
Optical clocks with trapped ions

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*Thesis submitted to the
Faculty of Mathematics, Computer Science and Physics
of the Leopold-Franzens University of Innsbruck
in partial fulfillment of the requirements for the degree of*

Doctor of Philosophy
(Physics)

February 7, 2023

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It's about time...

Abstract

The search for more precise and accurate frequency standards has played a key role in the development of basic science, precision measurements and technical applications. Nowadays, optical clocks are achieving fractional uncertainties at the low 10^{-18} range and below. This PhD thesis is focused on the development and characterization of optical clocks with trapped ions. Two different trapped ion clocks are presented: one with a single $^{40}\text{Ca}^+$ ion and one with a $^{40}\text{Ca}^+ / ^{27}\text{Al}^+$ mixed-ion crystal. The thesis starts with an overview of the theoretical basis necessary to operate and characterize trapped ion clocks as well as a description of the experimental setup. Followed by the results of three main projects:

The first project is centered around the absolute frequency measurement of the $4s^2S_{1/2} \leftrightarrow 3d^2D_{5/2}$ $^{40}\text{Ca}^+$ clock transition with respect to the Coordinated Universal Time at the Physikalisch-Technische Bundesanstalt, [UTC\(PTB\)](#). To perform this measurement a link between our laboratory in Innsbruck and the clocks in [PTB](#) was installed and characterized using the Global Navigation Satellite System [GNSS](#). The comparison between our clock and the ones at [PTB](#) was done using the Precise Point Positioning ([PPP](#)) technique. A ten-day campaign was held from the 16th to the 25th of June 2021. After the evaluation of the systematic shifts, the measured transition frequency is $(411\,042\,129\,776\,401.2 \pm 0.6)$ Hz with a fractional uncertainty of 1.4×10^{-15} . This value is in agreement with the latest measurements from the K. Gao group.

The second project concerns the measurement of the $^1S_0 \leftrightarrow ^3P_1$, $F=7/2$ intercombination transition in $^{27}\text{Al}^+$ using quantum logic spectroscopy with a $^{27}\text{Al}^+ / ^{40}\text{Ca}^+$ mixed-ion crystal. Through the implementation of Ramsey spectroscopy to probe the transition in $^{27}\text{Al}^+$ and the $(4s^2)S_{1/2} \leftrightarrow (4s3d)D_{5/2}$ clock transition in $^{40}\text{Ca}^+$ in interleaved measurements. By using the precisely measured frequency of the clock transition in $^{40}\text{Ca}^+$ as a reference, the frequency of the intercombination line is determined to be $\nu_{^1S_0 \leftrightarrow ^3P_1, F=7/2} = 1\,122\,842\,857\,334\,736(93)$ Hz and the Landé g-factor of the excited state to be $g_{^3P_1, F=7/2} = 0.428\,132(2)$. Additionally, the first observation of the $^1S_0 \leftrightarrow ^3P_0$ $^{27}\text{Al}^+$ clock transition in our experimental setup is presented.

The third project focuses on the investigation of trapped-ion kinetics due to background-gas collisions. Background-gas collisions affect the frequency of atomic clocks due to two main effects: on one hand they induce time dilations shifts due to changes in the motional state distribution, and on the other hand interactions during the collisions generate additional phase shifts of the atomic superposition. To properly characterize these shifts a better understanding of the trapped-ion kinetics due to background-gas collisions is necessary. This project proposes three different experimental techniques to determine the collision rate of particles that transfer a given energy to the ion. The three techniques together detect a range in energy due to collisions spanning seven orders of magnitude. The first technique uses a composite sequence of optical transitions in $^{40}\text{Ca}^+$ that allows us to determine its motional state, allowing the detection of collisions that impart a kinetic energy between 10^{-3} K to 10^{-1} K. The second technique is based on the detection of collisions that cause a reordering of a mixed-species ion pair and covers a range from 10^{-1} K to 10 K. The third technique is based on the characterization of the re-cooling dynamics of a single calcium ion after a collision and covers a range from 10 K to 10^4 K. The experimental characterization of trapped-ion kinetics due to background-gas collisions across such a broad range opens the door to a deeper understanding of the background-gas composition and its effect on trapped-ion experiments.

Zusammenfassung

Die Suche nach präziseren und genaueren Frequenznormalen hat eine Schlüsselrolle bei der Entwicklung von Grundlagenforschung, Präzisionsmessungen und technischen Anwendungen gespielt. Heutzutage erreichen optische Uhren (fraktionelle) Unsicherheiten im niedrigen 10^{-18} Bereich und darunter. Diese Dissertation befasst sich mit der Entwicklung und Charakterisierung von optischen Uhren mit gefangenen Ionen. Es werden zwei verschiedene Ionenfallenuhren vorgestellt: Eine mit einem einzelnen $^{40}\text{Ca}^+$ Ion und Eine mit einem $^{40}\text{Ca}^+ / ^{27}\text{Al}^+$ Mischkristall. Diese Arbeit beginnt mit einem Überblick über die theoretischen Grundlagen, die für den Betrieb und die Charakterisierung von Ionenfallenuhren notwendig sind und mit einer Beschreibung des experimentellen Aufbaus. Es folgen die Ergebnisse von drei Hauptprojekten:

Das erste Projekt konzentriert sich auf die absolute Frequenzmessung des $^{40}\text{Ca}^+ 4s^2S_{1/2} \leftrightarrow 3d\ ^2D_{5/2}$ Uhrenübergangs in Bezug auf die Koordinierte Weltzeit an der Physikalisch Technischen Bundesanstalt, UTC(PTB). Um dies zu verwirklichen wurde eine Verbindung zwischen unserem Labor in Innsbruck und den Uhren der PTB mit Hilfe des globalen Navigationssatellitensystems GNSS etabliert und charakterisiert. Der Vergleich zwischen unserer Uhr und den Uhren in der PTB wurde mit der 'Precise Point Positioning' (PPP) durchgeführt. Eine zehntägige Messkampagne fand vom 16 bis 25 Juni 2021 statt. Nach Auswertung der systematischen Verschiebungen beträgt die gemessene Übergangsfrequenz $(411\,042\,129\,776\,401.2 \pm 0.6)$ Hz mit einer fraktionellen Unsicherheit von 1.4×10^{-15} . Dieser Wert stimmt mit den jüngsten Messungen der Gruppe von K. Gao überein.

Das zweite Projekt betrifft die Messung des $^1S_0 \leftrightarrow ^3P_1, F=7/2$ Interkombinationsübergangs in $^{27}\text{Al}^+$ durch Quantenlogikspektroskopie mit einem $^{27}\text{Al}^+ / ^{40}\text{Ca}^+$ Mischkristall. Ramsey-Spektroskopie wurde zur Untersuchung des Übergangs in $^{27}\text{Al}^+$ und des $(4s^2)S_{1/2} \leftrightarrow (4s3d)D_{5/2}$ Uhrenübergang in $^{40}\text{Ca}^+$ in verschachtelten Messungen genutzt. Durch Verwendung der genau gemessenen Frequenz des Uhrenübergangs in $^{40}\text{Ca}^+$ als Referenz wird die Frequenz der Interkombinationslinie bestimmt als $\nu_{^1S_0 \leftrightarrow ^3P_1, F=7/2} = 1\,122\,842\,857\,334\,736(93)$ Hz und der Landé g-Faktor des angeregten Zustands als $g_{^3P_1, F=7/2} = 0.428\,132(2)$. Darüber hinaus wird die erste Beobachtung des $^{27}\text{Al}^+ ^1S_0 \leftrightarrow ^3P_0$ Uhrenübergangs in unserem Versuchsaufbau vorgestellt.

Das dritte Projekt befasst sich mit der Untersuchung der Kinetik von gefangenen Ionen aufgrund von Kollisionen mit Hintergrundgas. Hintergrundgaskollisionen beeinflussen die Frequenz von Atomuhren primär durch zwei Effekte: Zum Einen führen sie zu Zeitdilatationsverschiebungen aufgrund von Änderungen in der Verteilung der Bewegungszustände. Zum Anderen erzeugen Wechselwirkungen während der Kollisionen zusätzliche Phasenverschiebungen der atomaren Superposition. Um diese Verschiebungen hinreichend korrekt zu charakterisieren, ist ein besseres Verständnis der Kinetik der gefangenen Ionen aufgrund von Hintergrundgas-Kollisionen erforderlich. In diesem Projekt werden drei verschiedene experimentelle Techniken vorgeschlagen, um die Kollisionsrate von Teilchen zu bestimmen, die eine bestimmte Energie auf das Ion übertragen. Zusammen erfassen die drei Techniken einen durch Kollisionen verursachten Energiebereich von sieben Größenordnungen. Die erste Technik nutzt eine zusammengesetzte Sequenz optischer Übergänge in $^{40}\text{Ca}^+$, um Informationen über den Bewegungszustand des Ions genau zu bestimmen, was den Nachweis von Kollisionen mit einer kinetischen Energie zwischen 10^{-3} K und 10^{-1} K ermöglicht. Die zweite Technik basiert auf dem Nachweis von Kollisionen, die in einem Ionenkristall zweier Spezies zur Umsortierung führen. Diese Technik deckt einen

Bereich Kollisionen ab die kinetische Energien von 10^{-1} K bis 10 K. auf das Ion übertragen können. Die dritte Technik basiert auf der Charakterisierung der Rückkühlungsdynamik eines einzelnen Kalziumions nach einer Kollision und deckt einen Bereich von 10 K bis 10^4 K ab. Die experimentelle Charakterisierung der Kinetik von gefangenen Ionen aufgrund von Hintergrundgaskollisionen über einen so weiten Bereich öffnet die Tür zu einem tieferen Verständnis der Zusammensetzung des Hintergrundgases und seiner Auswirkungen auf Experimente mit gefangenen Ionen.

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Acronyms

AOM acoustic optic modulator.

BD beam dump.

BIPM International Bureau of Weights and Measures.

CCD Charge coupled device.

CGPM General Conference on Weights and Measures.

CIPM International Committee for weights and measures.

DC direct current.

ECDL external cavity diode laser.

EMCCD electron-multiplying-charge-coupled device.

EOM electro-optic modulator.

f_{CEO} carrier envelop offset frequency.

f_{CW} continuous wave frequency.

f_{REP} repetition rate frequency.

FALC fast analog linewidth control.

FC Frequency comb.

FI optical isolator.

FNC fiber noise cancellation.

GNSS Global Navigation Satellite System.

GPS Global Position System.

GTP Glan-Thompson polarizer.

GUM Guide to the expression of uncertainty in measurement.

HWP half-wave plate.

IAU International Astronomical Union.

IGS International GNSS Service.

IGST International GNSS Service Time.

IQOQI Institut for Quantum Optics and Quantum Information.

MAD Median Absolute Deviation.

maser microwave amplification by stimulated emission of radiation.

NEG non-evaporative getter.

NIST National Institute of Standards and Technology.

NRCan Natural Resources Canada.

PBS Polarized beam splitter.

PCF photonic crystal fiber.

PD Photo Diode.

PDH Pound-Drever-Hall.

PFS Primary frequency standard.

PID proportional–integral–derivative.

PMF polarization- maintaining fiber.

PMT photomultiplier tube.

PPP Precise Point Positioning.

PPS Pulse per second.

PTB Physikalisch-Technische Bundesanstalt.

QLS Quantum Logic Spectroscopy.

RF radio frequency.

RINEX Receiver Independent Exchange Format.

SC Sympathetic Cooling.

SI International System of Units.

SM single mode.

TA tapered amplifier.

TAI International Atomic Time.

TCG Geocentric Coordinate Time.

Ti:Sa titanium sapphire.

TrICS Trapped ion control system.

TT Terrestrial Time.

TTL transistor transistor logic.

UHV ultra high vacuum.

UTC Coordinated Universal Time.

VCO voltage-controlled oscillator.

WLM Wavelength meter.

Chapter 1

Introduction

"Never measure anything but frequency!"

Arthur Schawlow

Throughout history, humans have always tracked time [1]. Either for maintaining social activities, agricultural endeavors, navigation, avoiding airplane or train crashes and specially nowadays to keep track of the millions of telecommunication processes that happen every second. Time keeping and synchronization play an essential role in our daily lives.

A natural way to keep track of time is through the measurement of frequency. Measuring frequency consists in counting how often a given phenomenon is repeated during a given time. A "tick" is associated to every repetition. It can be every time a pendulum swings back and forth, the rotation of the earth or the frequency of oscillation of the light absorbed or emitted by an atom. To keep track of time it is only necessary to determine the period of oscillation, meaning the duration between two repetitive events and carefully count how often the event is repeated. Through history the art of building clocks has been focused, first, on finding the perfect oscillator: A system with a frequency of oscillation that is as constant and stable as possible. Second, on finding the best way to read its frequency: To unmistakably detect every "tick".

The first frequency measurements were done by recording the movement of celestial bodies such as the sun, the moon or bright stars. Given their very reliable periodicity, using astronomical events is a robust technique for keeping track of time on scales of months, days, or even hours. However, as society became increasingly complex the need for measuring time in smaller intervals became more important. To improve the resolution of time keeping, it became necessary to find periodic systems with a higher repetition rate. Instruments, such as water clocks or hourglasses, were used to time intervals by controlling the flow of sand or water. As human knowledge evolved so did clocks.

A crucial point in history came with the invention of the pendulum, attributed to the work of Galileo Galilei and Christiaan Huygens in the XVII century. The idea was to keep track of time using a swinging weight. Its frequency, dependent mostly on the length of the string holding the weight, was carefully studied and determined. In his Nobel lecture in 2006, Theodor Hänsch [2] gives an account of the evolution of precision measurements: Since the discovery of the pendulum clock time and frequency have been the quantities that we can measure with the highest precision. With the development of more sophisticated clocks it was discovered that through the measurement of frequency it was possible to indirectly measure other quantities and inherit, in the process, the same degree of precision. For this reason, his colleague and mentor, Arthur Schawlow advised his students to "Never measure anything but frequency!"

One of the main applications of precise clocks has been in navigation. During the XVII century, sailors that navigated through open seas realized that, to accurately determine their position it was necessary to measure time precisely. Through the precise determination of the time difference between the time at a reference point, such as the Greenwich meridian, and the ship's local time, the longitudinal position of the ship relative to the reference point could be calculated. To keep track of Greenwich's time a chronometer calibrated at the departure of the ship was used. To measure the local time, sextants were implemented. Sextants allowed the determination of coordinates of celestial objects from which the local time could be estimated. The local time of the ship was determined by comparing an accurate measurement of the angular distance between the moon and a fixed star to a set of pre-calculated tables. Given the rotation of the earth an error of four seconds in the determination of the time corresponds to an error of 1 nautical mile, equivalent to 1 minute of longitude or 1852 m in the east-west position. The very best pendulum clocks at that time had an accuracy of approximately 15 seconds per day. The performance of these chronometers was considerably affected when they were taken on board of ships in the open sea. Their frequency was affected by variations in temperature, pressure, humidity or by the movement of the boat in the sea. At that time, making a clock that was not only accurate but stable during long journeys in the sea, represented a formidable challenge [1].

It was not until the XVIII century, that the Harrison chronometer was developed. Using a fast-beating balance wheel controlled by a temperature-compensated spiral spring, this clock was easily transportable and only wrong by only 0.5 s per day [3]. Harrison observed that using high frequency oscillators he could increase the precision of his measurements. He also noticed that the variations of the oscillation frequency around its center, or its *linewidth*, should be as small as possible. The search for better marine chronometers established the ingredients that would lead to the development of modern clocks: the search for a high frequency oscillator with a narrow linewidth, that is either unaffected by the environment or whose perturbations are easy to characterize. The ratio of these two parameters defines the quality factor of an oscillator.

The next big step in time keeping technology came at the end of the 19th century with the discovery of quartz crystal oscillators. Based on electro-mechanical resonances, the oscillation period of these systems is faster and more stable than that of pendulum clocks. Quartz oscillators can achieve inaccuracies on the order of 1 second in 30 years. These kind of clocks have also the advantage that they can be easily miniaturized, making them available to be carried anywhere anytime. Unfortunately, quartz crystal oscillators do not exhibit a long-time stability and their natural oscillation frequency differs from one crystal to the other.

In 1879 a text written by Thomson (Lord Kelvin) and Tait introduced the idea of using the "time of vibration" of atoms as a frequency standard [4]. Atoms of the same species, as far as we know, show identical behavior, making them ideal clock candidates. With the discovery of quantum mechanics at the beginning of the 20th century, realizing this idea became a possibility. Quantum mechanics showed how the structure of atoms and molecules is composed by energy levels that can be accessed through absorption or emission of electromagnetic radiation at fixed frequencies. In an atomic clock, the natural frequency of a transition between two energy levels is used as reference to measure deviation of an external source. Depending on the atomic species chosen, the energy levels can be insensitive to external perturbations, making them a reliable and robust frequency reference. The beauty of using atoms as frequency standards relies on the fact that the clock oscillation should ideally be completely independent from any human influence, allowing identical atomic clocks to be

built anywhere.

The first prototype of an atomic clock, using the intense absorption line of the ammonia molecule lying at around 24 GHz, was devised in 1948 by H. Lyons [5] at the National Bureau of Standards in the USA, which is currently the National Institute of Standards and Technology (NIST). The resonance was broadened by the Doppler effect and collisions making its long term stability no better than that of a quartz clock. In 1945 I.I. Rabi introduced the idea of using a method he originally designed to probe the magnetic resonance of atoms as a way to probe atomic transitions using an oscillating magnetic field [6, 7]. This idea was further developed in 1950 by one of his students, Norman Ramsey, who added two separate oscillating fields [8]. In 1955, the first operational caesium atomic clock using *Ramsey spectroscopy* was built at the National Physical Laboratory [9]. Following the same ideas, the first masers (Microwave Amplification by Stimulated Emission of Radiation) using the ammonia molecular transition were designed by C. H. Townes in the USA and N. G. Basov and A. M. Prokhorov in the USSR, followed by the development of the hydrogen maser by Ramsey in 1959-1960. Further improvements implementing laser cooling techniques, reducing the thermal velocities from hundreds of meters per second to the scale of centimeter per second led to the realization of the fountain clock by another of Rabi's students, J.R. Zacharias [10]. The unrivaled precision and accuracy in time keeping provided by Cs clocks led to a new definition of time in 1967. The definition of the second today remains technically the same, except for some corrections that were added in 2019:

“The second, symbol s, is the SI unit of time. It is defined by taking the fixed numerical value of the caesium frequency $\Delta\nu_{Cs}$, the unperturbed ground-state hyperfine transition frequency of the caesium 133 atom, to be 9 192 631 770 when expressed in the unit Hz, which is equal to s^{-1} ”.

From this definition, time institutes around the world use Cs clocks to define their local contribution to the Universal Coordinated Time (UTC). This clock serves as a reference for all local dating procedures [9]. Each one of these clocks is regularly compared to each other and combined by the International Bureau of Weights and Measures (BIPM) for the realization of the International Atomic Time (TAI).

To characterize the performance of a clock it is necessary to determine its level of **precision** and **accuracy**.

- Precision is a measure of the (in)stability or the degree to which the time between "clock ticks" remains constant. The stability represents the repeatability of the measured clock frequency over an averaging time.
- Accuracy is a description of the systematic errors or how close the measured "tick frequency" is to the intrinsic frequency of the oscillator.

