavier barium isobar on one side and the lighter cerium isobar on the other, both of which have to be removed in order to obtain a precise lanthanum cyclotron frequency. These two isotopes of barium were challenging due to the short half-lives of 0.344 s and 0.3 s and small fission branches from 252 Cf of 4.04×10^{-3} and 3.27×10^{-4} ions per 100 fissions respectively. Both masses are within the extrapolated mass uncertainties from the 2012 mass evaluation, and 150 Ba represents the smallest fission branch measured at CARIBU so far.

 162 Sm: Following a successful measurement fo 162 Eu the samarium isobar was measured. The 162 Sm fission branch is approximately 10 times smaller than the europium and as a result the measurement took roughly twice as long to accrue sufficient statistics. In fact two separate measurements were in such good agreement the uncertainty for this isobar was actually smaller than that found for 162 Eu. The mass determined was within the uncertainty of the extrapolated value in the latest mass evaluation.

¹⁶⁴Eu: While a β -endpoint energy was measured by Hayashi *et al* in 2007, the resultant mass is still dependent on extrapolated mass values from the atomic mass evaluation. Therefore this is the first direct mass measurement of ¹⁶⁴Eu. It is interesting to note that our mass excess does agree within 1σ of the value extrapolated from this 2007 measurement. This isotope of europium has a small fission branch (3.5×10^{-3}) but with a half-life of approximately 2 s a quadrupole excitation of 500 ms was able to be carried out without significant loss of ions. Two consecutive measurements showed good agreement and a mass excess uncertainty of 5.9 keV was obtained. The value is outside 1σ of the extrapolated value, but no other common CARIBU contaminant ion was found to have a similar cyclotron frequency to the one measured.

¹⁶⁵**Gd**: The extrapolated mass from the mass evaluation is a second-order extrapolation since no mass has been measured of ¹⁶⁴Gd yet. After conducting a 500 ms excitation the mass excess was determined to be outside of 1σ of the doubly extrapolated value. Upon attempting to verify the legitimacy of various measurements we found that lanthanum isotopes forming molecules with either water or hydroxide ions tend to have similar masses to the many isotopes in this mass region. In fact

the cyclotron frequency of a ¹⁴⁷La·H₂O molecule was expected to be 1068696.68(8) Hz where the uncertainty is inferred from the uncertainty in the mass of ¹⁴⁷La. The measured cyclotron frequency of ¹⁶⁵Gd was 1068696.54(3) Hz. While they do not agree within uncertainty, if both ions were in the trap at the same time, the resultant cyclotron frequency fit might be a value in between the two species due to the Fourier line-width of approximately 2.2 Hz for a 500 ms quadrupole excitation. Another unfortunate coincidence is that both ¹⁴⁷La and ¹⁶⁵Gd have similar half-lives so we are unable to try and wait for one to decay in the trap while we measure the other. The ion numbers are also difficult to infer since we do not know the chemistry behind molecular formation of these rare lanthanum isotopes with either H₂O or OH. The ¹⁴⁷La has a large fission branch of 2% but it is difficult to determine how many of these fission products come out as single ions, or how many form molecules with H₂O over OH, or whether these yields are the same over time. The gas catcher at CARIBU can be baked, which should decrease the amount of water in the system overall. A follow-up measurement should be made once the system is cleaner or the chemistry issues in CARIBU are better understood.

In summary we see good agreement with 12 of the 15 measurements made in this thesis, while remeasurements of ¹⁰⁶Tc, ¹⁴²I, and ¹⁶⁵Gd should become priorities over the next few experimental campaigns at the CPT. Attempting measurements of even more neutron-rich nuclei with smaller fission branches and shorter half-lifes than were given in this thesis will be difficult given the current contaminant ion issues in the system. The ability to measure the cyclotron frequencies of ions more quickly while improving mass resolution and maintaining high accuracy is the next logical progression for the CPT. The next chapter will briefly introduce one possible method of studying nuclides farther from stability using the CPT.

CHAPTER 5

Future considerations for the CPT and a new measurement technique

The major limitation of the TOF-ICR measurement technique currently employed by the CPT is the time required for precision measurements to be carried out. As we tread farther into the neutron-rich side of the table of nuclides we lose activity from the ²⁵²Cf source and incur shorter-lived isotopes. With measurements in this thesis we have reached fission fragment branches on the order of 10^{-4} and half-lifes approaching 150 ms. In order to make these mass measurements, ω_c excitations as short as 50 ms , with Fourier line-widths of 20 Hz, and dipole ω_+ cleaning excitations of up to 300 ms had to be used. The shorter we apply the quadrupole excitations, the more challenging it is to distinguish the wanted species from contaminant ions from CARIBU as the line shapes of adjacent species can overlap. At branches of 10^{-4} and lower it is evident that contaminant ions from CARIBU are transported at equal and often greater yields than the sought-after ²⁵²Cf fission fragments. The installation of a 1.7 Ci at CARIBU provides more yield of the low fission branches – although it has yet to be determined if this new source also brought along with it much higher yields of contamination– but with the current capability of isobar separation at CARIBU we may only be able to go another neutron further from stability. In order to go further and really take advantage of the isotopes CARIBU is capable of delivering, we need to move on from ToF-ICR and towards a technique tested at SHIPTRAP at GSI called phase-imaging ion-cyclotron-resonance (PI-ICR). I will briefly introduce the PI-ICR technique and a possible excitation scheme in this chapter.

5.1 Basic Theory and Implementation

In PI-ICR the cyclotron frequency is determined by measuring the phases of the radial motions after a period of free revolution inside the Penning trap. Instead of measuring the cyclotron frequency directly as is currently done with the ToF-ICR technique, independent measurements of the magnetron and modified cyclotron frequency are carried out. Then the cyclotron frequency is simply found from the familiar relation,

$$\omega_c = \omega_- + \omega_+. \tag{5.1}$$

In this new method the phase difference, ϕ_{\pm} , resulting from the period of excitation-free revolution is measured. In combination with the phase accumulation time, t, and the number of revolutions in that time, N, the desired eigenmotion frequency (in Hz) can be calculated as:

$$\nu_{\pm} = \frac{\phi_{\pm} + 2\pi N}{2\pi t} \tag{5.2}$$

In equation 5.2 t is chosen by the experimentalist, N is an integer easily calculable knowing the approximate value of ν_{\pm} for the species of interest, leaving only ϕ_{\pm} to be measured. This measurement is done using a position-sensitive MCP discussed briefly in the next section.

5.1.1 Position-Sensitive Microchannel Plate Detector

The measurements will be made with a position-sensitive MCP detector from the German company RoentDek GmbH. The DLD40 has an active diameter of more than 40 mm with a position resolution of < 0.1 mm and a timing resolution of 10-20 ns [71]. Figure 5–1 shows the schematic directly from RoentDek of the detector mounted to an optional mounting flange.



Figure 5–1: Side and top view of the 40 mm-diameter delay-line position-sensitive detector as coupled to an optional mounting vacuum flange from RoentDek. All dimensions are given in mm.

The detector consists of two MCPs arranged in a chevron configuration and a grid of delay-line anode wires for positional determination in two dimensions. When an ion strikes the MCP a shower of electrons are created and drawn towards the anode where a signal can be processed. Position encoding comes from the difference in travel time of the signal along the anode wires in each direction. The readout from the detector gives us five signals: x_1, x_2, y_1, y_2 , and a signal from the MCP contact which is used as a trigger for which the other times are calculated from. So the position in the x-direction is proportional to $X = x_1 - x_2$ and the position in the y-direction is proportional to $Y = y_1 - y_2$. Actual position on the plates will be determined by multiplying X and Y by some conversion parameter which will need to be measured using a calibration mask with known dimensions.

5.1.2 Measurement Process

Equation 5.2 tells us that the only value we need to measure is ϕ_{\pm} . The positions of the ions at different times in the measurement can be projected onto our position-sensitive detector where the value of ϕ_{\pm} can be determined. There are three different projected images which need to be considered in determining this phase difference which in this thesis will be called the center position, reference phase, and final phase as illustrated by circles 1, 2, and 3 respectively in Figure 5–2. The distance from the center position to the reference phase is labeled as (x_i, y_i) and the distance to the final phase is labeled (x_f, y_f) .



Figure 5–2: Image of the ion motion on the position sensitive detector showing the center (1), the reference phase (2), and the final phase (3) alongside distances x_i, y_i and x_f, y_f .