Ideally, the instability of clocks using atomic transitions is only limited by shot-noise. This type of noise is associated with events that have a discrete output, which means that they can be modeled by a Poisson process. In other terms, the shot-noise gives an estimate on the error associated to the probability that a given event has a specific output. Its value is dependent on the number of "shots": the more times a given measurement is repeated the smaller its uncertainty is. The stability is expressed

as the Allan deviation, in fractional frequency units $\sigma_y(\tau)$. The instability of a shot-noise limited clock, using the Ramsey method of separated fields [8] with a waiting-time between pulses $T_m \approx 1/(2\pi\Delta f)$ can be estimated using [4]

$$\sigma_y(\tau) = \frac{1}{2\pi f_0 \sqrt{NT_m\tau}}, \quad (1.1)$$

where τ is the total measurement duration, N the number of atoms or repetitions and f_0 the reference transition frequency. To reach lower instabilities in a shorter measurement time τ it is better to use a system with high frequency f_0 , many atoms or repetitions N and long probing times T_m associated with narrow-linewidths.

The accuracy of an atomic clock depends on the level at which the transition frequency is affected by the environment and on how well these perturbations can be characterized. To determine the accuracy it is necessary to characterize all the environmental effects that can perturb the oscillation frequency of the atomic transition. The shifts generated by the interaction of the particles with the surrounding are listed in the error budget. This list includes the influence of electric and magnetic fields as well as of relativistic effects. These shifts are dependent on the species, the experimental setup and the probing method implemented, they need to be minimized and carefully characterized.

Nowadays, Cs fountains operated in time and frequency institutes all over the world, exhibit an inaccuracy at the low 10^{-16} level [11]. Cesium clocks operate using a microwave oscillator. Examining equation 1.1, it might appear obvious, that the instability can be reduced by clocks with higher frequencies, in the optical regime or even further. However, to operate this kind of clocks, it was necessary to: On one side, develop the technology to trap, cool-down, and probe atomic species exhibiting transitions in the optical regime. On the other side, to develop the technology necessary to measure optical frequencies.

This is nicely summarized in the review "Standards of time and frequency at the outset of the 21st Century" by Diddams et al. [9]: First, it was necessary to lower the temperature of the atoms and ions to milikelvin temperatures and below. The use of cooled atoms enables the extension of interaction times, facilitating the observation of narrow transition linewidths [12]. This was possible with the implementation of laser cooling. Second, to resolve these narrow transitions, it was necessary to reduce the linewidth of the lasers. The implementation of optical reference cavities and stabilization techniques permitted to reduce the linewidth of laser to the subhertz level. With this technology it was feasible to measure frequency differences below 1×10^{-17} for a 1-day measurement [13]. Finally, it was necessary to design a practical way to measure frequencies in the optical regime. This was possible through the development of the modelocked femtosecond laser frequency comb [14]. With these three major ingredients, optical clocks became possible.

There are two leading architectures for optical clocks: optical lattice clocks and trapped ion clocks. As suggested by the name, optical lattice clocks use many atoms trapped and separated in an optical lattice formed by the interference of counter-propagating laser beams. The idea to use optical lattices was first introduced by Vladilen Lethokov in the 1960s. However, it was only implemented in the late 1980s, when a team, led by William Philips, discovered by accident that the laser-cooled atoms were being held in an optical lattice [15]. Trapped ion clocks, are composed by a single or few atomic ions captured in an electro-magnetic trap, designed by Paul and Dehmelt in the 1950s. At that time, single trapped ions promised the ideal environment for precision spectroscopy: an unperturbed system with long trapping times [4].

Both technologies differ in the benefits and challenges with respect to frequency stability and systematic effects. Optical lattice clocks operate with thousands of atoms, which intrinsically increases the signal to noise ratio compared to that of a single-ion clock. This leads to higher clock stability in shorter times. However, having a large amount of particles comes with the prize of a higher and more complex sensitivity to environmental effects compared with single-ion clocks. Optical lattice clocks need to characterize not only the environmental effects on each one of the atoms but also the effects due to the interactions between them.

During the last decade, both kinds of optical clocks have shown an outstanding development. As seen in Table 1.1, state of the art optical clocks are nowadays achieving fractional uncertainties in the low 10^{-18} range. One of the main challenges for optical lattice clocks is to properly characterize and control the black body radiation shift. This shift originates from the interaction of the atoms with the thermal electromagnetic radiation. The difficulty lies on one side on the proper stabilization of the temperature and on the other side on the maintenance of a uniform temperature distribution of the surrounding. To meet these challenges, these experiments implement an active in situ calibration of the temperature. They use a combination of in-vacuum sensors, with an uncertainty of 5 mK and in-vacuum radiation shields, characterized using precision thermometry and thermal modeling [16].

The work on this thesis is focused on the development of trapped ion clocks. As shown in Table 1.1, the two leading atomic species: $^{27}\text{Al}^+$ and $^{171}\text{Yb}^+$, are achieving uncertainties in the low 10^{-18} and below. The $^{27}\text{Al}^+$ ion clock transition has the advantage of being less affected by environmental perturbations, such as electromagnetic fields or black-body radiations. However, one of the main challenges faced by this type of clock lies on the control of the motion of the ion(s) in the trap. The oscillation of the ion in the trap induces two kinds of shifts on the ion's clock transition: Quadratic Stark shifts generated when the ion is exposed to oscillating electric shifts and second-order Doppler shifts caused by the difference between the atom's transition frequency in its frame of reference and the probing laser in the laboratory frame. To minimize these shifts, new trap designs have being implemented that allow the operation of these clocks close to the three-dimensional motional ground state [17]. The $^{171}\text{Yb}^+$ ion has a relatively high atomic mass, which ensures that its clock transition is less affected by the Doppler shift at standard operating temperatures. This ion has the advantage of having a quadrupole and an octupole transitions available. However, $^{171}\text{Yb}^+$ clocks are limited by the black body radiation shift. Experiments working with this ion-specie have implemented extensive evaluations of the thermal radiation of the ion trap and a careful determination of the difference of the scalar polarizabilities of the ground and excited states [18].

Clock Specie	Transition	Absolute frequency (Hz)	Systematic uncertainty (Hz)
$^{27}\text{Al}^+$	$^1\text{S}_0, F = 5/2 \leftrightarrow ^3\text{P}_0, F = 5/2$	1 121 015 393 207 859.50 (0.36) [19]	9.4×10^{-19} [17]
$^{171}\text{Yb}^+$	$^2\text{S}_{1/2}, F = 0 \leftrightarrow ^2\text{F}_{7/2}, F = 3$	642 121 496 772 645.10(8) [20]	3×10^{-18} [21]
^{87}Sr	$^1\text{S}_0 \leftrightarrow ^3\text{P}_0$	429 228 004 229 873.19(0.15) [19]	2×10^{-18} [16]
^{171}Yb	$^1\text{S}_0 \leftrightarrow ^3\text{P}_0$	518 295 836 590 863.71(11) [22]	1.4×10^{-18} [23]

Table 1.1: State of the art optical clocks

Optical clocks with trapped ions using other species such as $^{88}\text{Sr}^+$ and $^{40}\text{Ca}^+$ are reaching uncertainties in the 10^{-17} level and lower [24, 25, 26, 27, 28]. These species have the combined advantages of exhibiting an excellent performance of frequency uncertainty and instability, and a relatively simple level scheme. The transitions necessary to operate these clocks can be accessed with commercially available laser sources and high quality optics. Experiments exploring these ions species, as well as other species such as $^{138}\text{Ba}^+$ and $^{176}\text{Lu}^+$ offer a test-bed for new theoretical and experimental techniques leading to high accuracy measurements [29, 30, 31, 32, 33].

Nowadays, Caesium remains the unique primary frequency standard (PFS) with which the SI second can be realized [34]. However, as can be seen in Table 1.1, the estimated uncertainty of several optical frequency standards has now been established two orders of magnitude lower than the accuracy of the bests Cs primary standards, measured to be in the low 10^{-16} . One could assume that it is soon time for a redefinition of the second in terms of an optical clock transition. Following this idea, a set of guidelines have been defined by the Bureau de Poids et mesure (BIPM) towards the redefinition of the second [35]. One of the key milestones states that:

"The time for a new definition is right when optical frequency ratios between a few (at least five) other optical frequency standards have been performed; each ratio measured at least twice by independent laboratories and agreement was found to be better than $\Delta\nu/\nu = 5 \times 10^{-18}$."

The next step lies in the implementation of frequency ratio measurements between different optical clocks. Following these guidelines, over the past years, an effort between frequency institutes around the world has been made to develop the required technology to create optical clock networks. The challenge is to find ways to transmit a clock signal with the same level of accuracy and precision over long distances, ideally all over the world. As it was previously mentioned the International Atomic Time, TAI, is based upon data from 60 different laboratories around the world via satellites using the Global Navigation Satellite Systems (GNSS) [10]. Efforts to improve the performance of this links using techniques such as Precise Point Positioning PPP [36, 22, 37] and the Two-Way Satellite Time and Frequency Transfer (TWSTFT) have achieved frequency comparison between primary and secondary frequency standards with overall uncertainties at the 10^{-16} level [11]. Optical fiber links, established both in Europe and the United States of America have achieved an stability on the 10^{-19} regime over distances up to 920 km [38, 39]. Recently, with the implementation of a 1.5-kilometre free-space link parallelly to a fiber and satellite link, a collaboration in Boulder (BACON), reached a fractional stability and reproducibility at the 10^{-18} level comparing clocks based on $^{27}\text{Al}^+$, ^{87}Sr and ^{171}Yb [37]. A recent similar collaboration in Europe (QSNET) proposes the implementation of a network of clocks for measuring the stability of fundamental constants including next-generation molecular and highly charged ion clocks [40].

These measurements contribute not only to the absolute determination of the frequencies of the different clock transitions [19] but provide new tools in fundamental and applied science: the characterization of the geodesy below the centimeter level [23], detection of dark matter [37], possible violations of local position invariance or variations of the fine structure constant [20, 21] among others. As stated by Arthur Schawlow [2], our understanding and comprehension of the laws of nature might be only limited by how well we can measure frequency.

This thesis is focused on the development and characterization of optical clocks with trapped ions. Two different trapped ion clocks are presented: one with a single

$^{40}\text{Ca}^+$ and one with a $^{40}\text{Ca}^+ / ^{27}\text{Al}^+$ mixed ion crystal. In this thesis, the characterization of both kind of clocks as well as the environment that surrounds them is presented. The first two chapters are focused on the theoretical basis to operate optical clocks with trapped ions: Chapter 2 lays the theoretical foundation to trap, cool and interrogate ions. Chapter 3 introduces all the theoretical elements necessary to fully characterize the systematic frequency shifts that can be encountered when operating trapped ion clocks. Chapter 4 gives a detailed description of the experimental setup used during this work. The remaining chapters, are focused on three specific projects: Chapter 5 presents the installation and characterization of a GNSS link between the Institute for Quantum Optics and Quantum Information (IQOQI) in Innsbruck and the Physikalisch-Technische Bundesanstalt (PTB) in Germany. Using the Precise Point Positioning technique an absolute frequency measurement of the $4s\ ^2S_{1/2} \leftrightarrow 3d\ ^2D_{5/2}$ $^{40}\text{Ca}^+$ clock transition respect to the UTC(PTB) is presented. Chapter 6 describes the implementation of Quantum Logic Spectroscopy with a $^{40}\text{Ca}^+ / ^{27}\text{Al}^+$ mixed ion crystal. The technique is implemented to probe the $^1S_0 \leftrightarrow ^3P_1$ intercombination line at 267 nm. The transition is measured with respect to the $4s\ ^2S_{1/2} \leftrightarrow 3d\ ^2D_{5/2}$ $^{40}\text{Ca}^+$ clock transition. These measurements are used to characterize the Landé g-factor of the excited state $g_{^3P_1, F'=7/2}$. This chapter presents also the first observation of $^1S_0 \leftrightarrow ^3P_0$ $^{27}\text{Al}^+$ clock transition in our experimental setup. In Chapter 7 the ions are used to characterize the background gas in the chamber. The chapters explores the implementation of three different techniques to characterize the differential rate of background gas collisions. Each technique is centered in a different range of energies and when combined cover a large energy spectrum that could facilitate the characterization of the composition of the background gas in the chamber as well as the determination of the background gas collision shift. A brief summary and an outlook of future projects is given in Chapter 8.

Chapter 2

Trapped ions for precision experiments

“...One may say that one does not realize experiments with single particles, any more than one raises ichthyosaurs in the zoo.”
Erwin Schrödinger (1952)

The 1989 Nobel prize in Physics was awarded half jointly to Hans G. Dehmelt and Wolfgang Paul "for the development of the ion trap technique" and half to Norman F. Ramsey "for the invention of the separated oscillatory fields method and its use in the hydrogen maser and other atomic clocks"[41]. These three major discoveries defined the path towards the realization and operation of single particle systems. As far as I know, ichthyosaurs have still not been raised in zoos, however, single particle systems are now commonly operated in laboratories all over the world. Trapped ions offer the possibility to have an unperturbed system with long trapping time, the ideal platform for precision spectroscopy experiments. This chapter gives an overview of the theoretical elements necessary for the implementation of trapped ions for precision experiments.

2.1 Ion trapping

Ion trapping has been described in great detail in literature (see [42, 43]). The main goal of this section is to give a reminder to the reader of the key elements involved in the operation of trapped ion clocks with a single and a mixed ion coulomb crystal.

2.1.1 Single ion

As illustrated in Figure 2.1, typically a Paul trap is composed by two pairs of electrodes (RF-blades) that confine the ion in the radial or xy-plane by means of dynamic electric fields and by a pair of electrodes (end-caps) held at a static electric field to ensure the axial (z-direction) confinement. The combination of these fields creates a time-dependent quadrupole potential Φ where charged particles can be captured. As can be seen in Figure 2.1 and following [43], the trapping potential Φ can be approximated by the lowest-order terms of a Taylor expansion around the center of the trap. It can be decomposed in a dynamical radial contribution Φ_{rad} and a static axial contribution Φ_{ax} :

$$\begin{aligned}\Phi_{rad}(x, y, z, t) &= \frac{U_r + V_{RF} \cos(\Omega_{RF} t)}{2r_0^2} (\alpha_x x^2 + \alpha_y y^2 + \alpha_z z^2), \\ \Phi_{ax}(x, y, z) &= \frac{U_{DC}}{2z_0^2} (\beta_x x^2 + \beta_y y^2 + \beta_z z^2),\end{aligned}\tag{2.1}$$

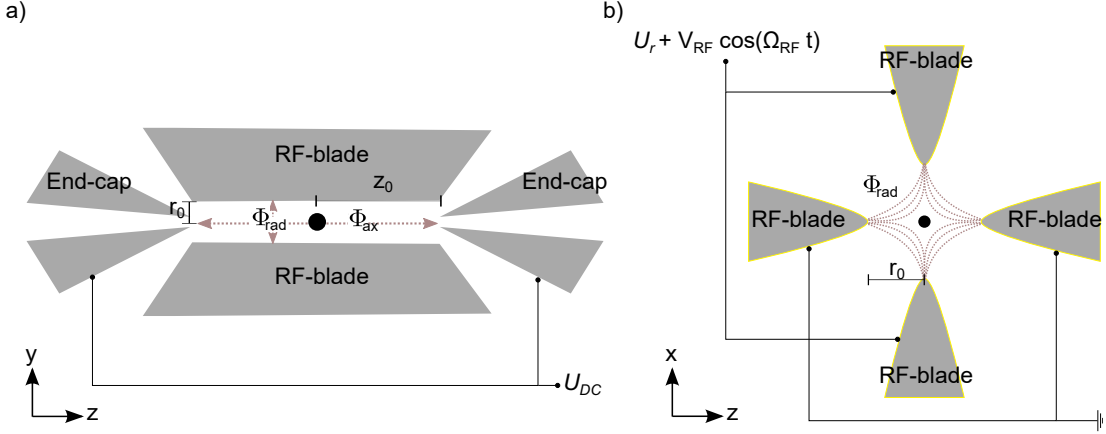


Figure 2.1: Schematic diagram of a linear Paul trap. The trap is composed by two pairs RF-blades and a pair of end-cap electrodes. A confining quadrupole potential Φ_{rad} in the xy -plane is created by a time-dependent voltage $U_r + V_{\text{RF}}\cos(\Omega_{\text{RF}}t)$ applied to one of the RF-blades pair. A DC voltage U_{DC} applied to the end-cap electrodes generates a static electric potential Φ_{ax} in the xz -plane along the z -axis. The trap center is located at a distance r_0 from the RF-blades and z_0 from the the end-cap electrodes.

where V_{RF} and Ω_{RF} correspond to the peak amplitude and the frequency of the applied RF field, U_r to a splitting voltage applied to the RF-blades, and U_{DC} to the voltage applied to the end-cap electrodes for the axial confinement. As illustrated in the figure, r_0 corresponds to the distance from the trap center to the RF-blades and z_0 the distance from the trap center to the end-cap electrodes. To trap an ion in an electromagnetic field, the Laplace equation $\Delta\Phi = 0$ needs to be satisfied for all times. To comply with this condition, the geometric factors α_i and β_i are bound by the relation $\sum_i \alpha_i = \sum_i \beta_i = 0$, which leads to the following relations:

$$\begin{aligned} \alpha_x &= -\alpha_y, \quad \alpha_z = 0, \\ -(\beta_x + \beta_y) &= \beta_z > 0. \end{aligned} \quad (2.2)$$

The classical motion of a particle with charge Q and mass m in the x direction can be described by:

$$\ddot{x} = -\frac{Q}{m} \frac{\partial \Phi}{\partial x} = -\frac{Q}{m} \left[(U_r + \cos(\Omega_{\text{RF}}t))\alpha_x x + \frac{U_{\text{DC}}}{z_0^2} \beta_x x \right] \quad (2.3)$$

and can be transformed to the standard form of the Mathieu equation

$$\frac{d^2 x}{d\tilde{\zeta}^2} + [a_x - 2q_x \cos(2\tilde{\zeta})]x = 0, \quad (2.4)$$

using the following substitutions:

$$\tilde{\zeta} = \frac{\Omega_{\text{RF}}t}{2}, \quad a_x = \frac{4Q}{m\Omega_{\text{RF}}^2} \left(\alpha_x \frac{U_r}{r_0^2} - \beta_x \frac{U_{\text{DC}}}{z_0^2} \right), \quad q_x = \alpha_x \frac{2QV_{\text{RF}}}{m\Omega_{\text{RF}}^2 r_0^2}. \quad (2.5)$$

The same approach can be used for the other directions y and z . Stable solutions in all three dimensions for a trapped particle can be estimated from the relations described in Equation 2.2. From these solutions, the experiment trapping parameters can be set.

In the limit that $a_i \ll q_i \ll 1$ the trajectory of the trapped particle is approximated to:

$$r_i(t) \approx A_i \cos(\omega_i t) \left(1 - \frac{q_i}{2} \cos(\Omega_{\text{RF}} t) \right), \quad (2.6)$$

with $i \in \{x, y, z\}$. We can see that the trajectory corresponds to a superposition of two motions: The first part of Equation 2.6 describes the so called *secular motion*, a harmonic oscillation with amplitude A_i and frequency $\omega_i = \Omega_{\text{RF}}/2 \cdot \sqrt{a_i + q_i^2/2}$, while the second part of the equation describes the fast driven oscillation at frequency Ω_{RF} denominated as "*micromotion*". Using the relations from Equation 2.2, the secular frequencies can be estimated as:

$$\begin{aligned} \omega_x &= \sqrt{\frac{\alpha_x Q U_r}{m r_0^2} + \frac{(q_x \Omega_{\text{RF}})^2}{8} - \frac{\omega_z^2}{4}}, \\ \omega_y &= \sqrt{-\frac{\alpha_x Q U_r}{m r_0^2} + \frac{(q_x \Omega_{\text{RF}})^2}{8} - \frac{\omega_z^2}{4}}, \\ \omega_z &= \sqrt{\frac{2\beta_x Q U_{\text{DC}}}{m z_0^2}}. \end{aligned} \quad (2.7)$$

From these equations we can see the effect of the axial trapping voltage U_{DC} on the radial modes: A stronger axial confinement increases the axial frequency and consequently decreases both radial frequencies. It is also clear that the application of a DC bias voltage U_r lifts the degeneracy of the two radial motional frequency ω_x and ω_y .

Another approach to describe the motion of the ion in the trap is by means of the so called secular approximation, which can be more convenient for the description of the normal modes of a two-ion crystal. In this approximation, the micromotion is neglected and the secular motion is reinterpreted as being generated by a harmonic potential of the form

$$\Psi = \sum_i \frac{1}{2Q} m \omega_i r_i^2. \quad (2.8)$$

For this case the ion's secular motion along the different axes can be estimated following [44] using the relations:

$$\begin{aligned} \omega_x &= \sqrt{\omega_p^2 - \alpha \omega_z^2}, \\ \omega_y &= \sqrt{\omega_p^2 - (1 - \alpha) \omega_z^2}, \\ \omega_z &= \sqrt{\frac{2Q\kappa U_{\text{DC}}}{m z_0^2}}, \end{aligned} \quad (2.9)$$

where κ is a geometric factor, $0 < \alpha < 1$ a parameter indicating the radial asymmetry of the static field, and

$$\omega_p = \frac{Q V_{\text{DC}}}{\sqrt{2} \Omega_{\text{RF}} m r_0^2} \quad (2.10)$$

is the contribution of the RF potential to the radial trap frequencies. The radial frequencies can be further simplified using the factor $\epsilon = \omega_p / \omega_z$:

$$\omega_x = \sqrt{\epsilon^2 - \alpha} \omega_z, \quad \omega_y = \sqrt{\epsilon^2 - (1 - \alpha)} \omega_z. \quad (2.11)$$

From this equation we can see that the parameters α and ϵ can be estimated experimentally through the measurement of the secular frequencies.

Quantum harmonic oscillator

A trapped ion in a quadratic potential in the quantum mechanical picture can be described as a harmonic oscillator in a static potential. Analogous to the classical case the Hamiltonian is

$$\mathcal{H}_{QHO} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2, \quad (2.12)$$

where $\hat{p}$ and $\hat{x}$ are the momentum and position operators of the ion. Introducing the creation and annihilation operators

$$a^\dagger = \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{x} - \frac{i}{m\omega}\hat{p} \right) \text{ and } a = \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{x} + \frac{i}{m\omega}\hat{p} \right), \quad (2.13)$$

the Hamiltonian takes the form

$$\mathcal{H}_{QHO} = \hbar\omega \left(a^\dagger a + \frac{1}{2} \right) = \hbar\omega \left(\hat{N} + \frac{1}{2} \right), \quad (2.14)$$

where $\hat{N}$ is the number operator. The eigenstates of the harmonic oscillator or *Fock states* indicate the number of phonons n in the system. As suggested by their names, the application of the creation or annihilation operator to a given state $|n\rangle$ raises or lowers its energy by one phonon, respectively:

$$a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle \text{ and } a|n\rangle = \sqrt{n}|n-1\rangle, \quad (2.15)$$

with $a|0\rangle = |0\rangle$. As shown in Figure 2.5, when this description is combined with the electronic levels, trapped ions appear to exhibit a ladder-like level structure.

2.1.2 Two-ion crystal

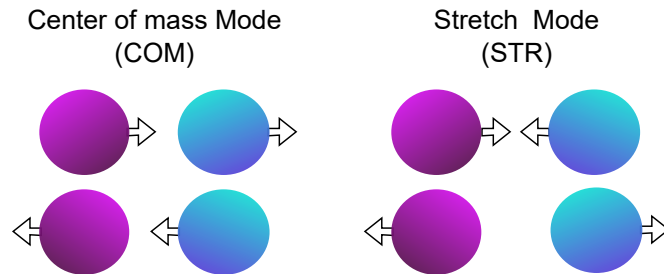


Figure 2.2: Collective motion of the two-ion crystal. There are two motional modes along each axis, the "center of mass" (COM) mode where the velocities of the two ions are in the same direction and the "stretch" (STR) mode where they are in the opposite direction.

The derivation of the normal modes of oscillation of a two-ion crystal are described in detail in [44]. In this section, as for the single trapped ion case, I will give a brief summary of the key elements.

When two ions are crystallized at near 0 K, they reach an equilibrium position along the trap z axis that is displaced from the trap center by a distance

$$z_{eq} = \left(\frac{Qd^2}{32U_{DC}\pi\epsilon_0} \right)^{1/3}. \quad (2.16)$$

As illustrated in Figure 2.2, the residual collective motion of the two-ion crystal around the equilibrium position is composed of two motional modes along each axis: The "center of mass" (COM or i) mode where the velocities of the two ions are in the same direction and the "stretch" (STR or o) mode where they are in opposite direction. Following the approach of [44], the motion q_1 and q_2 of each ion with masses m_1 and m_2 respectively along a chosen direction can be described with

$$\begin{aligned} q_1(t) &= z_i b_1 \sin(\omega_i t + \phi_i) + z_o b_2 \cos(\omega_o t + \phi_o) \\ q_2(t) &= \frac{z_i}{\sqrt{\mu}} \sin(\omega_i t + \phi_i) - \frac{z_o b_1}{\sqrt{\mu}} \cos(\omega_o t + \phi_o), \end{aligned} \quad (2.17)$$

where $\mu = m_2/m_1$ is a mass scaling factor, $\omega_{i,o}$, $\phi_{i,o}$ are the angular eigenfrequencies, and phases of the in-phase, and out-of-phase modes, and $b_{1,2}$ are the components of the normalized eigenvector of the in-phase mode such that $b_1^2 + b_2^2 = 1$. The $z_{i,o}$ factors correspond to the modal amplitudes. As explained in [44], the sum of the trap pseudopotential and the Coulomb potential generated from the ion-ion repulsion is developed around the equilibrium positions and the coupled equations of motions are solved in the lowest order. Neglecting higher order non-linear couplings, the result is the following set of equations:

$$\omega_{i,z} = \sqrt{\frac{1 + \mu - \sqrt{1 - \mu + \mu^2}}{\mu}} \omega_z, \quad (2.18)$$

$$\omega_{o,z} = \sqrt{\frac{1 + \mu + \sqrt{1 - \mu + \mu^2}}{\mu}} \omega_z, \quad (2.19)$$

$$b_{1,z}^2 = \frac{1 - \mu + \sqrt{1 - \mu + \mu^2}}{2\sqrt{1 - \mu + \mu^2}}, \quad (2.20)$$

$$\omega_{i,x,y} = \sqrt{-\frac{\mu + \mu^2 - \epsilon^2(1 + \mu^2) - a}{2\mu}} \omega_z, \quad (2.21)$$

$$\omega_{o,x,y} = \sqrt{-\frac{\mu + \mu^2 - \epsilon^2(1 + \mu^2) + a}{2\mu}} \omega_z, \quad (2.22)$$

$$b_{1,x,y}^2 = \frac{\mu - \mu^2 + \epsilon^2(-1 + \mu^2) + a}{2a}, \quad (2.23)$$

where

$$a = \sqrt{\epsilon^4(\mu^2 - 1)^2 - 2\epsilon^2(\mu - 1)^2\mu(1 + \mu) + \mu^2(1 + (\mu - 1)\mu)}. \quad (2.24)$$

2.2 Laser ion interaction

The core of trapped ion clocks relies on our ability to control and manipulate the state of ion(s) with lasers. Lasers are used not only to interrogate the clock transition, but

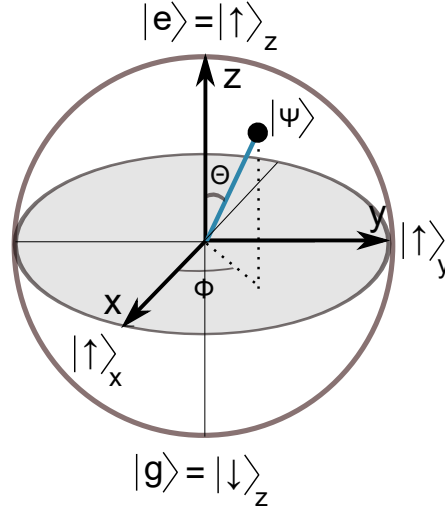


Figure 2.3: Bloch sphere: A tool to visually represent the state of a two-level system. A quantum state $|\Psi\rangle$ is represented by a *Bloch vector*, defined by the angles $(\theta$ and ϕ). Pure quantum states lie on the surface while fully mixed states lie at the center of the sphere. The ground $|g\rangle$ and excited $|e\rangle$ states are represented at the south and north pole of the sphere, respectively.

also to cool down the ion or to prepare it in any necessary quantum state. The following section focuses on the description of the interaction of an ion with laser radiation. A simplified model of a free two-level atom is introduced: the state of the ion is represented by two quantum states commonly denominated as ground $|g\rangle$ and excited $|e\rangle$ states. To visually represent the system's state, the so-called *Bloch sphere* representation is introduced. The second part of this section describes the interaction of the two-level system with light as well as the different types of transitions that are involved in the operation of the trapped-ion clock.

2.2.1 The Bloch sphere: a representation of a two-level atom

To study the interaction of the light with the atom a simplified model of a two-level system is used. Two distinguishable quantum states are identified; the ground state $|g\rangle$, or $|\downarrow\rangle$, and the excited state $|e\rangle$, or $|\uparrow\rangle$. In the quantum mechanical domain, the system can be in either of these two states or in a superposition state $|\Psi\rangle$ composed by a linear combination of the two

$$|\Psi\rangle = \alpha|g\rangle + \beta|e\rangle \quad (2.25)$$

where α and β are two complex numbers such that $|\alpha|^2 + |\beta|^2 = 1$. Here, $|\alpha|^2$ and $|\beta|^2$ correspond to the probabilities of find the state $|\Psi\rangle$ to be in the ground or excited state, respectively. The probability p that the system is in a given state can only be measured after a number of repetitions N with an uncertainty limited by the *quantum projection noise* [45], calculated using the following relation:

$$\Delta p = \sqrt{\frac{p(1-p)}{N}}. \quad (2.26)$$

A convenient way to rewrite Equation 2.25 is to identify the two levels as column vectors $|\downarrow\rangle_z = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $|\uparrow\rangle_z = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ and to use spherical coordinates. The state $|\Psi\rangle$ takes the following form

$$|\Psi\rangle = \cos\left(\frac{\theta}{2}\right) |\downarrow\rangle_z + e^{i\phi} \sin\left(\frac{\theta}{2}\right) |\uparrow\rangle_z, \quad (2.27)$$

where θ and ϕ are real numbers. This relation can be mapped onto the *Bloch sphere*, illustrated in Figure 2.3. Points on the surface of the sphere are identified by polar angles (θ and ϕ) corresponding to the values of the pure qubit state $|\Psi\rangle$. The north Pole ($\theta = 0$) is assigned to the excited state $|e\rangle$ and the south pole ($\theta = \pi$) to the ground state $|g\rangle$. The vectors lying on the x and y directions can be easily calculated using Equation 2.27

$$\begin{aligned} |\uparrow\rangle_x &= \frac{1}{\sqrt{2}}(|\uparrow\rangle_z + |\downarrow\rangle_z), \\ |\uparrow\rangle_y &= \frac{1}{\sqrt{2}}(|\uparrow\rangle_z + i|\downarrow\rangle_z). \end{aligned} \quad (2.28)$$

In this representation, rotations around the axes $\{x, y, z\}$ shown in Figure 2.3 can be described by means of the Pauli matrices [46]

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \text{and} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (2.29)$$

2.2.2 Two-level atom interaction with light

In the following, the interaction of a bare two-level atom with an electric field is described. The atom's energy is described by the Hamiltonian

$$\mathcal{H}_a = \frac{\hbar\omega_0}{2}\sigma_z, \quad (2.30)$$

where $\hbar\omega_0$ corresponds to the energy difference between the ground $|g\rangle = |\downarrow\rangle$ and excited $|e\rangle = |\uparrow\rangle$ states and σ_z is the Pauli Z operator. The Hamiltonian describing the perturbation of a two-level atom by an electric field $E = E_0\cos(\omega_l t + \phi_l)$, with a frequency ω_l close to resonance, a phase ϕ_l , and amplitude E_0 applied for a time t is

$$\mathcal{H}_l = \hbar\Omega\sigma_x\cos(\omega_l t + \phi_l). \quad (2.31)$$

When the laser is on resonance with the ion transition the population oscillates between the ground and excited state at the so-called *Rabi frequency* Ω . This frequency accounts for the coupling strength between the energy levels and the laser field. To have a better understanding of the laser-atom interaction, the joint Hamiltonian $\mathcal{H} = \mathcal{H}_a + \mathcal{H}_l$ is transformed to an interaction picture with respect to $\mathcal{H}_a$. After applying the rotating wave approximation, neglecting sum frequency terms that oscillate much faster than the time scale of the induced dynamics of interest, the interaction Hamiltonian takes the following form

$$\mathcal{H}_{int} = \hbar\frac{\Omega}{2} (\cos(\Delta \cdot t + \phi_l)\sigma_x + \sin(\Delta \cdot t + \phi_l)\sigma_y), \quad (2.32)$$

where $\Delta = \omega_l - \omega_0$ is the detuning of the laser frequency from the atomic transition. Using the electronic raising and lowering operators $\sigma_{\pm} = (\sigma_x \pm i\sigma_y)/2$, the Hamiltonian can be rewritten as

$$\mathcal{H}_{int} = \hbar \frac{\Omega}{2} \left(e^{-i(\Delta \cdot t + \phi_l)} \sigma_+ + e^{i(\Delta \cdot t + \phi_l)} \sigma_- \right). \quad (2.33)$$

From this expression we can distinguish two different cases; resonant and non-resonant interactions with the laser field.

Resonant laser field $\Delta = 0$

In this case the interaction takes the form of the unitary operation

$$\mathcal{U}(\theta, \phi_l) = e^{-i \frac{\mathcal{H}_{int} t}{\hbar}} = \begin{pmatrix} \cos \frac{\theta}{2} & -ie^{-i\phi_l} \sin \frac{\theta}{2} \\ -ie^{-i\phi_l} \sin \frac{\theta}{2} & \cos \frac{\theta}{2} \end{pmatrix}, \quad (2.34)$$

where $\theta = \Omega \cdot t$ corresponds to the *pulse area*. This has a geometric interpretation, in that θ represents the magnitude of a rotation of the state vector $|\Psi\rangle$ around an axis in the Bloch sphere which is determined by the optical phase ϕ_l in the equatorial plane. For the case of a laser on resonance to the atomic transition the rotation angle θ depends on the duration t for which the laser is applied and the Rabi frequency Ω , which in turn depends on the light intensity and coupling efficiency to the corresponding transition. A transfer of the population from $|g\rangle$ to $|e\rangle$ is commonly designated as a π -pulse, which is achieved by applying a resonant laser pulse for a duration $t = \pi/\Omega$. When the laser is continuously applied to the ion, a periodical exchange between both energy levels denominated as *Rabi oscillations* or *Rabi-flops* is observed, as illustrated in figure 2.4.

Non-resonant laser field $\Delta \neq 0$

For values close to resonance frequency, a population transfer between the ground and excited state is still observed. To estimate the probability p_e to excite the atom from the $|g\rangle$ to the $|e\rangle$ state as a function of the time t that a laser detuned by a frequency Δ interacts with the ion, the following expression can be derived from a solution of the optical Bloch equations [47, 48]:

$$p_e(t, \Delta) = \frac{\Omega^2}{\Omega^2 + \Delta^2} \sin^2 \left(\frac{\sqrt{\Omega^2 + \Delta^2} t}{2} \right) = \frac{\Omega^2}{\Omega_{eff}^2} \sin^2 \left(\frac{\Omega_{eff} t}{2} \right). \quad (2.35)$$

As shown in Figure 2.4, the non-resonant Rabi oscillations follow an effective Rabi frequency $\Omega_{eff} = \sqrt{\Omega^2 + \Delta^2}$ at a reduced amplitude $\propto \Omega^2/\Omega_{eff}^2$. In the figure, notice how for large detunings $\Delta \gg \Omega$ the population exchange is almost completely suppressed. Off-resonant fields are also responsible for shifts of the atomic levels. As it was previously described, the presence of oscillating electric fields induces so-called *AC-Stark shifts*. These shifts are described in a generalized frame in the context of the trapped ion systematic shifts in Section 3, however in this section their effect is introduced from the laser-ion interaction perspective.

AC-Stark shift To estimate the magnitude of *AC-stark shifts*, we transform our Hamiltonian to the interaction picture with respect to the frequency of the applied laser field.

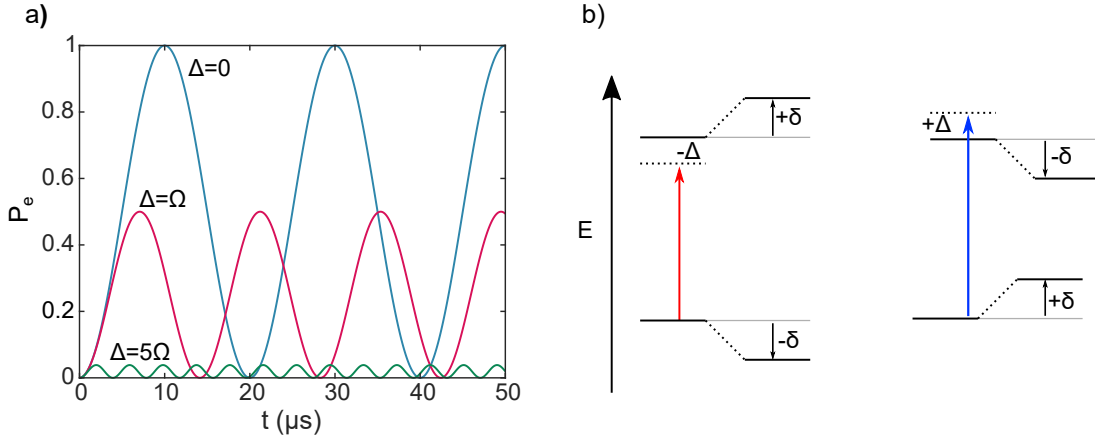


Figure 2.4: Resonant and non-resonant photon-ion interactions. a) Rabi oscillations with $\Omega = 2\pi \times 50$ kHz for different laser detunings: $\Delta = 0$ (blue), $\Delta = \Omega$ (pink), $\Delta = 5\Omega$ (green). b) Energy level shifts $\pm\delta$ induced by red detuned ($\Delta < 0$) or blue detuned ($\Delta > 0$) laser frequency with respect to the atomic transition.

The perturbation introduced by the laser field is expressed as

$$\mathcal{H}_{int}^{AC} = -\frac{\Delta}{2}\sigma_z + \frac{\Omega}{2}\sigma_x = \begin{pmatrix} -\Delta/2 & \Omega/2 \\ \Omega/2 & \Delta/2 \end{pmatrix}. \quad (2.36)$$

The eigenvalues $\lambda_{\pm} = \pm\frac{\hbar}{2}\sqrt{\Omega^2 + \Delta^2}$ determine the energy shift:

$$\delta = \lambda_{\pm} - \lambda_{\pm}(\Omega = 0) = \pm\frac{\Omega^2}{4\Delta}. \quad (2.37)$$

As illustrated in Figure 2.4, the detuning Δ determines the sign of δ for the individual energy levels. The overall AC-Stark shift Δ for a detuned laser is

$$\Delta E_{AC} = -\frac{\Omega^2}{2\Delta} \quad (2.38)$$

Rabi frequency

The *Rabi frequency* Ω accounts for the coupling strength between the light and the atomic transition and for the amplitude of the light's electric field. This coupling mechanism is dependent on the type of atomic transition. In the context of trapped ion clocks, electric dipole and quadrupole transitions need to be considered.