Part of the calibration process will be accurately determining the center position and reference phase for a given set of parameters. These will likely need to be measured within days of data collection given the typical magnetic field decay and instability. The center position can be measured by repeatedly trapping and cooling a number of known ions and ejecting them towards the detector. Assuming welltuned ion optics between the trap and the MCP, this should result in narrowly Gaussian distributed data in the xy plane which can easily be fit to determine the measurement center of the detector. Once the trap center has been established we can conduct the magnetron frequency measurement. This is a mass-independent measurement that will consist of a dipole excitation for approximately 10 ms, which will bring the contents of the trap out to a certain orbital radius, followed by an immediate

ejection from the trap. Reloading the Penning trap and repeating this cycle many times will give us the statistics necessary to determine our reference phase. To find the final phase we again trap the ions and increase the radius by dipole excitation at ω_{-} of the same duration used to find the reference phase, then after some time of free revolution, t, we eject the ions out of the trap. A cartoon of this pulse scheme is shown in Figure 5–3a. If we take the magnetron frequency to be $\nu_{-} \approx 1550 \, Hz$ and $t = 30 \, ms$, then equation 5.2 allows us to determine the integer number of revolutions in the trap. By taking $\phi_{-} = 0$, $N = \nu_{-}t \approx 46.5$. This means N = 46 and an angle of $\phi_{-} \approx \pi$ between the reference and final phases. The position sensitive detector allows us to measure the exact phase and thus determine the magnetron frequency. Measuring the modified cyclotron frequency is done with a similar pulse scheme. We again transport the ions to the trap where they are captured and cooled, then we apply a dipole pulse at roughly the value of ν_+ of the isotope we wish to measure, but for a short length of time, say 10 ms, such that the Fourier line-width of the pulse is large. This will bring the contents of the trap to some radius r. After the excitation pulse is complete we convert the ω_+ motion into ω_{-} motion by using a quadrupole π -pulse just as we did in section 2.2, and eject the ions out of the trap. This is repeated a number of times in order to establish the reference phase. To ascertain the final phase we reload the trap and apply the same dipole excitation at ν_+ as before but now we allow for free revolution for some time t where a phase of $\phi_+ + 2\pi N$ is accumulated. Then we apply the exact same π -pulse as was used to determine the reference phase, and eject the ions from the trap giving us the projected image of the final phase on the detector. A nice feature of the ToF-ICR technique was that it was simple to determine the rf amplitude required for a π pulse to perfectly convert from magnetron to modified-cyclotron motion. In this PI-ICR method we will be applying the π -pulse at a strong amplitude to make up for the lack of degree of freedom that scanning frequencies allowed us. We will instead have to tune the duration of the π -pulse to determine approximately when the conversion takes place. In the pulse scheme summarized here we do not need to know the exact time when conversion occurs since we apply the same conversion pulse at the end of the reference phase as we do for the final phase. Thus the precisely controlled phase accumulation time will not depend on the parameter used on the conversion pulse. The analysis then simply comes down to calculating ϕ_{\pm} . A representation of this possible pulse scheme is shown in Figure 5–3b. The resolution of our frequency measurement in PI-ICR is not limited by the Fourier line-width as it is when conducting a ToF-ICR measurement. The resolution is now found from the simple geometry



Figure 5–3: Possible pulse schemes for measurement of ω_{-} and ω_{+} frequencies.

between the three detected phases and is given in equation 5.3:

$$\Delta \nu_{\pm} = \frac{\Delta \phi}{2\pi t} = \frac{2sin^{-1}(\Delta r/r)}{2\pi t} \approx \frac{\Delta r}{\pi tr}$$
(5.3)

where r is the radius of the ions as projected onto the detector. Taking even more conservative values than those quoted from SHIPTRAP [72] of $\Delta r = 70 \,\mu\text{m}$ and $r = 0.7 \,\text{mm}$ the gain in resolving power is an easy factor of 30. Measurements given in this thesis were the quickest measurements made yet at the CPT with excitation times as low as 50 ms, but only out of necessity. We needed time to clean contaminants within the Penning trap before the quadrupole excitation was even applied, and for some measurements 50 ms was all the time that could be spared without significant loss of activity due to decay. With the PI-ICR technique and this factor of 30 we can obtain the same (albeit poor) resolution with a phase accumulation time of less than 2 ms.

The uncertainty of the frequency measurement δ_{ω_c} will depend on how well we can fit the position of the three phases:

$$\delta_{\nu_c} = \frac{\sqrt{\sum_{i,f} ((y\delta x)^2 + (x\delta y)^2)}}{2\pi r^2 t}$$
(5.4)

where $(x \pm \delta x, y \pm \delta y)_{i,f}$ are the coordinates and uncertainties of the reference (i), and final (f) phases with respect to the center position.