Electric dipole transition The Rabi frequency Ω of an electric dipole transition is defined by the dipole matrix element

$$\Omega_{dip} = \frac{1}{\hbar} \langle g | \vec{d} \cdot \vec{E} | e \rangle, \quad (2.39)$$

where $\vec{d} = e\vec{r}$ is the induced dipole moment and $\vec{E}$ is the light's electric field at the position of the atom. Following [49], the decay rate of the excited state for a two-level

system can be calculated using

$$\Gamma = \frac{\omega_0^3}{3\pi\epsilon_0\hbar c^3} |\langle g | \vec{d} \cdot \vec{E} | e \rangle|^2. \quad (2.40)$$

Combining this equation with Equation 2.39, the Rabi-frequency for a dipole transition can be calculated using

$$\Omega_{dip} = \sqrt{\frac{3\pi\epsilon_0\hbar c^3\Gamma}{\omega_0^3}} |E| = \sqrt{\frac{3\pi c^2\Gamma I}{\omega_0^3}}, \quad (2.41)$$

where the intensity is related to the magnitude of the electric field by $I = 2\epsilon_0 c |E|^2$. The Stark-shift by far-detuned light from dipole transitions is

$$\Delta E_{AC}^{dip} = \pm \frac{3\pi c^2}{2\omega_0^3} \frac{\Gamma}{\Delta} I. \quad (2.42)$$

For a multi-level atom with transition substructure, it is necessary to include the dipole matrix elements $\mu_{ij} = \langle e_i | \mu | g_i \rangle$ between specific electronic ground states $|g_i\rangle$ and excited states $|e_i\rangle$. Following [49], the specific transition matrix element

$$\mu_{ij} = c_{ij} ||\mu||, \quad (2.43)$$

can be written as a product of a reduced matrix element $||\mu||$ and a real transition coefficient c_{ij} . The fully reduced matrix element is dependent on the electronic orbital wave functions and is related to the spontaneous decay rate. The coefficients c_{ij} take into account the coupling strength between specific sub-levels i and j of the electronic ground and excited state, depend on the laser polarization, the electronic and nuclear angular momenta involved. The energy shift on an electronic ground state $|g_i\rangle$ can be calculated using

$$\Delta E_{AC}^{dip} = \pm \frac{3\pi c^2\Gamma}{2\omega_0^3} I \times \sum_j \frac{c_{ij}^2}{\Delta_{ij}}, \quad (2.44)$$

where the summation is carried out over all electronically excited states $|e_j\rangle$. c_{ij}^2 corresponds to the relevant line strengths and Δ_{ij} to the respective detuning.

Electric quadrupole transition The electromagnetic coupling strength for a quadrupole transition is defined by the interaction of the atomic quadrupole moment $\hat{Q}$ with the electric field gradient, as described by the Hamiltonian: $\mathcal{H}_l = \hat{Q} \cdot \nabla E$. Following the derivation in [50, 51], the Rabi frequency is

$$\Omega_{quad} = \frac{eE}{2\hbar} \sqrt{\frac{15\lambda^3\Gamma}{c\alpha_0 8\pi^3}} \Lambda(m_g, m_e) g_{\Delta m_j}, \quad (2.45)$$

where α_0 is the fine structure constant, Γ the spontaneous decay rate (or natural line width) of the excited state, λ the laser wavelength, $\Lambda(m_g, m_e)$ are the corresponding Clebsch-Gordan coefficients of the transition with corresponding Zeeman sublevels m_g , and m_e [46] and $g_{\Delta m_j}$ is the geometric factor that accounts for the polarization and the angle between the laser beam's wave vector and the defined quantization axis [52, 53]. Given that the Rabi frequency for electric quadrupole transitions depends on the experimental conditions, it is easier to estimate directly the coupling strength by

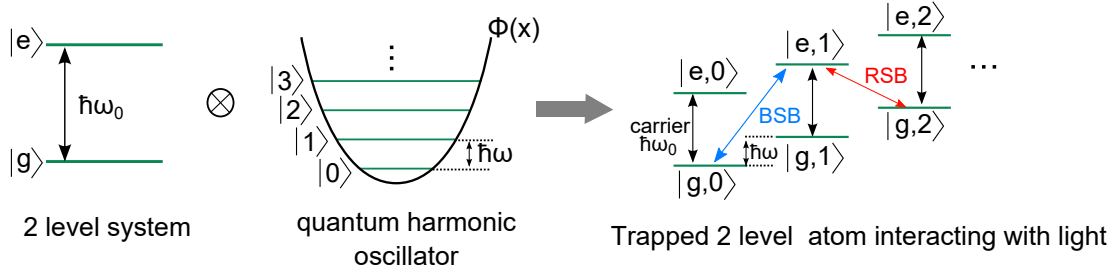


Figure 2.5: Trapped two-level atom interacting with light. The combination of the two-level system with the quantum harmonic oscillator picture reveals the ladder-like structure of the trapped two-level atom interacting with light.

experimentally measuring the Rabi oscillation frequency. Once the coupling strength is determined, the AC-Stark shift for quadrupolar transitions can be estimated using Equation 2.38.

2.3 Trapped two-level atom interaction with light

To have a full description of the interaction of a trapped ion with a laser it is necessary to combine the two pictures described in the previous sections. As illustrated in Figure 2.5, the combination of the simplified two-level system (Section 2.2) with the quantum harmonic oscillator picture (Section 2.1.1) reveals a ladder-like structure. The oscillating motion of the ion in the trap at a frequency ω affects the phase ϕ_l of the incident light field as a function of the ion's position. The Doppler shift caused by the motion of the ion results in an effective frequency modulation of the incident light: motional sideband transitions appear at $\omega_0 \pm \omega$. As illustrated in Figure 2.5, the red and blue sidebands at each side of the carrier give access to the ion's electronic and external degrees of freedom. As expected, the Hamiltonian describing the interaction of the laser with the trapped ion includes all the terms described in the previous sections:

$$\begin{aligned}\mathcal{H} &= \mathcal{H}_a + \mathcal{H}_l + \mathcal{H}_{QHO} \\ &= \frac{\hbar\omega_0}{2}\sigma_z + \hbar\Omega(\sigma_+ + \sigma_-)\cos(k\hat{x} - \omega_l t - \phi_l) + \hbar\omega(a^\dagger a + \frac{1}{2}),\end{aligned}\quad (2.46)$$

where ω_0 corresponds to the bare atomic transition frequency, ω to the oscillation frequency of the ion in the harmonic potential, and k and ω_l to the lasers wave vector and frequency respectively. Following the same approach as in section 2.2, the Hamiltonian is transformed to the interaction picture with respect to the atomic terms $\mathcal{H}_a + \mathcal{H}_l$ and the rotating wave approximation is implemented. Terms which oscillate at optical frequencies are neglected, giving

$$\mathcal{H}_{int} = \frac{\hbar\Omega}{2} \left(\sigma_+ e^{-i(\Delta t + \phi_l)} e^{i\eta(ae^{-i\omega t} + e^{a^\dagger i\omega t})} + \sigma_- e^{i(\Delta t + \phi_l)} e^{-i\eta(ae^{-i\omega t} + e^{a^\dagger i\omega t})} \right), \quad (2.47)$$

where η is the *Lamb-Dicke* parameter that relates the position operator $\hat{x}$ to the creation and annihilation operators $a, a^\dagger$ by

$$k\hat{x} = \eta(a + a^\dagger). \quad (2.48)$$

The Lamb-Dicke parameter accounts for the ratio of the ion's ground state wave packet size x_0 and both the laser's wavelength and the propagation angle θ respect to the

ion's direction of motion. The Lamb-Dicke parameter estimates how well the laser light field couples to the ion's motion in the harmonic trap:

$$\eta = |\mathbf{k}| \cos(\theta) x_0 = |\mathbf{k}| \cos(\theta) \sqrt{\frac{\hbar}{2m\omega}}. \quad (2.49)$$

If the extension of the wave function is small compared to the laser wavelength, such that $\eta^2(2\bar{n} + 1) \ll 1$, which occurs if the mean phonon number $\bar{n}$ is small enough that the coupling of the laser to the motional state is not too strong, the ion is said to be in the Lamb-Dicke regime. In this regime the exponential term in $\mathcal{H}_{int}$ can be simplified using a Taylor expansion:

$$e^{i\eta(ae^{-i\omega t} + a^\dagger e^{i\omega t})} = \mathbb{1} + i\eta(ae^{-i\omega t} + a^\dagger e^{i\omega t}) + \mathcal{O}(\eta^2). \quad (2.50)$$

Using this simplification, the interaction Hamiltonian takes the form

$$\mathcal{H}_{int} = \frac{\hbar\Omega}{2} \left(\sigma_+ e^{-i(\Delta t + \phi_l)} \left[\mathbb{1} + i\eta(ae^{-i\omega t} + a^\dagger e^{i\omega t}) + \mathcal{O}(\eta^2) \right] + h.c. \right) \quad (2.51)$$

In the resolved sideband regime ($\omega \gg \Omega$), a second rotating wave approximation can be performed, neglecting terms equal or higher than ω . From this approximation, three types of transition can be distinguished depending on their detuning Δ with respect to the resonant transition:

- **Carrier transition $\Delta = 0$:** The Hamiltonian takes the form:

$$\mathcal{H}_{car} = \frac{\hbar\Omega_{n,n}}{2} \left(\sigma_+ e^{-i\phi_l} + \sigma_- e^{i\phi_l} \right). \quad (2.52)$$

Represented as black arrows in Figure 2.5. It couples $|g, n\rangle \leftrightarrow |e, n\rangle$ with a strength $\Omega_{n,n} = \Omega(1 - \eta^2 n)$.

- **Red sideband transition $\Delta = -\omega$:** The Hamiltonian takes the form:

$$\mathcal{H}_{rsb} = \frac{i\hbar\Omega_{0,0}}{2} \left(e^{i\phi_l} a \sigma_+ - e^{-i\phi_l} a^\dagger \sigma_- \right). \quad (2.53)$$

Represented as red arrows in Figure 2.5, the excitation of this transition reduces the motional quantum number n . It couples $|g, n\rangle \leftrightarrow |e, n-1\rangle$ with a strength $\Omega_{n-1,n} = \eta\sqrt{n}\Omega$.

- **Blue sideband transition $\Delta = \omega$:** The Hamiltonian takes the form:

$$\mathcal{H}_{bsb} = \frac{i\hbar\Omega_{0,0}}{2} \left(e^{i\phi_l} a^\dagger \sigma_+ - e^{-i\phi_l} a \sigma_- \right). \quad (2.54)$$

Represented as blue arrows in Figure 2.5, the excitation of this transitions increases the motional quantum number n . It couples $|g, n\rangle \leftrightarrow |e, n+1\rangle$ with a strength $\Omega_{n,n+1} = \eta\sqrt{(n+1)}\Omega$.

Each one of these transition can be interrogated, provided that the linewidth of the laser is small compared to the trap frequency. Sideband transitions act as mediators between the internal and external degrees of freedom of the trapped ion, giving us the possibility to manipulate the ion's state. As it was described in Section 2.1.2, when there is more than a single ion in the trap potential, each ion influences each of the others through their Coulomb interaction. For N ions, a total of $3N$ sidebands are observed. By means of the sideband frequencies, the spin excitation of one ion in the

chain can be transferred to any other ion in the chain that shares the motional mode. The collective motion of the ions is used as a bus system to mediate the interaction between the ions in the trap. Quantum logic spectroscopy, a technique described in Section 2.4.3, allows the interrogation of species that do not have a suitable detection transition and relies on this motional "bus system" of communication between two or more ions in a trap.

2.4 Spectroscopy

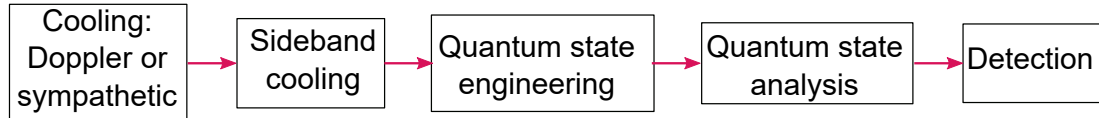


Figure 2.6: Pulsed sequence. commonly used to perform spectroscopic investigations. Once the ion is captured in the trap it is cooled to its ground state using Doppler or sympathetic cooling followed by sideband cooling. The next step prepares the ion in the desired state by means of quantum state engineering. Finally a set of pulses is implemented to probe the quantum state of the ion and detect it through the observation of the ion's fluorescence.

Spectroscopic experiments, implemented to measure the resonance frequency of a trapped ion, commonly follow the pulsed scheme described in Figure 2.6. The scheme is summarized in the following steps:

- **Doppler cooling:** A fast cycling transition is used to cool down the ion. Sometimes depending on the ion's energy level scheme, the cooling laser is used in conjunction with a repumper laser to pump out any undesired state that the ion might decay and make sure that the ion stays in the cooling-detection cycle. The minimum temperature depends on the linewidth Γ of the cooling transition $T_D = \hbar\Gamma / (2k_B)$ and is achieved at a detuning of $-\Gamma/2$ [54].
- **Sympathetic cooling:** In the absence of a "good" cooling transition, the ion is trapped jointly with one or more ions from a different species that can be Doppler cooled. Through the strong mutual electro-static interaction between both ion species, the laser-cooled ion *sympathetically* cools down the ion that does not interact with the cooling laser [44, 55].
- **Sideband cooling:** The narrow linewidth of a clock transition is used to create a sideband-resolved cooling cycle that prepares the ion with high probability in the motional ground state [56, 57]. The clock laser is set to be on resonance with the motional red sideband (RSB), as illustrated in Figure 2.5, with the help of an auxiliary laser that "extinguishes the excitation", using an auxiliary state, from which a spontaneously emitted photon at 393 nm provides the desired energy dissipation. The ion decays back to the lower electronic state, emitting a phonon. The cycle is repeated until the motional ground state is achieved and coupling to a RSB transition is no longer possible.
- **Quantum state engineering:** A set of pulses is used to manipulate the quantum state of the ion(s) to prepare the system in the configuration necessary to probe the clock transition.

- **Quantum state analysis:** Two types of pulse sequences are commonly implemented: *Rabi spectroscopy*, composed of a single π -pulse or *Ramsey spectroscopy*, using two $\pi/2$ -pulses separated by a waiting time. Both spectroscopy methods are described in detail in the following subsections (2.4.1 and 2.4.2). For the case of ion species with no proper cooling and detection transition, quantum logic spectroscopy is implemented. This method, described in detail in the next subsection 2.4.3, takes advantage of the collective motional mode of two different ions to transfer the information from one ion to the other [58].
- **Detection:** The fast transition used for Doppler cooling is excited and used to monitor the fluorescence of the ion for several milliseconds. The number of counts detected permits a discrimination of whether the ion is in the ground or excited state.

2.4.1 Rabi spectroscopy

In the 1930s, Isidor Isaac Rabi developed and pioneered a new method for measuring the nuclear magnetic moment [6, 7]. The so called *molecular-beam magnetic resonance method* used to measure the Larmor frequency consists of three different stages. In the first stage, atoms are passed through an inhomogeneous magnetic field that splits the beam into either the spin up or spin down state. The sequence is followed by the selection of one of the two beams which is then sent through the second stage. In this section the atoms are exposed to a rotating field whose frequency ω is scanned. When the frequency matches the Larmor frequency, the state of the atoms undergoes population inversion. The state is then detected when the atoms pass through the third stage where another inhomogeneous magnetic field is applied. We can adapt this method to trapped ions. The ion is first prepared in a initial given state. In the second stage, the ion is probed with a pulse for which frequency and length can be varied. Finally, in the third stage, fluorescence state detection is implemented. The transition frequency is measured by sweeping the frequency of the probing pulse using a fixed length that assures a maximum excitation (commonly denominated as π -pulse). A maximum or minimum (depending on the chosen state) fluorescence is detected when the resonance frequency is reached. The sequence is illustrated in Figure 2.7. If the π -pulse is on resonance with the transition, the ion initially prepared in the ground state $|\downarrow\rangle_z$ is excited to the $|\uparrow\rangle_z$ of the Bloch sphere (solid pink line). The excitation probability of the ion as a function of the detuning can be determined using Equation 2.35. The *Rabi pattern* obtained is illustrated in Figure 2.7 and 2.8. Examining at the points P_A and P_B in Figure 2.8 and Equation 2.35, we can see that the detuning frequencies for which the excitation is halved ($\pm\Delta\nu$) correspond to the points where the pattern has the steepest slope with respect to the detuning (solid green lines in the figure). Measurements at these points are more sensitive to frequency variations and are used during the so-called *Rabi-experiments* to determine frequency variations. The excitation probability in the points P_A and P_B is measured and the detuning $\Delta\nu$ is determined using:

$$\Delta\nu = \frac{(P_B - P_A)}{2} \left(\frac{1}{\frac{\partial p_e}{\partial \Delta\nu}} \right), \quad (2.55)$$

where $\frac{\partial p_e}{\partial \Delta\nu}$ corresponds to the slope of the pattern at the two measuring points, obtained from the partial derivation of Equation 2.35. The central peak of the pattern gets narrower for longer interrogation times, demonstrating the Fourier transform relationship between the time and frequency domain in spectroscopy. The interrogation

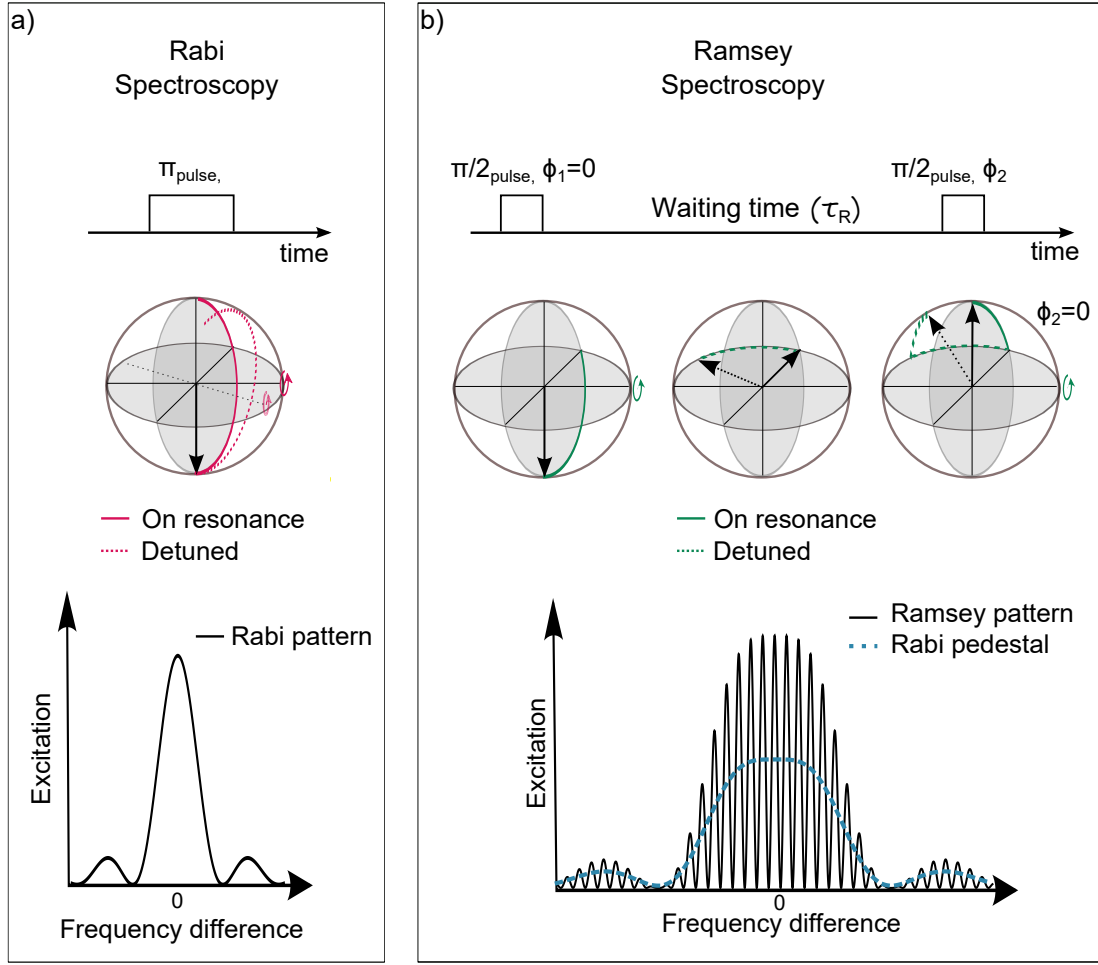


Figure 2.7: Illustrative summary of the Rabi and Ramsey spectroscopy methods. **a) Rabi spectroscopy:** The frequency of a single π -pulse is scanned. If the frequency is on resonance with the transition, the Bloch vector (black arrow) gets rotated from south to north (solid pink line), which is equivalent to the initially prepared state being excited with the highest probability (maximum point on the pattern). When the frequency is not on resonance, the rotation is no longer through the centered axis (dotted pink line), so the vector does not reach the north point of the sphere. However, the measured projection corresponds to the excitation probability as a function of the detuning obtained using Equation 2.35. **b) Ramsey spectroscopy.** The sequence consists of two $\pi/2$ pulses separated by a waiting time τ_R . The first pulse rotates the Bloch vector into the equatorial plane of the sphere where the ion is in a superposition state of the ground and excited state. During the waiting time, the system is let to evolve freely. If the laser is on resonance with the transition the second pulse rotates the vector to the north pole (solid green line). If the laser is not on resonance, any detuning $\Delta\omega$ from the resonance will rotate the Bloch vector during the waiting time by an amount $\delta = \Delta\omega\tau_R$ (dotted green line). In this case, the second pulse rotates the vector into a measurement basis. The Ramsey pattern illustrates how the measured probability of excitation evolves depending on the detuning for a given waiting time.

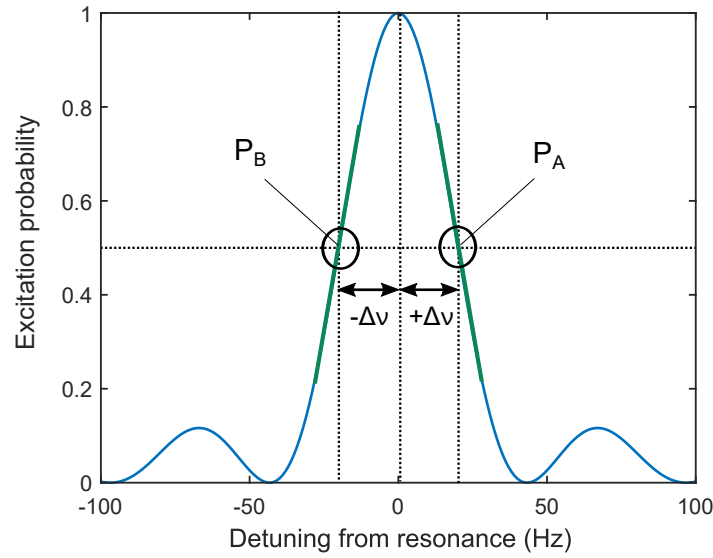


Figure 2.8: Illustration of Rabi experiments. The theoretical solid blue line is obtained using Equation 2.35. The points P_A and P_B correspond to the frequencies at which the excitation probability is halved. At these points the slope of the pattern (green solid line), calculated by evaluating the partial derivation of Equation 2.35 at the two respective points, is maximum. These two points have the optimal sensitivity to detect frequency variations as a function of the excitation probability.

time is limited by higher motional excitation or decoherence processes, such as electric or magnetic field noise. This can be observed as a damping of the Rabi oscillations over time, which consequently reduces the contrast of the Rabi pattern. It is also important to notice that when implementing this technique, care needs to be taken to minimize and characterize any intensity fluctuations of the laser source.

Figure 2.9 shows two measured Rabi patterns on the $^{40}\text{Ca}^+ S_{1/2}, m_j = 1/2 \leftrightarrow D_{5/2}, m_j = 1/2$ transition using a pulse length of 5.3 ms and 40 ms. The experimental points in green and pink, respectively, match the theory predictions shown in purple and blue obtained using Equation 2.35. The linewidth of the pattern becomes narrower at longer interrogation times. A slight reduction of the contrast in Figure 2.9b) can be explained by the presence of electric or magnetic field noise during the measurement.

2.4.2 Ramsey spectroscopy

The Ramsey spectroscopy method of separated oscillatory fields was invented by Norman Ramsey [8], a student of Isidor Isaac Rabi. Ramsey introduced a variation to Rabi's spectroscopy method: The single probing section is split into two very short interaction zones, each applying a $\pi/2$ -pulse, separated in space by a non-interacting zone. As illustrated in Figure 2.7 b, when the method is applied to trapped ions, two $\pi/2$ pulses are separated by a waiting time τ_R . In simple terms, the first pulse puts the ion in a superposition state of the ground and excited states, then is let free to evolve. Its evolution during the waiting time depends of the electromagnetic variations that surround the ion. Finally a second pulse maps any variation that altered the state of the ion to the energy eigenstate basis.

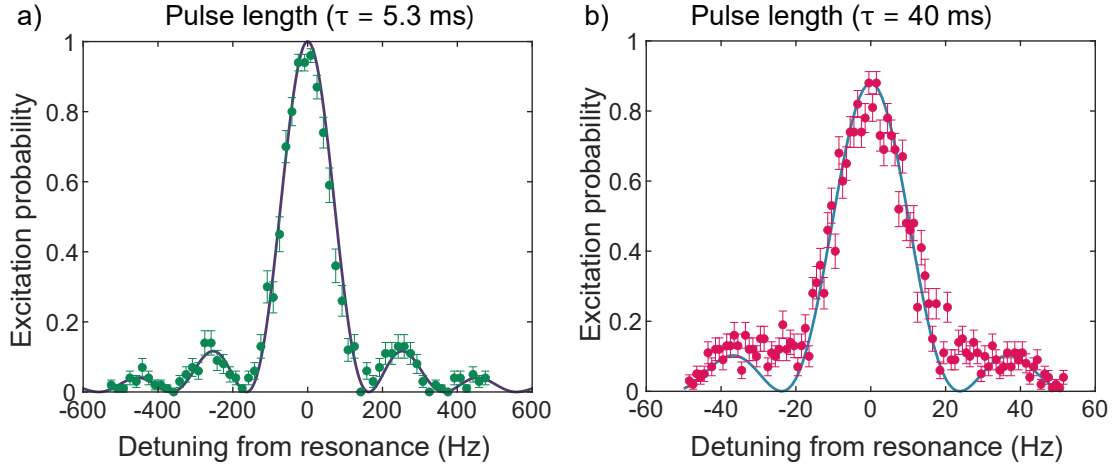


Figure 2.9: Rabi patterns on the $^{40}\text{Ca}^+ \text{S}_{1/2}, m_j = 1/2 \leftrightarrow \text{D}_{5/2}, m_j = 1/2$ transition with a: a) 5.3 ms and b) 40 ms pulse length. The green and pink points are measured experimentally with the corresponding error bars obtained from the quantum projection noise. The purple and blue solid lines correspond to the theoretical prediction using Equation 2.35. A slight reduction of the contrast can be explained by the presence of electric or magnetic field noise during the measurement.

In a more formal description, as shown in the Figure 2.7 b, the ion starts in the electronic ground state $|\downarrow\rangle_z$ and the first $\pi/2$ pulse rotates the vector into the Bloch sphere's equatorial plane in the state $|\uparrow\rangle_y$. Here the ion is in an equal superposition of the ground and excited state. During the Ramsey waiting time τ_R , the system freely evolves and can be described by the state vector

$$|\Psi\rangle = \frac{1}{\sqrt{2}}(|\downarrow\rangle_z + ie^{i\omega_0\tau_R}), \quad (2.56)$$

where ω_0 corresponds to the transition frequency. In a rotational frame with respect to the ion's transition frequency, the vector takes the form

$$|\Psi\rangle = \frac{1}{\sqrt{2}}(|\downarrow\rangle_z + ie^{-i\Delta\omega\tau_R}|\uparrow\rangle_z). \quad (2.57)$$

The state rotates in the equatorial plane around the z-axis by an amount $\delta = \Delta\omega\tau_R$ where $\Delta\omega$ corresponds to the detuning between the laser and the transition. The detuning can either be caused by variations of the atomic transitions due to interaction with the environment or by the laser variations (drifts or fluctuations). As illustrated by the dotted green line in Figure 2.7 b, the Bloch vector picks up a phase, according to the detuning and as long as the laser is on resonance (solid green line) the vector remains stationary. The second $\pi/2$ pulse rotates the state vector back onto the measurement basis. If there is no difference between the phase ϕ_1 of the first pulse and ϕ_2 of the second pulse, the state vector ends in $|\uparrow\rangle_z$. If the phase difference is π , it would go back to $|\downarrow\rangle_z$. The phase accumulated during the waiting time is then related to the mean excitation probability at the end of the experiment and can be easily measured by looking at the emitted fluorescence. With knowledge of the Ramsey time τ_R , the detuning frequency can be directly extracted. The transition probability can be calculated as a function of the detuning Δ for a pulse length τ [59] using the

following expression:

$$P(\Delta\omega) = \frac{4\Omega}{\sqrt{\Omega^2 + \Delta\omega^2}} \sin^2\left(\frac{1}{2}\sqrt{\Omega^2 + \Delta\omega^2}\tau\right) \left[\cos\left(\frac{1}{2}\sqrt{\Omega^2 + \Delta\omega^2}\tau\right) \cos\left(\frac{1}{2}\Delta\omega\tau_R + \phi\right) - \frac{\Delta\omega}{\sqrt{\Omega^2 + \Delta\omega^2}} \sin\left(\frac{1}{2}\sqrt{\Omega^2 + \Delta\omega^2}\tau\right) \sin\left(\frac{1}{2}\Delta\omega\tau_R + \phi\right) \right]^2, \quad (2.58)$$

where $\phi = \phi_2 - \phi_1$ is the phase difference between the two pulses and Ω is the Rabi frequency. The characteristic Ramsey pattern, illustrated in Figure 2.7, shows the appearance of fringes with a periodicity $1/\tau_R$. The so-called Rabi pedestal, illustrated with blue dashed lines in Figure 2.7, corresponds to the Fourier transform of the rectangular pulse distribution and can be calculated by replacing the rapidly oscillating terms in Equation 2.58 by their mean values

$$P_{Rabi} = \frac{\Omega}{2\sqrt{\Omega^2 + \Delta\omega^2}} \left(\sin^2(\Omega\tau) + \frac{\Delta\omega^2}{\Omega^2} (1 - \cos(\Omega\tau))^2 \right). \quad (2.59)$$

Figure 2.10 shows an example of a Ramsey pattern of the $^{40}\text{Ca}^+ \text{S}_{1/2} \leftrightarrow \text{D}_{5/2}$ transition. The pink points represent the measured excitation as a function of the laser detuning for Ramsey pulses of 100 μs duration and a waiting time of 5 ms. The data is fitted using Equation 2.58 (solid blue line) and the Rabi pedestal is obtained using Equation 2.59 (solid green line).¹ The standard deviation of the residuals between the measured excitation and the theory fit is equal to 0.04, which is in agreement with the expected deviation due to quantum projection noise, indicating great agreement between the theory and the experiment. The deviations can most likely be explained by magnetic field fluctuations during the measurement. The figure illustrates the theory previously described, and we can see the appearance of the *Ramsey fringes* with a periodicity $1/\tau_R = 200$ Hz. Also seen in the figure is that the maximum excitation probability in the data taken does not reach the value of 1. This is due to a loss of contrast caused by decoherence effects such as laser phase noise or magnetic field fluctuations. To estimate the detuning using Ramsey experiments, we start by simplifying Equation 2.58 by considering the case where $\Delta \ll \Omega$:

$$P(\Delta\omega) = \frac{1}{2} \left[1 + \cos\left(\Delta\omega\left(\tau_R + \frac{4\tau}{\pi}\right) + \phi\right) \right] \sin^2(\Omega\tau). \quad (2.60)$$

From this equation, it is clear when the phase difference between the two $\pi/2$ pulses is 0 ($\phi = 0$) and the laser is on resonance with the ion transition frequency ($\Delta\omega = 0$). Figure 2.11 a) shows the variations of the excitation probability in a Ramsey experiment when the laser frequency is on resonance with the transition ($\Delta\omega = 0$) but the phase of the second pulse (ϕ_2) is varied. It is clear that a maximum probability is achieved when the phase is equal to 0 and it is reduced to half for a phase of $\pm\pi/2$. Phase shifts δ , accumulated during the waiting time, shift the fringe pattern left or right depending on their sign. Figure 2.11 b) shows how as the frequency is scanned, if the phase difference between the two pulses is $\pm\pi/2$, the pattern is shifted by half a fringe. Referring again to Figure 2.11 a), in the two regions where the phase is equal to $\pm\pi/2$ we can see that the pattern has the steepest slope (green solid line) with respect to the detuning. Consequently, measurements around these points are more sensitive

¹The quantum projection noise for each respective point with a probability p for N repetitions is calculated using $\Delta p = \max(\sqrt{p(1-p)/N}, 1/(N+2))$ [45].

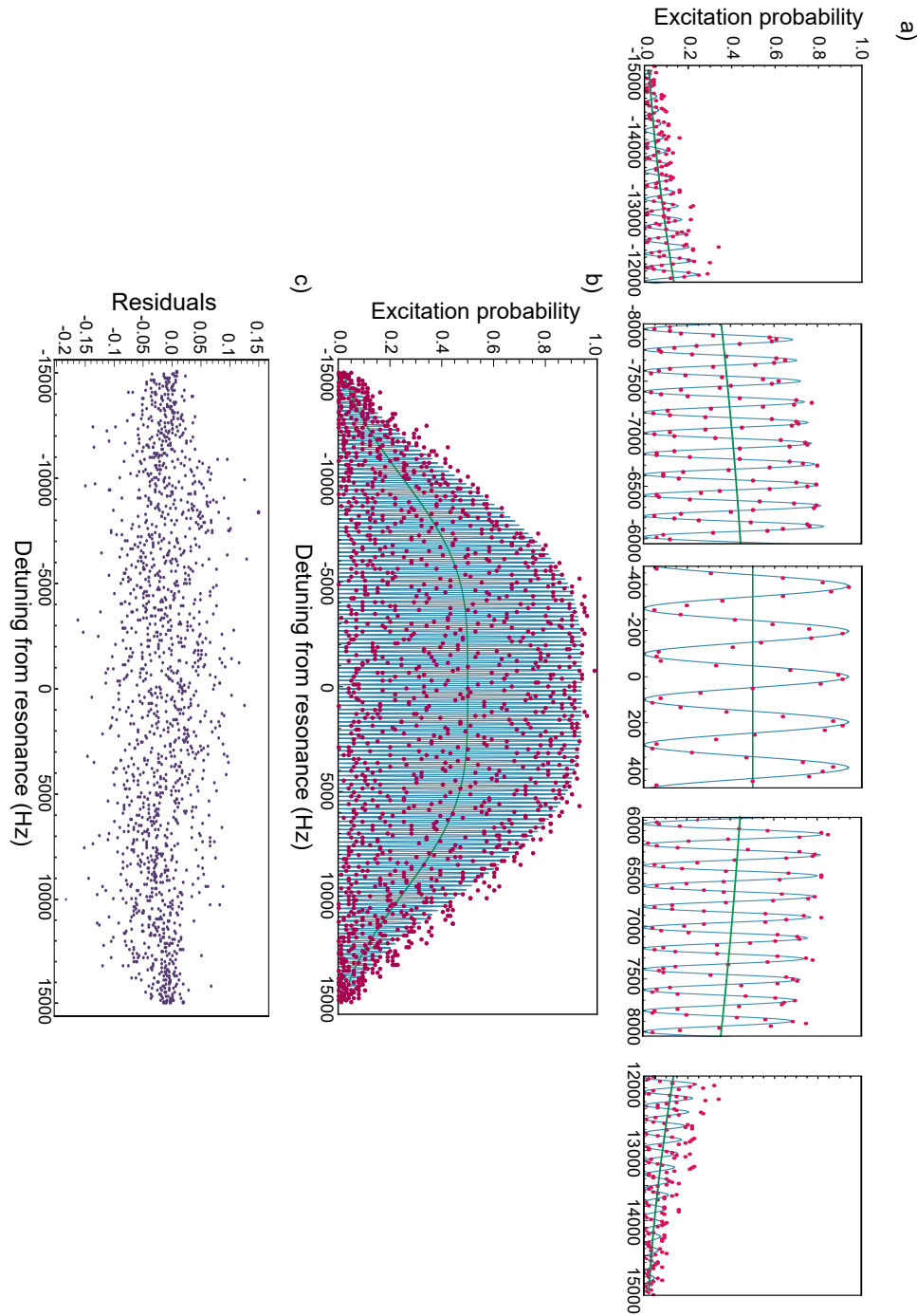


Figure 2.10: Ramsey experiments on the $^{40}\text{Ca}^+ S_{1/2} \leftrightarrow D_{5/2}$ transition. Measured excitation as a function of the laser detuning (pink points) for Ramsey pulses of $100\ \mu\text{s}$ duration and a waiting time of 5 ms. The solid blue line corresponds to the theoretical estimation using Equation 2.58. The Rabi pedestal is obtained using Equation 2.59 (solid green line). a) Corresponds to a set of zoomed-in sections from the longer frequency scan plotted in b). c) The residuals between the measured excitation and the theory fit are plotted as a function of the detuning from resonance.

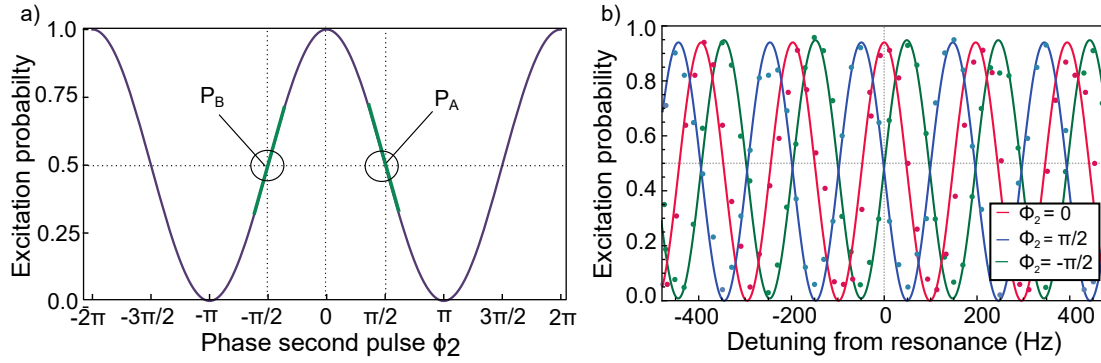


Figure 2.11: Ramsey experiments with a variable phase of the second pulse. ϕ_2 a) Variations of the excitation probability of the Ramsey experiments when the laser frequency is on resonance with the transition ($\Delta\omega = 0$) as a function of the phase of the second pulse (ϕ_2). The two regions marked as p_A and p_B correspond to the measured excitation when the phase difference is $\pm\pi/2$ and to the points where the pattern has the steepest slope (green solid line). b) Center fringes of the Ramsey experiment illustrated in Figure 2.10 repeated using 3 different phases ϕ_2 . Phase shifts $\delta\phi = \phi_1 - \phi_2$ accumulated during the waiting time shift the fringe pattern left or right, depending on their sign.

to frequency variations. Using Equation 2.60, we can calculate the excitation probability for the two phase settings p_A for $\phi_2 = \pi/2$ and p_B for $\phi_2 = -\pi/2$. Combining these two calculations, the detuning can be estimated using:

$$\frac{\Delta\omega}{2\pi} = \frac{1}{2\pi(\tau_R + 2\tau_{pi}/\pi)} \arcsin\left(\frac{p_B - p_A}{(p_A + p_B)C}\right), \quad (2.61)$$

where C accounts for the loss of the fringe contrast. To keep track of any variations of the fringe contrast during a measurement, Ramsey experiments are repeated using different values for the phase of the second pulse. Notice in Equation 2.61 that the detuning does not depend on the Rabi frequency Ω , meaning that the measurements are not directly affected by laser intensity fluctuations. The resolution of the measurement depends of the waiting time τ_R . It is important to notice also that the contrast of the fringes is intrinsically related to the maximum coherence time experimentally achieved and limits the maximum waiting time that can be used. Consequently, the maximum resolution that can be achieved is also limited by the maximum coherence time. Figure 2.12 illustrates this concept. The two plots show measured Ramsey patterns of the $^{40}\text{Ca}^+ S_{1/2}, m_j = 1/2 \leftrightarrow D_{5/2}, m_j = 1/2$ transition using Ramsey pulses of $100 \mu\text{s}$ with a waiting time of 28 ms for one and 44 ms for the other. The fringe periodicity changes accordingly, $1/\tau_R \approx 36 \text{ Hz}$ and $1/\tau_R \approx 23 \text{ Hz}$, and the fringe contrast is reduced for longer waiting times.