5.2 Possible systematic uncertainties

While this measurement system has yet to be fully installed and tested, there are a few concerns that must be addressed beforehand. Firstly, the ion optics currently used to transport ions from the Penning trap to detector will have to be retuned. Simulations will be carried out to determine what potentials along the existing ToF line are needed and whether the addition of more lensing elements is required. There should also be a concern about the stability of the magnetic field since, with the proposed excitation scheme, two different measurements will have to be made in order to determine the cyclotron frequency. The measurements of ω_{-} and ω_{+} will be carried out at different times so we will need to be even more vigilant about taking calibration data in a timely fashion. Early work with this method [72][73] has shown that the distortion of the projected phases onto the detector is a major hurdle. The alignment of the magnetic field, trap, and detector all have to be in sync for an accurate position to be read. In a well-tuned system, however, these systematic uncertainties have been shown to be much smaller than the required precision of masses for r-process calculations. Distortion of the projection gives $\delta \nu_c / \nu_c < 10^{-11}$, non-simultaneous measurement of phases results in $\delta \nu_c / \nu_c \approx 10^{-10}$, and fluctuations in magnetic field and trapping voltages produce $\delta \nu_c / \nu_c \approx 10^{-10}$ each [74]. The extent of these systematic uncertainties are not unlike what we experience now with the ToF-ICR technique, and are actually much smaller than the systematics quoted in this thesis. Whether this is underestimation on the part of SHIPTRAP or insight into the stability of this new measurement procedure, has yet to be determined.

Appendix A

A.1 Multiple peak fitting function

We generalize our fitting function from section 4.2 to N resonantly excited species as:

$$t'_{tof} = (b'+s)\sum_{i=1}^{N} \left(1 - n_i + \frac{n_i}{\sqrt{1 + \frac{E_r(\nu_{c_i})}{E_{r,0}} \left[\left(\frac{b'+s}{b'+s-d}\right)^2 - 1\right]}}\right) - s$$
(A.1)

where the overall depth of the spectrum, d, remains fixed as in the single-peak case from a well-known calibrant, and the parameters n_i model the relative depths of each resonant peak at frequency ν_i . An N = 2 example used to determine the cyclotron frequencies of ¹³⁴La^{g,m} is shown in Figure A.1.



Figure A.1: Example of double-peak fitting function where both the ground and excited state of 134 I are measured at the same time with the CPT. The black dotted lines denote the fitted centroids used to determine the masses.

A.2 Damped fitting function

For completeness an example of our fitting function where we take the damping due to ion-ion interaction into account by letting the γ parameter be greater than zero in the functions E_r and $E_{r,0}$ (equations 4.7,4.8) is shown in Figure A.2. In this figure we show a calibration measurement

of 52 Cr where the number of ions entering the Penning trap is a given shot was not cut back. This measurement was made with an average of approximately 15 ions per shot.



Figure A.2: An example of our fitting function where the damping constant γ is allowed to vary while determining the cyclotron frequency of stable ⁵²Cr.