2.4.3 Quantum logic spectroscopy

Quantum logic spectroscopy (QLS) is implemented to probe the transition of species that lack a "suitable" cooling and detection transition. To be able to perform Doppler cooling and internal state detection, the ion needs to have a fast or broad cycling transition. However, care needs to be taken also that the cooling transitions is not too broad, since the Doppler-cooling limit is dependent on the transition width. It is important to consider also that the necessary lasers to probe such transition are commercially

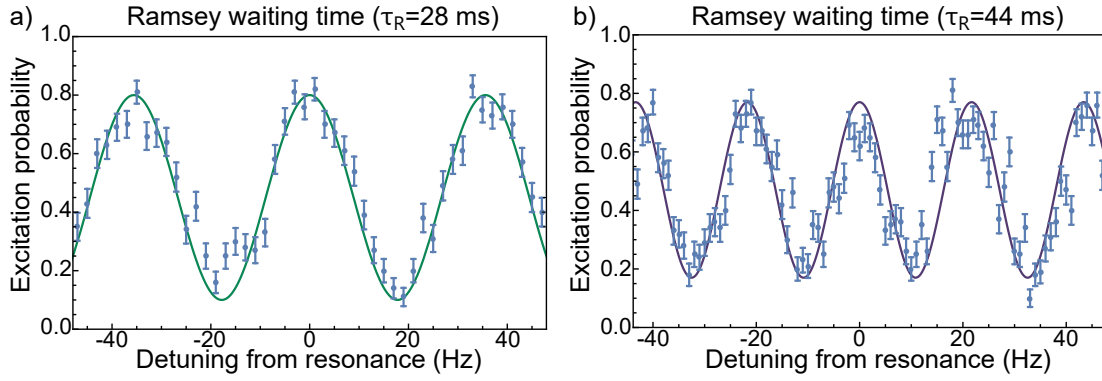


Figure 2.12: Ramsey patterns with 28 ms and 44 ms waiting times. Measurement excitation of the $^{40}\text{Ca}^+ \text{S}_{1/2}, m_j = 1/2 \leftrightarrow \text{D}_{5/2}, m_j = 1/2$ transition as a function of the laser detuning for Ramsey pulses of $100 \mu\text{s}$ duration taken with a Ramsey waiting time of: a) 26 ms, and b) 44 ms. The solid lines in green for a) and purple b) correspond to the theoretical estimations using Equation 2.58.

available and not too difficult to operate. Given these requirements, dipole-allowed transitions are usually implemented. However, not all species possess such transitions, limiting the selection of species that could potentially be good trapped-ion clock candidates. To circumvent this problem, **QLS** can be implemented: The *spectroscopy* ion is co-trapped together with a so-called *logic* ion that possesses a "good" cooling and detection transition. The ion is sympathetically cooled by means of the Coulomb interaction between both ions. Taking advantage of the collective motion of the ions, described in Section 2.3, the internal state of the *spectroscopy* ion is mapped into the state of the *logic* ion. This technique was first developed to probe the Al^+ clock transition [58] and is now implemented to probe highly charged ions and molecular ions [60, 61, 62]. The sequence implemented for **QLS** follows the same structure as the one described in Figure 2.6. In particular, sympathetic cooling is utilized to cool down the ions and an extra set of pulses are added during the *quantum state analysis* stage to map the internal state of the spectroscopy ion onto the state of the logic ion. To transfer the quantum information from one ion to the other, different quantum logic spectroscopy schemes can be implemented. They all take advantage of the collective motion of the ions in the trap and use combinations of blue and/or red side band pulses. Figure 2.13 illustrates a **QLS** scheme that can be described by the following steps:

- Both ions are cooled down to the ground state. The *spectroscopy* ion is prepared in the ground electronic level $|g\rangle$ while the *logic* ion is prepared in the excited electronic level $|e\rangle$. The transition of the *spectroscopy* ion is probed either using Rabi or Ramsey spectroscopy. The probability to excite the *spectroscopy* ion into the excited clock level is represented by a blue disk and the remaining population on the ground state by a pink disk.
- A π -pulse in the blue sideband of the *spectroscopy* ion excites the remaining population on the ground state into the first motional state of the excited state, mapping the ground state amplitude onto the first excited motional state of the excited level of the *logic* ion (pink disk).
- Another π -pulse is applied, but now on the blue sideband of the *logic* ions. This maps the first excited motional state of the excited level onto the ground motional state of the ground level (pink disk). At this point the internal state of the

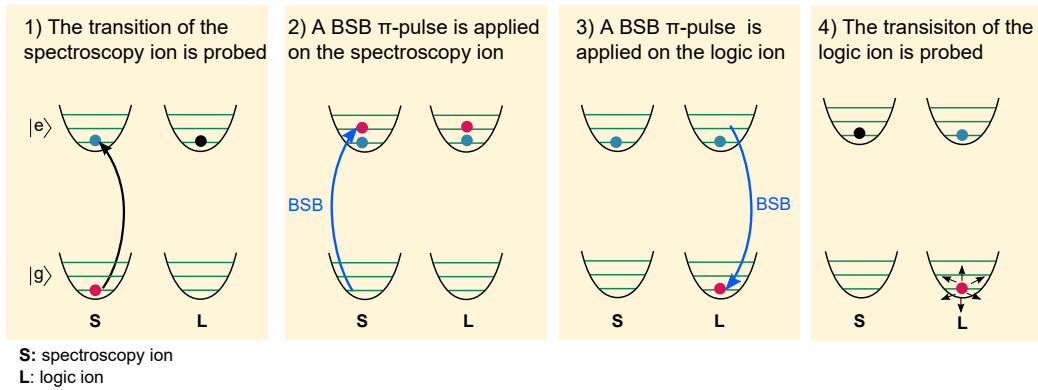


Figure 2.13: Quantum logic spectroscopy scheme. The ground and excited electronic states of the spectroscopy **S** and logic **L** ion are represented by $|g\rangle$ and $|e\rangle$, respectively. The levels in green represent the motional states. The probability to excite the spectroscopy ion to the $|e\rangle$ electronic state is represented by a blue disk while the population remaining in the ground state is illustrated by a pink disk. Following the steps described in the text, by means of two blue side band (BSB) pulses, the internal state of **S** is mapped onto the one of **L**. Finally the probability to excite the ion is measured by detecting the fluorescence on the logic ion.

spectroscopy ion has been successfully mapped onto the internal state of the *logic* ion.

- Finally, the state of the *logic* ion is probed by measuring the emitted fluorescence on the fast detection transition. The detection procedure can be carried out multiple times in order to lower the detection error rate.

Chapter 3

Systematic frequency shifts for trapped ions

"If you thought before that science was certain
-well, that is just an error on your part"

Richard Feynman
The Character of Physical Law (1965)

As it is nicely stated by Richard Feynman: Science is not certain. Once we accept this fact, the question that we need to answer is how certain or uncertain we are about a measurement. This question lies at the center of any clock experiment and by answering it we learn not only about the fundamental aspects of our system, in our case the trapped ion, but also about the environment that surrounds it. This chapter focuses on the theoretical background necessary to characterize the systematic frequency shifts that limit our knowledge about the clock transition and allows us to answer how (un)certain we are about our measurement.

The degree of sensitivity of a "clock transition" to the environment is intrinsically related to the atomic structure. Interactions with the environment are going to be perceived as frequency shifts that perturb the clock transition. When choosing the ideal "clock transition" it would be ideal to select an element whose clock transition is very insensitive to the environment. However it is also important to remember that when selecting an ion species, cooling, detection and state preparation transitions need to be considered. Choosing the right element becomes a trade between insensitivity and ease of manipulation. Most of trapped-ion clock candidates are singly-charged ions with one and two valence electrons. These atomic species offer the advantage to have a relatively simple electronic level structure. They exhibit closed shells that form a spherically symmetric core of electrons surrounded by valence electrons. The core screens the nuclear charge in such a way that at large distances the valence electrons behave similar to the electrons of atoms with just one or two electrons with a singly or doubly charged nucleus. The study of these species follows the same theoretical approach as for the well known cases of the hydrogen or helium atoms. These calculations allow us to have a deep understanding of the interactions between the ion and the external electro-magnetic fields and precisely estimate the frequency shifts generated on the clock transition. In the following section a brief summary of the key aspects necessary for the determination of these shifts is given. In this more theoretical section the development and notation implemented for the study of many-electron atoms is followed, keeping in mind that the final calculations are usually greatly simplified due to the inner properties of the used atomic species.

To describe the electronic level structure of atomic species the spectroscopy notation $n^{2S+1}L_J$ is used, where n is the principal quantum number, L the electronic orbital (identified either by quantum numbers or roman letters such that $0 \equiv S$, $1 \equiv P$,

$2 \equiv D \dots$) and S the spin quantum number. The factor $(2S+1)$ denotes the spin multiplicity. The spin-orbit interaction induces energy shifts such that the levels with quantum number L split into $(2S+1)$ sublevels with a total electronic angular momentum $-|L+S| \leq J \leq |L+S|$. For atoms with a nuclear magnetic moment, the coupling between the magnetic moment of the electron and the nuclear magnetic moment generates a hyperfine structure. The net nuclear spin number defined by the quantum number I (analogous to the net electron spin S) in combination with the magnetic moment J define the total atomic angular momentum $F=I+J$ of each of the $(2F+1)$ hyperfine levels, which take on the values $-|J+I| \leq F \leq |J+I|$. The quantum numbers n and S are not always necessary to identify the energy levels addressed, so in some parts of the thesis the notation is simplified to: $n^{2S+1}L_J \rightarrow L_J$.

3.1 Interaction with magnetic fields

Magnetic fields are omnipresent in any laboratory: coming from the earth's core, generated by electronic equipment, the next door elevator or even from a rotating desk chair. Sources of environmental magnetic fields are innumerable. To minimize their effect trapped ions are usually placed inside shielding enclosures that can block fields spanning from high AC down to DC fields. However, their effective amplitude cannot be completely canceled. Additionally to this unwanted magnetic field sources, for the operation of trapped-ion clocks, a static homogeneous magnetic field on the order of few Gauss (3 G or 4 G in our experiments) is applied to assure the control of the quantization axis for the interaction with the different laser fields. In this section I will give a brief summary on how to derive the fine structure and hyperfine structure elements involved in the calculations of the linear and quadratic Zeeman shift of a clock transition in the presence of a weak magnetic field. To estimate both the linear and quadratic Zeeman shift for trapped ion clocks we followed the approach described in the Atomic Physics Lecture Notes by J.T.M Walraven [63].

3.1.1 Linear Zeeman shift

The interaction of the atom's magnetic moment with a weak magnetic field induces the so-called Zeeman effect, lifting the degeneracy of the electronic levels.

The Hamiltonian describing the magnetic fine structure in first order perturbation theory for given values of n and L , assuming no nuclear spin, can be written as:

$$\mathcal{H} = \mathcal{H}_{\text{CF}} + \mathcal{H}_{\text{LS}} + \mathcal{H}_{\text{Z}} \quad (3.1)$$

where $\mathcal{H}_{\text{CF}}$ is the central-field Hamiltonian, $\mathcal{H}_{\text{Z}}$ the Zeeman Hamiltonian and $\mathcal{H}_{\text{LS}}$ the spin-orbit Hamiltonian. The magnetic field interactions are studied in two separate regimes denominated as low-field and high-field. The intersection point between these two regimes is defined by the absolute value of the fine-structure field $|B_{fs}|$ denominated as *fine-structure crossover*. The fine-structure field B_{fs} represents an effective internal magnetic field and is a measure of the spin-orbit splitting in magnetic field units. The value of the fine-structure field is determined by the spin-orbit coupling constant ζ_{nL} . This constant can be determined experimentally through the measurement of the spin-orbit splitting in zero magnetic field or theoretically through lengthy numerical calculation requiring the knowledge of the effective charge distribution. Trapped ion clocks operate usually in the low-field limit ($B \ll |B_{fs}|$). In this regime, the angular momenta $\mathbf{L}$ and $\mathbf{S}$ are spin-orbit coupled to form the total electronic angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$. Under these conditions the Hamiltonian 3.1 is

best analyzed in the coupled representations $\{|nLSJM_J\rangle\}$, where the first two terms are diagonal and $\mathcal{H}_Z$ acts as the perturbation. If the quantization axis is chosen along the direction of the $\mathbf{B}$ field the expression for the linear Zeeman energy shift is simplified to:

$$\Delta E_{linZ_{fine}}(J, M_J) = g_J \mu_B B \langle JM_J | (J_z/\hbar) | JM_J \rangle = g_J \mu_B M_J B, \quad (3.2)$$

where the Landé g_J factor is calculated using:

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}. \quad (3.3)$$

The energy level is split in $(2J+1)$ energy sublevels labeled by the magnetic quantum number $M_J = -|L+S| \leq J \leq |L+S|$.

The procedure is analogous for atomic species exhibiting a hyperfine structure. In this case, the effects related to the nuclear spin I need to be considered. The Hamiltonian describing the nuclear spin Zeeman contribution, with the quantization axis (z axis) chosen along the magnetic field direction, is:

$$H_{Znuc} = -\gamma_I \mathbf{I} \cdot \mathbf{B} = -g_I \mu_N B (I_z/\hbar), \quad (3.4)$$

where γ_I is the gyromagnetic ratio of the nucleus, g_I the nuclear g -factor and μ_N is the nuclear magneton $\mu_N \equiv e\hbar/2m_p = (m_e/m_p)\mu_B$, where (m_e/m_p) corresponds to the ratio of the electron to proton mass. Following the same approach as for atomic species exhibiting a fine structure, the interactions with the magnetic field are studied in two different regimes: low-field and high-field. The intersection point between these two regimes is determined by the absolute value of the hyperfine field $|B_{hfs}|$ denominated as *hyperfine crossover field*. The field B_{hfs} is an effective internal magnetic field that depends on the hyperfine coupling constant a_{hfs} analogous to ζ_{nL} . For small fields ($B \ll |B_{hfs}|$) the angular momentum $\mathbf{J}$ and $\mathbf{I}$ are strongly hyperfine-coupled to form the total electronic angular momentum $\mathbf{F} = \mathbf{J} + \mathbf{I}$. The expression for the linear Zeeman energy shift is then simplified to:

$$\Delta E_{linZ_{hyperfine}} = g_F \mu_B B \langle FM_F | (F_z/\hbar) | FM_F \rangle = g_F \mu_B M_F B, \quad (3.5)$$

where the Landé g_F factor can be calculated using:

$$g_F = g_J \frac{F(F+1) - I(I+1) + j(j+1)}{2F(F+1)}. \quad (3.6)$$

The energy levels are split in $(2F+1)$ energy sublevels labeled by the magnetic quantum number $M_F = -|J+I| \leq F \leq |J+I|$.

3.1.2 Quadratic Zeeman shift

A common origin of the quadratic Zeeman shift in trapped ion clock transitions occurs when two fine-structure levels, J' and $J = J' - 1$ are coupled by the spin-orbit interaction. To calculate the quadratic Zeeman shift, second-order perturbation theory can be used.

To calculate the shift of the fine structure splitting in the low-field regime ($B \ll |B_{fs}|$) the following general formula can be employed:

$$\Delta E_{J,M}^{quadZ_{fine}}(n^{2s+1}L_j) = \pm \sum_{J'} \frac{|\langle LSJ'M | g_L \mu_B L_z + g_S \mu_B S_z | LSJM \rangle B/\hbar|^2}{E_{J',M} - E_{J,M}}. \quad (3.7)$$

To calculate the shift of the hyperfine structure splitting also in the low-field regime ($B \ll |B_{hfs}|$) the following formula is implemented:

$$\Delta E_{F,M_F}^{quadZ_{Hfine}}(n^{2s+1}L_j) = \sum_{F'} \frac{|\langle IjF'M_F | g_J \mu_B J_z - g_I \mu_N I_z | IjFM_F \rangle B / \hbar|^2}{E_{F',M_F} - E_{F,M_F}} \quad (3.8)$$

The full development and calculation of this shift are described in detail in the Atomic Physics Lecture Notes by J.T.M Walraven [63] and result in:

$$\Delta E_{J'/J,M}^{quadZ_{fine}}(n^{2s+1}L_j) = \pm \frac{1}{4} \zeta_{nLS} J' (B/B_{fs})^2 (1 - \tilde{M}^2) R(LSJ'), \quad (3.9)$$

where ζ_{nLS} corresponds to the *Russell-Saunders coupling constant*

$$B_{fs} \equiv \zeta_{nLS} J' / \mu'_B, \quad (3.10)$$

$\mu'_B \equiv (g_S - g_L) \mu_B$ corresponds to the fine structure crossover field, $\tilde{M} = M_J / J'$ and

$$R(LSJ') \equiv \frac{(L + S + 1 + J')(J' - L + S)(J' + L - S)(L + S + 1 - J')}{(2J' - 1)(2J' + 1)}. \quad (3.11)$$

For the case of alkaline-like one valence electron ions such as Ca^+ , Sr^+ or Hg^+ , the quadratic Zeeman effect is caused by mixing of the $^2D_{5/2}$ and $^2D_{3/2}$ sublevels. States with the same M_J in the doublet interact and repel each other shifting the energy of the sublevels of the $^2D_{5/2}$. Using Equation 3.9 the quadratic Zeeman shifts for a given magnetic sublevel M_J of the clock transition can be simplified to [24]:

$$\Delta \nu_{quadZ}(S, D) = K \frac{(\mu'_B B)^2}{h^2 \nu_{FS}} \quad (3.12)$$

where $\nu_{FS} = \zeta_{nLS} J'$ is the fine structure splitting and $K = \frac{1}{4} (1 - \tilde{M}^2) R(LSJ')$. For $L=2$, $S=1/2$, $J'=5/2$ the constant is:

$$\begin{aligned} K &= \frac{6}{25} \quad \text{for } M_J = \pm \frac{1}{2}, \\ K &= \frac{4}{25} \quad \text{for } M_J = \pm \frac{3}{2}, \\ K &= 0 \quad \text{for } M_J = \pm \frac{5}{2}. \end{aligned} \quad (3.13)$$

With this tool it is possible to characterize the effects of the magnetic field for most ion-trapped species. However, there are some exceptions where a more complex analysis is required. This is the case for trapped ion clocks based on elements from the group 13 of the periodic table. These ions have clock transitions between states with vanishing angular momentum such as the $^1S_0 \leftrightarrow ^3P_0$. The clock transitions of these ions offer promising advantages: They are narrow transitions in the ultra-violet regime. They also have the advantage that their frequency is not affected by electric quadrupole shifts and have smaller linear and quadratic Zeeman shifts. These narrow transitions rely on the hyperfine interaction that couples the 3P_0 , 3P_1 and 1P_1 states with the same F quantum number. As a consequence the so called 3P_0 contains admixtures of these other states, thus inheriting some of their properties, including a modified g -factor. As expected, the precise estimation of the g -factor of both the

ground and excited state for this kind of trapped ion clocks has been the focus of theoretical and experimental research [64, 65, 66, 67, 68].