References

- Klaus Blaum and Yuri A. Litvinov. 100 years of mass spectrometry. International Journal of Mass Spectrometry, 349350(0):1 – 2, 2013. 100 years of Mass Spectrometry.
- K.S. Sharma. Mass spectrometry early years. International Journal of Mass Spectrometry, 349350(0):3 – 8, 2013. 100 years of Mass Spectrometry.
- [3] G. Mnzenberg. Development of mass spectrometers from thomson and aston to present. *Inter*national Journal of Mass Spectrometry, 349350(0):9 – 18, 2013. 100 years of Mass Spectrometry.
- [4] Klaus Blaum. High-accuracy mass spectrometry with stored ions. *Physics Reports*, 425(1):1 78, 2006.
- [5] W. Paul and M. Raether. Das elektrische massenfilter. Zeitschrift fr Physik, 140(3):262–273, 1955.
- [6] R. F. Wuerker, H. Shelton, and R. V. Langmuir. Electrodynamic containment of charged particles. *Journal of Applied Physics*, 30(3):342–349, 1959.
- [7] R. M. Yee, N. D. Scielzo, P. F. Bertone, F. Buchinger, S. Caldwell, J. A. Clark, C. M. Deibel, J. Fallis, J. P. Greene, S. Gulick, D. Lascar, A. F. Levand, G. Li, E. B. Norman, M. Pedretti, G. Savard, R. E. Segel, K. S. Sharma, M. G. Sternberg, J. Van Schelt, and B. J. Zabransky. β. *Phys. Rev. Lett.*, 110:092501, Feb 2013.
- [8] J.R. Pierce. Theory and Design of Electron Beams. D. van Nostrand Co., New York, 1949.
- [9] H.-Jrgen Kluge. Penning trap mass spectrometry of radionuclides. *International Journal of Mass Spectrometry*, 349350(0):26 37, 2013. 100 years of Mass Spectrometry.
- [10] Hans Dehmelt. Experiments with an isolated subatomic particle at rest. *Rev. Mod. Phys.*, 62:525–530, Jul 1990.
- [11] G. Bollen, P. Dabkiewicz, P. Egelhof, T. Hilberath, H. Kalinowsky, F. Kern, H. Schnatz, L. Schweikhard, H. Stolzenberg, R.B. Moore, H.-J. Kluge, G.M. Temmer, and G. Ulm. First absolute mass measurements of short-lived isotopes. *Hyperfine Interactions*, 38(1-4):793-802, 1987.
- [12] R. B. Cakirli, D. S. Brenner, R. F. Casten, and E. A. Millman. Proton-neutron interactions and the new atomic masses. *Phys. Rev. Lett.*, 94:092501, Mar 2005.
- [13] H. Schatz. Nuclear masses in astrophysics. International Journal of Mass Spectrometry, 349350(0):181 – 186, 2013. 100 years of Mass Spectrometry.
- [14] Jason Clark and Guy Savard. Precision masses for studies of the astrophysical r process. International Journal of Mass Spectrometry, 349350(0):81 – 86, 2013. 100 years of Mass Spectrometry.

- [15] Tommi Eronen and Ari Jokinen. High-precision atomic mass measurements for a CKM unitarity test. International Journal of Mass Spectrometry, 349350(0):69 – 73, 2013. 100 years of Mass Spectrometry.
- [16] S. Sturm, F. Kohler, J. Zatorski, A. Wagner, Z. Harman, G. Werth, W. Quint, C. H. Keitel, and K. Blaum. High-precision measurement of the atomic mass of the electron. *Nature*, 506:467–470.
- [17] Guilhem Douysset, Tomas Fritioff, Conny Carlberg, Ingmar Bergström, and Mikael Björkhage. Determination of the ⁷⁶ge double beta decay Q value. Phys. Rev. Lett., 86:4259–4262, May 2001.
- [18] J. Van Schelt, D. Lascar, G. Savard, J. A. Clark, S. Caldwell, A. Chaudhuri, J. Fallis, J. P. Greene, A. F. Levand, G. Li, K. S. Sharma, M. G. Sternberg, T. Sun, and B. J. Zabransky. Mass measurements near the r-process path using the canadian penning trap mass spectrometer. *Phys. Rev. C*, 85:045805, Apr 2012.
- [19] J. Van Schelt, D. Lascar, G. Savard, J. A. Clark, P. F. Bertone, S. Caldwell, A. Chaudhuri, A. F. Levand, G. Li, G. E. Morgan, R. Orford, R. E. Segel, K. S. Sharma, and M. G. Sternberg. First results from the CARIBU facility: Mass measurements on the *r*-process path. *Phys. Rev. Lett.*, 111:061102, Aug 2013.
- [20] Hans E. Suess and Harold C. Urey. Abundances of the elements. Rev. Mod. Phys., 28:53–74, Jan 1956.
- [21] E. Margaret Burbidge, G. R. Burbidge, William A. Fowler, and F. Hoyle. Synthesis of the elements in stars. *Rev. Mod. Phys.*, 29:547–650, Oct 1957.
- [22] M. Arnould, S. Goriely, and K. Takahashi. The r-process of stellar nucleosynthesis: Astrophysics and nuclear physics achievements and mysteries. *Physics Reports*, 450(46):97 213, 2007.
- [23] J.A. Clark. Precise mass measurements of nuclides approaching the r-process. The r-Process: The Astrophysical Origin of Heavy Elements and Related Rare Isotope Accelerator Physics. Proceedings from the Institute for Nuclear Theory, 13:11–19, 2004.
- [24] Y.-Z. Qian. The origin of the heavy elements: Recent progress in the understanding of the r-process. Progress in Particle and Nuclear Physics, 50(1):153 – 199, 2003.
- [25] M. Wang, G. Audi, A.H. Wapstra, F.G. Kondev, M. MacCormick, X. Xu, and B. Pfeiffer. The Ame2012 atomic mass evaluation. *Chinese Physics C*, 36(12):1603, 2012.
- [26] Matthew R. Mumpower, G. C. McLaughlin, and Rebecca Surman. The rare earth peak: An overlooked r-process diagnostic. *The Astrophysical Journal*, 752(2):117, 2012.
- [27] S. Goriely, N. Chamel, and J. M. Pearson. Further explorations of skyrme-hartree-fockbogoliubov mass formulas. xiii. the 2012 atomic mass evaluation and the symmetry coefficient. *Phys. Rev. C*, 88:024308, Aug 2013.
- [28] Hiroyuki Koura, Takahiro Tachibana, Masahiro Uno, and Masami Yamada. Nuclidic mass formula on a spherical basis with an improved even-odd term. *Progress of Theoretical Physics*, 113(2):305–325, 2005.
- [29] Y. Aboussir, J.M. Pearson, A.K. Dutta, and F. Tondeur. Nuclear mass formula via an approximation to the hartreefock method. Atomic Data and Nuclear Data Tables, 61(1):127 – 176, 1995.