The approach derived above can be implemented for the characterization of the $|^3P^1, F = 7/2 >$ level [69],[70]: The fine-structure mixing effect of a non-zero magnetic field giving rise to a small second-order Zeeman shift of the $|^3P^1, F = 7/2, m_F = \pm 7/2 >$ states due to the coupling to the $^3P^2$ states with the same magnetic quantum number can be calculated using Equation 3.9.

3.2 Interaction with electric fields

Electric fields are as ubiquitous as magnetic fields in the laboratory. They can originate from the trap itself, the presence of neighboring ions, laser fields, black-body radiation or even by the motion of the ion. Electric fields are responsible mainly of two types of shifts: the so-called quadrupole shift and quadratic Stark-shifts. The quadrupole shift appears from the coupling of the multipole moments of the atom to external electric field gradients. Quadratic Stark-shifts arise when the ion is exposed to oscillating electric fields. In this section I will present a brief summary on how to calculate these shifts. I will introduce the different sources of the electric fields that affect the ion and will describe how to calculate and if possible minimize their effects on the ion.

3.2.1 Quadrupole shift

For any atomic state with $J > 1/2$ (and consequently $F > 1/2$) the electronic charge distribution can have multipole moments. Quadrupole shifts originate from the coupling of these multipole moments to electric field gradients. The Hamiltonian describing the interaction of the electric quadrupole operator $\Theta^{(2)}$ with an external field gradient $\nabla E^{(2)}$ can be simplified to [71, 4]:

$$H_Q = \nabla E^{(2)} \cdot \Theta^{(2)} \quad (3.14)$$

Following [72], this expression is simplified in the principal axis frame, using the Wigner-Eckart theorem and assuming that the quadrupole shift is small compared to the Zeeman shift to:

$$H_Q = \frac{1}{4} \frac{dE_z}{dz} \Theta \frac{(F(F+1) - 3M^2)}{F(2F-1)} (3\cos^2\beta - 1), \quad (3.15)$$

where $\frac{dE_z}{dz}$ corresponds to the electric field gradient along the principal trap axis, Θ the quadrupole moment and β the angle between the quantization axis and the principal axis of the trap. A key element to note is that this expression possesses symmetry properties that can be used for the cancellation of the quadrupole shift without previous knowledge of the orientation or strength of the electric field gradient. The quadrupole shift vanishes if the clock transition is measured and averaged over three mutually perpendicular orientations of the magnetic field respect to the quantization axis [73, 74, 75]. Another technique consists in taking advantage of the fact that:

$$\sum_{M=-F}^F = (F(F+1) - 3M^2) = 0. \quad (3.16)$$

From this expression and 3.15 we can see that an average of the transition over all Zeeman sublevels also cancels the quadrupole shift. Depending on the quantum numbers,

different schemes can be designed in such a way that the quadrupole shift is canceled [76, 24, 73].

Expression 3.15 is valid for generic hyperfine states with non-vanishing angular momentum, however for the case of transitions such as the $^1S_0 \leftrightarrow ^3P_0$ clock transition in group 13 singly-charged ions a special care needs to be taken. As it was previously described, the 3P_0 contains admixtures of the 3P_1 and 1P_1 states with the same F quantum number, which results in a nonzero but very small electric quadrupole moment. As described in [72] to estimate the quadrupole shift for ion clocks using species such as Al^+ or In^+ it is necessary to extend the analysis through third order perturbation theory and include the hyperfine coupling of the electrons to both the magnetic dipole and electric quadrupole moment of the nucleus. However these analyses have concluded that for the case of the Al^+ ion clock a fortuitous cancellation leads to a highly suppressed quadrupole shift that would affect the uncertainty of the most recent Al^+ clocks on the order of a fractional uncertainty of 1.7×10^{-20} assuming an electric field gradient on the order of 4.7×10^7 V/m² [72].

Electric field gradient

There are two main contributions to the electric field gradient at the position of the clock ion: one due to the static axial confining trap potential and a second one originating from the presence of neighboring ions. The static trapping potential applied to the tips in linear Paul traps gives rise to an electric field gradient along the axial or z -direction:

$$\frac{dE_z}{dz} = \frac{m\omega_{ax}^2}{e}, \quad (3.17)$$

where ω_{ax} is the frequency of oscillation of one single ion in the axial direction, m is the mass of the ion and e is the elementary charge. Spurious electric field gradients originating from patch potentials might also be present but they are usually negligible compared to dE_z/dz . In a multi-ion string, each ion generates an additional E-field gradient for its neighbors. For the case of two ions the electric gradient from the presence of the neighbor ion can be calculated following [72] as

$$\frac{dE}{dz} = \frac{e}{2\pi\epsilon_0} \frac{1}{\Delta z^3}, \quad (3.18)$$

where Δz is the equilibrium inter-ion distance equal to:

$$\Delta z = \left(\frac{e^2}{2\pi m_1 \epsilon_0 \omega_{ax}^2 \left(\frac{\mu}{1+\mu-\sqrt{1-\mu+\mu^2}} \right)} \right)^{1/3}. \quad (3.19)$$

where m_1 and $m_2 = \mu m_1$ are the respective masses of the two ions. From this formula we can see for the case of two ions with the same mass m , the E-field gradient is $dE/dz = 2m\omega_{ax}^2/e$.

Quadrupole moment

The quadrupole moment arises when the electronic charge distribution of an atom departs from its spherical symmetry. As described in [71] atomic quadrupole moments were first measured by determining the shift in energy levels due to applied electric-field gradients in atomic-beam resonance experiments. The same methods

implemented for the treatment of the electric quadrupole hyperfine interaction of an atom have been adapted to describe the interaction of external electric-field gradients with the atomic quadrupole moment. Following this procedure, quadrupole moments have been calculated for ion species such as $^{99}\text{Hg}^+$, $^{171}\text{Yb}^+$, $^{88}\text{Sr}^+$ and $^{40}\text{Ca}^+$ [71, 77] and experimentally determined by measuring the change in the clock transition frequency in the presence of static electric field gradients [74, 75, 78] or by preparing a pair of ions in an entangled state insensitive to magnetic field fluctuations but sensitive to the quadrupole shift [79]. As previously mentioned for the case of Al^+ or In^+ , the calculations require third-order perturbation theory and the inclusion of hyperfine coupling of the electrons to both the magnetic dipole and electric quadrupole moment of the nucleus [72].

3.2.2 Quadratic Stark shift

Even if trapped ions in Paul traps are located at the point where the DC electric field vanishes, they can be exposed to oscillating electric fields due to laser fields, black-body radiation or by the motion of the ion around the RF null position. The exposure of the ion to oscillating fields displaces the magnetic sublevels of the clock transition via the quadratic Stark effect. Following [71] the quadratic Stark shift is treated as small perturbation of the linear Zeeman splitting and can be calculated for a state $|\gamma J F M\rangle$ as a function of the mean squared oscillating electric field $\langle E^2 \rangle$ using

$$\Delta E^{quadS}(\gamma, J, F, M, E) = -(2\alpha_s(\gamma, J) + \alpha_T(\gamma, J, F)g(F, M, \beta))\frac{\langle E^2 \rangle}{4}, \quad (3.20)$$

where

$$g(F, M, \beta) = \frac{3M^2 - F(F+1)}{F(2F-1)}(3\cos^2\beta - 1), \quad (3.21)$$

β is the angle between the electric field vector and the quantization axis, α_s and α_T the scalar and tensorial polarizabilities. The $g(F, m, \beta)$ factor has the exact same symmetry properties as the quadrupole shift described in equation 3.15 so the same techniques that cancel the quadrupole shift will also cancel the tensorial contribution of the polarizability to the quadratic Stark shift and the calculation of the clock energy shift is simplified to:

$$\Delta E^{quadS} = -\frac{1}{2}\Delta\alpha_0\langle E^2 \rangle, \quad (3.22)$$

where $\Delta\alpha_0 = \alpha_s(\text{excited}) - \alpha_s(\text{ground})$ is the polarizability difference between the two energy levels of the clock transition. The calculation of the quadratic shift requires on one hand the determination of the differential scalar polarizability $\Delta\alpha_0$ and on the other hand the measurement of the mean squared amplitude of all the electric fields perceived by the ion. In the following I discuss possible origins of these fields namely the motion of the ion around the RF null position, laser fields and black body radiation.

Motion of the ion and oscillating electric field

The motion of the ion in a Paul trap can be separated in three different kinds of motions: secular motion, micromotion and excess micromotion. To characterize the motion of the ion in the pseudopotential we use the Mathieu equations, introduced in Section 2.1.1. Following [24] in a simplified approach the first-order solution takes the form

$$u_i(t) = u_{0i}\cos(\omega_i t + \phi_i)\left(1 - \frac{q_i}{2}\cos(\Omega t)\right) \quad (3.23)$$

where $u_i(t)$ correspond to the position of the ion along the principal axes of motion of the secular motion with an amplitude u_{0i} , an angular frequency ω_i and ϕ_i the initial phase. The parameters q_i for the case where no dc voltage is applied to the end-cap electrodes are:

$$q_x = q_y = -\frac{q_z}{2} = \frac{-4eV_0}{m\Omega^2(r_0^2 + 2z_0^2)} \quad (3.24)$$

where V_0 is the amplitude of the voltage applied, r_0 the radius of the end-cap electrode, z_0 the distance between the center of the trap and the end-cap faces. The first term of the equation 3.23 describes the secular motion and the second term the micromotion. The secular motion can be described as the oscillation of the ion assuming that it is trapped in a pseudo-potential. The micromotion corresponds to the modulated oscillation generated by the interaction of the ion with the RF field of the trap. Finally, the excess micromotion is generated by static electric stray fields that push the ion away from the RF null position, increasing its interaction with the RF field of the trap. The level of interaction with the RF field determines the magnitude of the mean-squared electric field and consequently the magnitude of the quadratic shift. In order to measure and minimize the effect of these shifts, two parameters need to be considered: the motional energy of the ion and the compensation of the excess micromotion. The shifts generated by both the secular motion and micromotion are linked to how well we can cool down the ion. Additionally, the mitigation of the shifts originating from the excess micromotion is limited by how well we can compensate stray fields and push back the ion to the RF null position. Following the procedure described in [24] I will describe how to estimate the magnitude of the shift for each one of the motion categories.

Excess micromotion The magnitude of the excess micromotion, in the limit of low modulation β_i , is determined from the intensity ratio of the micromotion sideband to the carrier of one of the Zeeman transitions [80]:

$$R_i = \frac{J_1(\beta_i)^2}{J_0(\beta_i)^2} = \frac{\Omega_{SB}^2}{\Omega_{car}^2} = \frac{\beta_i^2}{4}, \quad (3.25)$$

where J_n are Bessel functions of order n that relate the micromotion strength to the modulation index β_i and Ω_{car} and Ω_{SB} correspond to the Rabi frequency of the carrier and the micromotional sideband. The modulation index is related to the vector amplitude of the ion velocity $\mathbf{v}_0$ at the angular frequency Ω by [24]:

$$\beta_i = \left(\frac{\omega_0}{\Omega}\right) \frac{|\hat{\mathbf{n}}_i \cdot \mathbf{v}_0|}{c} \quad (3.26)$$

where ω_0 corresponds to the probe laser frequency, $\hat{\mathbf{n}}_i$ a unit vector in the direction of propagation of the laser beam and c the speed of light. By solving the equation of motion for this kind of motion, we find that the vector amplitude of the ion velocity $\mathbf{v}_0$ is related to the vector amplitude of the electric field $\mathbf{E}_0$ by:

$$\mathbf{E}_0 = \left(\frac{m\Omega}{e}\right) \mathbf{v}_0 \quad (3.27)$$

where m denotes the ion mass and e is the electric charge of the ion. Since $|\hat{\mathbf{n}}_i \cdot \mathbf{v}_0|^2 = |\mathbf{v}_0|^2 \cos^2 \theta_i = 2 \cos^2 \theta_i \langle v^2 \rangle$ we get the following relation for the mean square velocity

and the sideband to carrier intensity ratio:

$$R_i = \left(\frac{\omega_0}{\Omega}\right)^2 \frac{\langle v^2 \rangle}{2c^2} \cos^2 \theta_i, \quad (3.28)$$

where θ_i is the angle between $\hat{n}_i$ and $\mathbf{v}_0$. Since the angle between the laser beam and the ion motion is not easily determined, to estimate the mean-square electric field due to the excess micromotion $\langle E^2(t) \rangle = |\mathbf{E}_0^2|/2$ it is necessary to measure the amplitude of the ratio R_i in three orthogonal directions such that:

$$\langle E_{\text{excess}\mu}^2(t) \rangle = 2 \left(\frac{m\Omega^2 c}{\omega_0 e} \right)^2 \sum_{x,y,z} R_i. \quad (3.29)$$

The quadratic Stark shift due to the excess micromotion can be determined by applying this expression to Equation 3.20. It becomes obvious that to minimize this shift the excess micromotion has to be minimized too. In Paul traps this can be done by shifting the ion back to the RF null position with the help of compensation electrodes.

Secular motion and micromotion Following a similar approach as the one used to characterize the effect of the excess micromotion [24] we describe how the motion of the ion determines its interaction with the electric field. The secular motion and micromotion are linked to the mean motional energy of the ion. To determine the energy of the ion at each direction T_i the thermal velocity can be measured using a similar technique as for the excess micromotion which consist in evaluating the ratio of secular sideband to carrier intensities. The total energy of the ion is determined by evaluating its kinetic energy at each direction i , provided that the harmonic oscillator distribution is thermal. The thermal energy U_i at a given direction i can be calculated using:

$$U_i = \frac{m\langle v_i^2 \rangle}{2} = \frac{m u_{0i}^2 \omega_i^2}{2} \approx kT_i, \quad (3.30)$$

where k is the Boltzmann's constant. The motion of the ion is described by the expression 3.23. The amplitude of the motion is determined by the temperature of the ion, using equation 3.30. The mean-squared electric field perceived by the ion due to the micromotion $\langle E_\mu^2(t) \rangle$ is evaluated over the three principal axes of motion

$$\langle E_\mu^2(t) \rangle = \frac{-3kT}{2} \left(\frac{m\Omega^2}{e^2} \right) \quad (3.31)$$

The quadratic Stark shift due to micromotion can be determined applying this expression to Equation 3.20. To minimize this shift great care needs to be taken to reduce the temperature of the ion.

Black body radiation shift

The thermal electromagnetic radiation field interacting with the ion shifts the two clock energy levels by off-resonant coupling to other levels. This shift can be approximated to a quadratic Stark shift that follows equation 3.20. Assuming that the thermal radiation field is isotropic the tensor contribution averages to zero. The mean squared electric field is obtained from the integration of Planck's radiation law and depends on the environmental temperature that surrounds the ion T and can be estimated using

[81]:

$$\langle E^2(t) \rangle = (831.9 \text{ V/m})^2 \left(\frac{T(\text{K})}{300} \right)^4. \quad (3.32)$$

The generated shift can be approximated using Equation 3.22 as a quadratic Stark shift of the form [82]:

$$\Delta E_{BBR} = -\frac{1}{2} \langle E^2(t) \rangle \Delta \alpha_0 (1 + \eta) \quad (3.33)$$

where $\Delta \alpha_0$ is the differential scalar polarizability and η is a small dynamic correction due to the frequency distribution of the black body radiation field.

Laser fields and AC stark shifts

Trapped-ion clocks rely on the laser-ion interaction not only to excite the clock transition but also for cooling and state preparation. A detailed description of the properties of this interaction for different types of electronic transitions is presented in the previous Section 2.2. The interaction of the ion with electromagnetic radiation produces a dynamic Stark effect that shifts the clock transition. To estimate this shift we follow a similar approach as the one previously used to described the quadratic shift due to the motion of the ion. We consider only the scalar contribution of the quadratic shift in Equation 3.20, assuming that a symmetric probing scheme that cancels the tensorial contribution is implemented. The scalar polarizabilities α_0 are replaced by frequency-dependent dynamic polarizabilities $\Delta \alpha_{AC}(\lambda)$ and the mean-squared electric field contribution is determined in terms of the light intensity $I = c\epsilon_0 \langle E^2 \rangle$, where ϵ_0 is the vacuum permittivity. Following [24] the shift can be estimated with:

$$\Delta E_{AC}(\lambda) = -\frac{\Delta \alpha_{AC}(\lambda)}{2c\epsilon_0} I. \quad (3.34)$$

The dynamical polarizability is mainly composed of the contributions from the off-resonant coupling of dipole and quadrupole transitions to the levels of the clock transition. The determination of these contributions for each kind of transition was previously described in detail in Section 2.2.

3.3 Relativistic shifts

3.3.1 Second-order Doppler shift

The motion of the ion in the trap generates a relativistic Doppler shift that reduces the center frequency ν_0 measured in the laboratory frame as a function of the atom's velocity v . The shift can be calculated using [4]:

$$\frac{\Delta \nu_D}{\nu_0} = \frac{\langle v_{||} \rangle}{c} - \frac{\langle v^2 \rangle}{2c^2} + \frac{\langle v_{||} \rangle^2}{c^2} + O(v/c)^3 \quad (3.35)$$

where c is the speed of light and $v_{||}$ is the atom's velocity along the probe laser beam direction which averages down to zero for long trapping duration ($\langle v_{||} \rangle = 0$). For trapped ion clocks the shift is reduced to the so-called second order Doppler shift:

$$\frac{\Delta \nu_{D2}}{\nu_0} = -\frac{\langle v^2 \rangle}{2c^2}. \quad (3.36)$$

The mean-squared velocity $\langle v^2 \rangle$ is related to the motion of the ion in the trap and its determination is linked to the three kinds of motions described in 3.2.2. As it was presented in this section the determination of the mean square electric field for each kind of motion is actually related to the calculation of the mean square velocity so the same formulas can be adapted to determine the second-order Doppler shift.

Excess micromotion

As it was previously described in Equation 3.25, the excess micromotion can be determined through the measurement of the intensity ratio of the micromotion sideband to the carrier. Using Equation 3.28 we get a relation between the mean square velocity as a function of the sideband intensity ratio, using the obtained expression with Equation 3.36 the second-order Doppler shift is equal to [24]:

$$\frac{\Delta\nu_{D2, Excess}}{\nu_0} = - \left(\frac{\Omega}{\omega_0} \right)^2 \sum_{x,y,z} R_i. \quad (3.37)$$

Secular and micro-motion

These two motions are related to the temperature through Equation 3.30. In the pseudopotential approximation, the contribution to the second order Doppler shift is equal for both kind of motions. Using Equation 3.36 the second-order Doppler shifts are:

$$\frac{\Delta\nu_{D2, s}}{\nu_0} = \frac{\Delta\nu_{D2, \mu}}{\nu_0} = - \frac{3kT}{2mc^2}. \quad (3.38)$$

3.3.2 Gravitational Red-shift

As predicted by Einstein's general relativity theory, clocks will run at different rates with respect to a common or coordinate timescale if they move or are under the influence of a gravitational field [83]. The Geocentric Coordinate Time (TCG) defines the "proper time" of a clock at rest in a coordinate frame moving with the center of the earth. In simple terms the TCG is the idealized definition of a second not influenced by the gravitational time dilation. The Terrestrial Time (TT) defines the time of a clock on the geoid (Earth surface at mean sea level) such that TT differs from TCG just by a constant rate $(1-L_G)$, where L_G is a conversion constant with a fixed value and zero uncertainty, directly linked to a corresponding (zero) reference gravity potential value W_0 by the relation $L_G = W_0/c^2$. The value recommended by the IAU from the year 2000 and the resolution 2 of the 26th CGPM 2018 for W_0 is equal to:

$$W_0 = 62\,636\,856.00 \frac{\text{m}^2}{\text{s}^2}. \quad (3.39)$$

The International Atomic Time or TAI, corresponds to the principal realization of the Terrestrial Time (TT) and the basis for the Coordinated Universal Time (UTC). The UTC realizations of each individual time institute around the world are regularly compared to each other and combined by the International Bureau of Weights and Measures for the realization of the TAI. The offset of every UTC realization with respect to the TAI is evaluated every 5 days and can be accessed through the circular-T reports of the BIPM [84]. The gravitational red shift for a clock at rest on the Earth's surface can be calculated with [83]:

$$\frac{\Delta\nu_{GR}}{\nu_0} = \frac{gH}{c^2} \quad (3.40)$$

where g is the gravity acceleration and H is the height of the clock with respect to the zero potential.