- [30] J. Duflo and A.P. Zuker. Microscopic mass formulas. Phys. Rev. C, 52:R23–R27, Jul 1995.
- [31] Min Liu, Ning Wang, Yangge Deng, and Xizhen Wu. Further improvements on a global nuclear mass model. *Phys. Rev. C*, 84:014333, Jul 2011.
- [32] P. Moller, J.R. Nix, W.D. Myers, and W.J. Swiatecki. Nuclear ground-state masses and deformations. Atomic Data and Nuclear Data Tables, 59(2):185 – 381, 1995.
- [33] Lawrence C. Evans. *Parital Differential Equations*. American Mathematical Society, 2nd edition, 2008.
- [34] Dieter Gerlich. Inhomogeneous RF Fields: A Versatile Tool for the Study of Processes with Slow Ions, pages 1–176. John Wiley & Sons, Inc., 2007.
- [35] W Paul. Electromagnetic traps for charged and neutral particles. Reviews of Modern Physics, 62:531–540, 1990.
- [36] C.W. Van Fong. Phase Space Dynamics in a Linear RFQ Trap for Time-of-Flight Mass Spectrometry. PhD thesis, McGill University, 2001.
- [37] E.T. Whittaker. On the general solution of Mathieu's equation. Proc. Edinburgh Math. Society, 32:75–80, 1914.
- [38] L Ruby. Applications of the Mathieu equation. American Journal of Physics, 64:39–44, 1996.
- [39] G Li. Electron-Neutrino Angular Correlation Measurement in the Decay of ⁸Li. PhD thesis, McGill University, 2012.
- [40] Jae C Schwartz, Michael W Senko, and John E.P Syka. A two-dimensional quadrupole ion trap mass spectrometer. Journal of the American Society for Mass Spectrometry, 13(6):659 – 669, 2002.
- [41] M Kretzschmar. Particle motion in a Penning trap. European Journal of Physics, 12(5):240, 1991.
- [42] M. Mukherjee, D. Beck, K. Blaum, G. Bollen, J. Dilling, S. George, F. Herfurth, A. Herlert, A. Kellerbauer, H.-J. Kluge, S. Schwarz, L. Schweikhard, and C. Yazidjian. Isoltrap: An on-line penning trap for mass spectrometry on short-lived nuclides. *The European Physical Journal A*, 35(1):1–29, 2008.
- [43] K Blaum, G Bollen, F Herfurth, A Kellerbauer, H-J Kluge, M Kuckein, S Heinz, P Schmidt, and L Schweikhard. Recent developments at ISOLTRAP: towards a relative mass accuracy of exotic nuclei below 10⁻⁸. Journal of Physics B: Atomic, Molecular and Optical Physics, 36(5):921, 2003.
- [44] M. König, G. Bollen, H.-J. Kluge, T. Otto, and J. Szerypo. Quadrupole excitation of stored ion motion at the true cyclotron frequency. *International Journal of Mass Spectrometry and Ion Processes*, 142(12):95 – 116, 1995.
- [45] G. Bollen. Mass measurements of short-lived nuclides with ion traps. Nuclear Physics A, 693(12):3 – 18, 2001. Radioactive Nuclear Beams.
- [46] H. Hayashi, Y. Akita, O. Suematsu, M. Shibata, M. Asai, T.K. Sato, S. Ichikawa, I. Nishinaka, Y. Nagame, A. Osa, K. Tsukada, T. Ishii, Y. Kojima, and A. Taniguchi. Q measurements of

158, 159pm , 159, 161sm , 160-165eu , 163gd and 166tb using a total absorption BGO detector. The European Physical Journal A, 34(4):363–370, 2007.

- [47] A.H. Wapstra, G. Audi, and C. Thibault. The ame2003 atomic mass evaluation: (i). evaluation of input data, adjustment procedures. *Nuclear Physics A*, 729(1):129 – 336, 2003. The 2003 {NUBASE} and Atomic Mass Evaluations.
- [48] T.R. England and B.F. Rider. Evaluation and compilation of fission product yields 1993. LA-UR-94-3106 ENDF-349, 1994.
- [49] J. Tuli. Nuclear wallet cards. National Nuclear Data Center, 2011.
- [50] I.W. Osbourne-Lee and C.W. Alexander. Californium-252: A remarkably versatile radioisotope. Oak Ridge National Laboratory for the U.S. Department of Energy, 1995.
- [51] N. Nica. Nuclear data sheets for a = 252. Nuclear Data Sheets, 106:813–834, 2005.
- [52] W. W. T. Crane, G. H. Higgins, and H. R. Bowman. Average number of neutrons per fission for several heavy-element nuclides. *Phys. Rev.*, 101:1804–1805, Mar 1956.
- [53] J. Van Schelt. Precision Mass Measurements of Neutron-Rich Nuclei, and Limitations on the r-Process Environment. PhD thesis, The University of Chicago, 2012.
- [54] D. Lascar. Precision Mass Measurements of Short-Lived, Neutron-Rick, R-Process Nuclei about the N = 82 Waiting Point. PhD thesis, Northwestern University, 2012.
- [55] G. Savard, J. Clark, C. Boudreau, F. Buchinger, J.E. Crawford, H. Geissel, J.P. Greene, S. Gulick, A. Heinz, J.K.P. Lee, A. Levand, M. Maier, G. Mnzenberg, C. Scheidenberger, D. Seweryniak, K.S. Sharma, G. Sprouse, J. Vaz, J.C. Wang, B.J. Zabransky, and Z. Zhou. Development and operation of gas catchers to thermalize fusionevaporation and fragmentation products. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 204(0):582 – 586, 2003. 14th International Conference on Electromagnetic Isotope Separators and Techniques Related to their Applications.
- [56] Cary N. Davids and Don Peterson. A compact high-resolution isobar separator for the CARIBU project. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 266(1920):4449 – 4453, 2008. Proceedings of the {XVth} International Conference on Electromagnetic Isotope Separators and Techniques Related to their Applications.
- [57] Michael P. Bradley, James V. Porto, Simon Rainville, James K. Thompson, and David E. Pritchard. Penning trap measurements of the masses of ^{133}cs , $^{87,85}rb$, and ^{23}na with uncertainties ≤ 0.2 ppb. *Phys. Rev. Lett.*, 83:4510–4513, Nov 1999.
- [58] J. Fallis. The Masses of Proton-Rich Isotopes Nb, Mo, Tc, Ru, and Rh and their Influence on the astrophysical rp and νp processes. PhD thesis, University of Manitoba, 2009.
- [59] Data Design Corporation. DG11A Digital Delay Generator. 7851-A Beechcraft Avenue, Gaithersburg, Maryland.
- [60] Jorway Corporation. The programming and use of the Model 221A timing and sequence module.
- [61] Lowell S. Brown and Gerald Gabrielse. Geonium theory: Physics of a single electron or ion in a penning trap. Rev. Mod. Phys., 58:233–311, Jan 1986.

- [62] F. Dyson. Turning points: A meeting with enrico fermi. Nature, 427:297, 2004.
- [63] S. George, K. Blaum, M. Block, M. Breitenfeldt, M. Dworschak, F. Herfurth, A. Herlert, M. Kowalska, M. Kretzschmar, E. Minaya Ramirez, D. Neidherr, S. Schwarz, and L. Schweikhard. Damping effects in penning trap mass spectrometry. *International Journal of Mass Spectrometry*, 299(23):102 – 112, 2011.
- [64] H. Raimbault-Hartmann, G. Audi, D. Beck, G. Bollen, M. de Saint Simon, H.-J. Kluge, M. König, R.B. Moore, S. Schwarz, G. Savard, and J. Szerypo. High-accuracy mass determination of neutron-rich rubidium and strontium isotopes. *Nuclear Physics A*, 706(12):3 – 14, 2002.
- [65] G. Savard, J.C. Wang, K.S. Sharma, H. Sharma, J.A. Clark, C. Boudreau, F. Buchinger, J.E. Crawford, J.P. Greene, S. Gulick, A.A. Hecht, J.K.P. Lee, A.F. Levand, N.D. Scielzo, W. Trimble, J. Vaz, and B.J. Zabransky. Studies of neutron-rich isotopes with the CPT mass spectrometer and the CARIBU project. *International Journal of Mass Spectrometry*, 251(23):252 259, 2006. ULTRA-ACCURATE MASS SPECTROMETRY AND RELATED TOPICS Dedicated to H.-J. Kluge on the occasion of his 65th birthday anniversary Jrgen Kluge Special Issue.
- [66] U. Hager, T. Eronen, J. Hakala, A. Jokinen, V. S. Kolhinen, S. Kopecky, I. Moore, A. Nieminen, M. Oinonen, S. Rinta-Antila, J. Szerypo, and J. Äystö. First precision mass measurements of refractory fission fragments. *Phys. Rev. Lett.*, 96:042504, Feb 2006.
- [67] U. Hager, V.-V. Elomaa, T. Eronen, J. Hakala, A. Jokinen, A. Kankainen, S. Rahaman, S. Rinta-Antila, A. Saastamoinen, T. Sonoda, and J. Äystö. Precision mass measurements of neutron-rich tc, ru, rh, and pd isotopes. *Phys. Rev. C*, 75:064302, Jun 2007.
- [68] M. Matoš. Isochronous mass measurements of short-lived neutron rich nuclides at the FRS ESR facilities. PhD thesis, University of Giessen, 2004.
- [69] M. Graefenstedt et al. Beta decay energies and nuclear masses of ¹⁴⁸Ba, ¹⁴⁸La, and ¹⁵²Pr. Zeitschrift für Physik A - Atomic Nuclei, 336:247–252, 1990.
- [70] B. Sun, R. Knbel, Yu.A. Litvinov, H. Geissel, J. Meng, K. Beckert, F. Bosch, D. Boutin, C. Brandau, L. Chen, I.J. Cullen, C. Dimopoulou, B. Fabian, M. Hausmann, C. Kozhuharov, S.A. Litvinov, M. Mazzocco, F. Montes, G. Mnzenberg, A. Musumarra, S. Nakajima, C. Nociforo, F. Nolden, T. Ohtsubo, A. Ozawa, Z. Patyk, W.R. Pla, C. Scheidenberger, M. Steck, T. Suzuki, P.M. Walker, H. Weick, N. Winckler, M. Winkler, and T. Yamaguchi. Nuclear structure studies of short-lived neutron-rich nuclei with the novel large-scale isochronous mass spectrometry at the frs-esr facility. *Nuclear Physics A*, 812(14):1 – 12, 2008.
- [71] RoentDek Handels GmbH. MCP Delay Line Detector Manual. RoentDek.
- [72] S. Eliseev et al. A phase-imaging technique for cyclotron-frequency measurements. *Applied Physics B: Lasers and Optics*, 114:107–128, 2014.
- [73] G. Eitel, M. Block, A. Czasch, M. Dworschak, S. George, O. Jagutzki, J. Ketelaer, J. Ketter, Sz. Nagy, D. Rodrguez, C. Smorra, and K. Blaum. Position-sensitive ion detection in precision penning trap mass spectrometry. *Nuclear Instruments and Methods in Physics Research Section* A: Accelerators, Spectrometers, Detectors and Associated Equipment, 606(3):475 – 483, 2009.
- [74] Mikhail Leonidovich Goncharov. High-precision Penning-trap mass spectrometry at SHIPTRAP and PENTATRAP for neutrino physics research. PhD thesis, Ruperto-Carola-University of Heidelberg, 2014.