3.4 Calcium and Aluminum ion clocks

The focus of this thesis is centered on the development of ion clocks with $^{40}\text{Ca}^+$ and $^{27}\text{Al}^+$ ions. I will start by presenting their atomic structure and the particular properties that make these two species good clock candidates. At the end of this section a summary table 3.4.2 with all the important atomic parameters for both ion species is included.

3.4.1 Atomic structure of $^{40}\text{Ca}^+$

^{40}Ca is the most abundant isotope of the alkaline-earth element calcium. It has two outer valence electrons in the $4s$ shell and no nuclear spin, which consequently means that it does not exhibit a hyperfine structure. As illustrated in Figure 3.1 a) the atom can be ionized following a two-step photoionization process. In its singly ionized form $^{40}\text{Ca}^+$ has a single valence electron in the $4s$ shell and therefore an electronic level structure similar to that of hydrogen. This kind of singly-charged ion with one and two valence electrons, similar to Sr^+ , Hg^+ , and Yb^+ , belongs to the so-called group of "*Alkaline-like-one-valence-electron*" systems that have been studied extensively due to their relatively simple electronic level structure and due to the fact that they exhibit a fast almost closed cycling transition, ideal for laser cooling and internal state discrimination [4].

As illustrated in Figure 3.1 b), the $3^2D_{5/2}$ level used for the $4^2S_{1/2} \leftrightarrow 3^2D_{5/2}$ quadrupole clock transition at 729 nm has a life time of 1.17 s resulting in a linewidth of $2\pi \cdot 136$ mHz. The fast, $4^2S_{1/2} \leftrightarrow 4^2P_{1/2}$ transition at 397 nm with a comparably large linewidth of $\Gamma/(2\pi) = 22.4$ MHz is used for laser cooling and internal state discrimination in combination with the $3^2D_{3/2}$ transition at 866 nm that ensures that any electron that decays is brought back into the cycle via the $4^2P_{1/2}$ level. The short lived $4^2P_{3/2}$ state couples to the $3^2D_{3/2}$, $3^2D_{5/2}$ and $4^2S_{1/2}$ via electric dipole transitions at 850 nm, 854 nm and 393 nm. The $3^2D_{5/2} \leftrightarrow 4^2P_{3/2}$ is used as a repumper for efficient state preparation.

The $3^2D_{5/2}$ level has a Landé g -factor $g_{2D_{5/2}} = 1.2003340(3)$ [76] and the $4^2S_{1/2}$ of $g_{2S_{1/2}} = 2.00225664(9)$ [85], as can be seen in Figure 3.2 in the presence of a magnetic field the magnetic sublevels are splitted by about 1.7 MHz/G for the upper level and 2.8 MHz/G for the lower level. An extra quadratic Zeeman shift of the upper level transition is on the order of a few Hertz and needs to be also considered. The quadrupole moment of the $^2D_{5/2}$ responsible for a quadrupole shift, if not properly canceled, on the order of few Hertz has been carefully calculated and measured [77, 79, 76].

3.4.2 Atomic structure of $^{27}\text{Al}^+$

The level structure of the $^{27}\text{Al}^+$ is "slightly" more complicated than the one of $^{40}\text{Ca}^+$. The ion has two valence electrons in the $3s$ shell which makes its level structure similar to the one of Helium and has a nuclear spin of $I = 5/2$ exhibiting a hyperfine structure. As illustrated in Figure 3.3 a), similarly to the calcium atom, the aluminum atom is ionized following a two-step photoionization process. The $^{27}\text{Al}^+$ belongs to the singly-charged ions of the so-called "*group 13*". The ions from this group, even with their more complex level structure, captured the attention of metrologists due

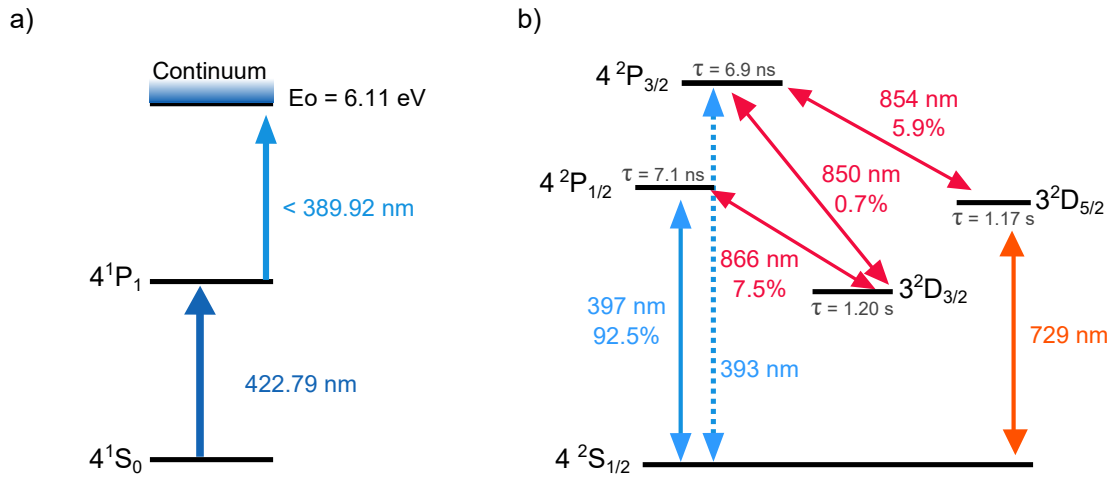


Figure 3.1: Reduced energy level scheme of calcium.

a) Energy levels and laser wavelengths used in the photoionization process of neutral calcium. b) Energy level scheme of $^{40}\text{Ca}^+$ with wavelengths and decay probabilities (in %) for the relevant transitions necessary in the experiments presented in this work. The $4^2S_{1/2} \leftrightarrow 3^2D_{5/2}$ quadrupole transition at 729 nm with a linewidth of $\Gamma/(2\pi) = 136$ mHz is used as a clock transition. Doppler cooling and state detection are carried out on the fast cycling dipole transition $4^2S_{1/2} \leftrightarrow 4^2P_{1/2}$ at 397 nm with a linewidth of $\Gamma/(2\pi) = 22.4$ MHz. Two infrared lasers at 866 nm and 854 nm pump out the metastable D-states to prevent population trapping.

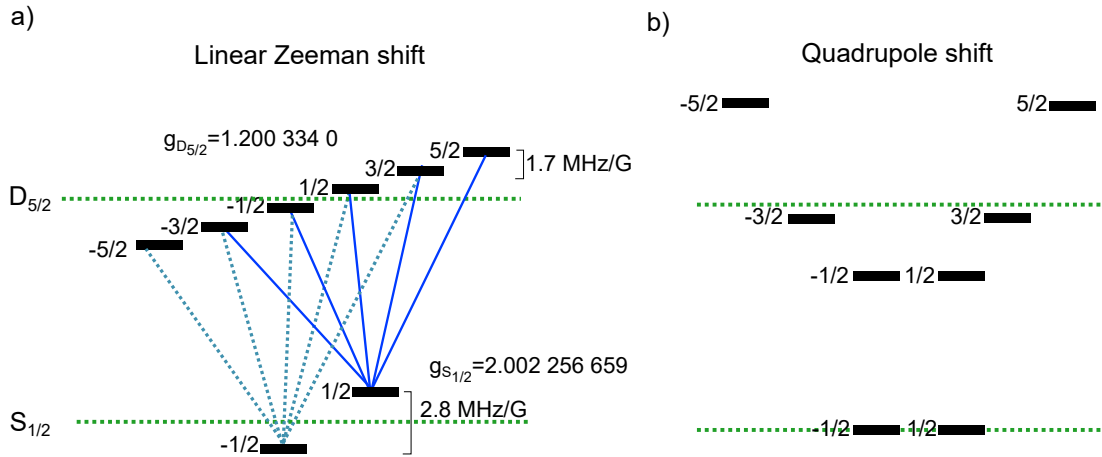


Figure 3.2: Linear Zeeman shift and quadrupole shift of the $^{40}\text{Ca}^+$ clock.

a) The $D_{5/2}$ level has a Landé g-factor $g_{D_{5/2}} = 1.2003340(3)$ and the $S_{1/2}$ has a Landé g-factor $g_{S_{1/2}} = 2.00225664(9)$. Due to the Zeeman effect both levels split into 6 and 2 sub-levels, respectively. Following the selection rules, a total of 10 transitions can be probed. b) The sub-transitions of the the $D_{5/2}$ level are also shifted by the interaction with the electric field gradient. The quadrupole shift for $m_j = \pm 5/2$ is equal to the combined shifts of $m_j = \pm 3/2$ and $m_j = \pm 1/2$.

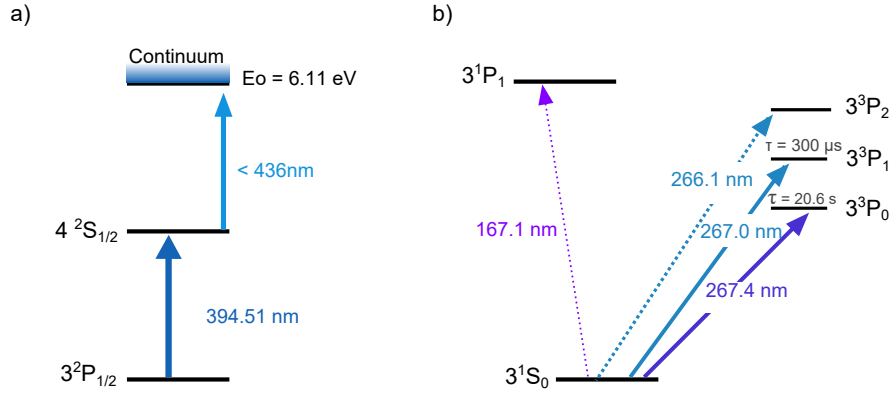


Figure 3.3: Reduced energy level scheme of aluminum.

a) Energy levels and laser wavelengths used in the photoionization process of neutral aluminum. b) Energy levels and transition wavelengths in aluminum relevant for the experiments presented in this work.

to the fact that they exhibit clock transitions between states with vanishing angular momentum such as the $^1S_0 \leftrightarrow ^3P_0$ transition. These transitions theoretically promise to have very small (nuclear) linear and quadratic Zeeman shift and to not be affected by electric quadrupole shifts. In principle, a single photon transition between these two pure states is strictly forbidden by angular momentum rules. However due to the hyperfine interaction, the 3P_0 state couples to the 3P_1 and 1P_1 states with the same F quantum number, resulting in that the 3P_0 state is no longer a pure state. As described in [4] the so called 3P_0 state is actually an admixture of these other states and inherits consequently some of their properties, such as a modified Landé g-factor ($g_{^3P_0} = -0.00197686$) [68], a decay to the ground state and a non vanishing but considerably small quadrupole moment.

Figure 3.3 b) presents a simplified illustration of the level structure. The 3P_0 state used for the hyperfine-induced clock transition $^1S_0 \leftrightarrow ^3P_0$ at 267.4 nm has a life time of 20.6 s [68] which results in a natural linewidth of $2\pi \cdot 7.6$ mHz. The 3P_1 state has shorter life time of 305 μs and a Landé g-factor of $g_{^3P_1} = -0.0428132$. The $^1S_0 \leftrightarrow ^3P_1$ intercombination line at 267 nm is used for initializing the ion in a pure electronic state by optical pumping. The 1S_0 state has a Landé g-factor of $g_{^1S_0} = -0.00079248$. The small Landé g-factors for both energy levels of the clock transition result in low magnetic field sensitivity. As can be seen in Figure 3.3, the large separation of the clock energy levels from any other state with a strong transition assures that any black-body radiation shifts are considerably reduced.

The $^1S_0 \leftrightarrow ^3P_0$ transition of $^{27}\text{Al}^+$ with its high frequency, small linewidth and insensitivity to environmental effects seems to fulfill almost completely the requirements for an ideal clock. However, as can be seen in Figure 3.3, the dipole transition $3^1S_0 \leftrightarrow 3^1P_1$ that could be used for direct laser cooling and detection has a wavelength of 167.1 nm and a spectral width of $2\pi \cdot 224$ MHz. This poses several difficulties: on one hand the necessary crystals for frequency doubling to that wavelength are not commercially available (to the knowledge of the author), on the other hand due to the strong absorption of 167 nm light it would be necessary to assure vacuum conditions for the whole optical path. Finally even if the two previous conditions could be fulfilled given that the linewidth of the transition is rather large it would not be possible to achieve low enough temperatures with Doppler cooling. To circumvent the cooling difficulties sympathetic cooling is implemented. To solve the detection issues quantum logic spectroscopy, described in Section 2.4.3, is implemented.

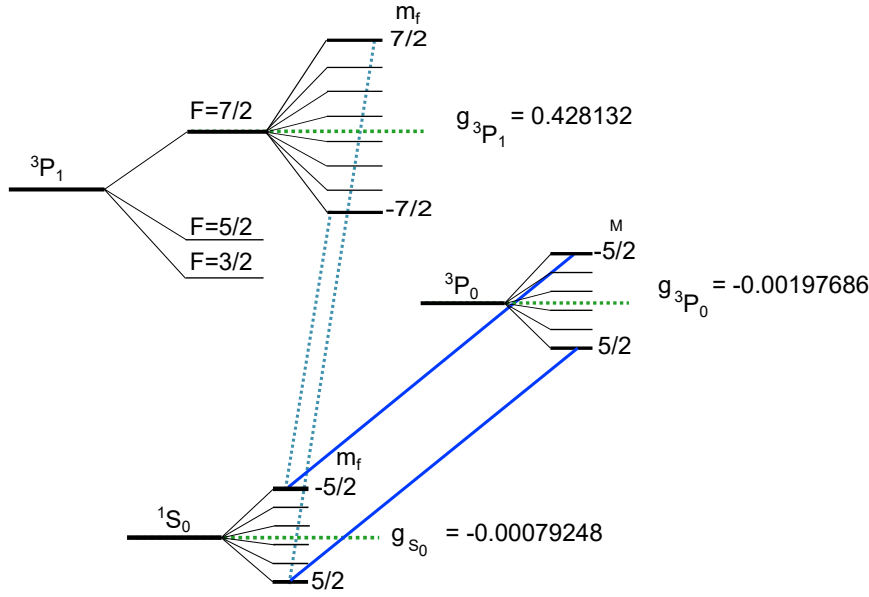


Figure 3.4: Linear Zeeman shift for the $^{27}\text{Al}^+$ clock levels.

The 3P_0 energy level has a Landé g-factor of $g_{^3P_0} = -0.00197686$, the 3P_1 of $g_{^3P_1} = -0.0428132$ and the 1S_0 of $g_{^1S_0} = -0.00079248$. The 3P_1 level is split in 7 magnetic sublevels while the ground and excited clock state split in 5 magnetic sublevels each. Taking advantage of this "ladder" configuration the $^1S_0 \leftrightarrow ^3P_1$ intercombination line at 267 nm is used for initializing the ion in a pure electronic state by optical pumping.

	$^{40}\text{Ca}^+$	$^{27}\text{Al}^+$
Atomic mass m (u)	39.962	26.981
Nuclear Spin I	0	5/2
Clock transition	$^2S_{1/2} \leftrightarrow ^2D_{5/2}$	$^1S_0, F = 5/2 \leftrightarrow ^3P_0, F = 5/2$
Frequency of clock transition (THz)	411.042	1 121.02
Natural linewidth (mHz)	136	7.6
Landé g-factor excited state	1.200 334 0(3) [79]	-0.001 976 86(21) [68]
Landé g-factor ground state	2.002 256 659 [85]	-0.000 792 48(14)[68]
Quadratic Zeeman coefficient (Hz/mT ²)	14.355(17) ¹ [76]	-71.944(24)[67]
Scalar differential polarizability $\Delta\alpha_s$ (10^{-40} Jm ² /V ²)	-7.2677(21) [27]	0.0702(95)[17]
Black body radiation shift (Hz)	0.37913(12) ² [27]	-0.0038(5) ³ [17]
Quadrupole moment θ (e a ₀ ²)	1.83(0.01)[33]	-1.7(6) $\times 10^{-6}$ [72]

Table 3.1: Atomic parameters of $^{40}\text{Ca}^+$ and $^{27}\text{Al}^+$ clocks

¹Averaged over 6 transitions

²At a temperature of approximately 300 K

³At a temperature of approximately 295 K

Chapter 4

Experimental setup

"Machines, he said, are an effect of art
which is nature's ape, and they reproduce not its forms
but the operation itself"
Umberto Eco
The name of the rose

The experiments described in this thesis were focused on the development of techniques to perform precision spectroscopy with calcium and aluminum ions. A key aspect of the work was centered around the experimental setup necessary to load, cool, detect and manipulate the state of the ions. The ion trap, vacuum vessel and laser system, used for these experiments, were originally set up by Michael Guggemos and Daniel Heinrich and are described in their respective theses [69, 86]. In this chapter, I give a condensed overview of the current setup and describe the new extensions that have not yet been described.

4.1 Ion trap

Our ion trap setup was designed with the main goal of performing high precision spectroscopy and ultimately operate as a frequency standard. The focus of the design was centered around minimizing the influence of any external perturbation to the trapped ions. Our ion trap is based on the macroscopic linear Paul trap designs successfully implemented in different experiments in our group over the past 15 years [87, 59, 88, 52]. The main differences of our design reside in the selection of different materials to mitigate heating and vibrations and in the implementation of ablation loading. The ion trap, depicted in Fig. 4.1, is composed of four blade-shaped electrodes, symmetrically aligned within the radial plane and two tip-shaped electrodes located at each side in the axial direction. The electrodes of the trap are made of titanium, coated with a 10 μm thick layer of gold, and held together by sapphire pieces. This combination of materials was chosen because it assures a reduction of temperature variations during daily trap operations [69]. One pair of opposite blades carries a radio frequency (RF) voltage and is driven at a frequency $\Omega/2\pi \approx 32$ MHz. The other two blades are held at a fixed DC voltage. The ion-to-RF blade distance is about 500 μm . The two tip electrodes, or *end-caps*, situated at each side of the trapping center, separated by a distance of 4.5 mm, are held at a fixed voltage, typically around 400 V, to supply the axial confinement of the ion. In order to provide optical access along the trap axis, both *end-caps* have 0.5 mm holes. Two pairs of "compensation electrodes" are implemented to shift the radial ion position either in the horizontal or vertical direction. Two targets for ablation-loading, one made of pure aluminum, and the second of an aluminum-calcium alloy, are located above the trap. An electrode situated at the

bottom of the trap is used to generate a variable controlled RF field by applying an RF voltage, denominated hereafter “tickle voltage”.

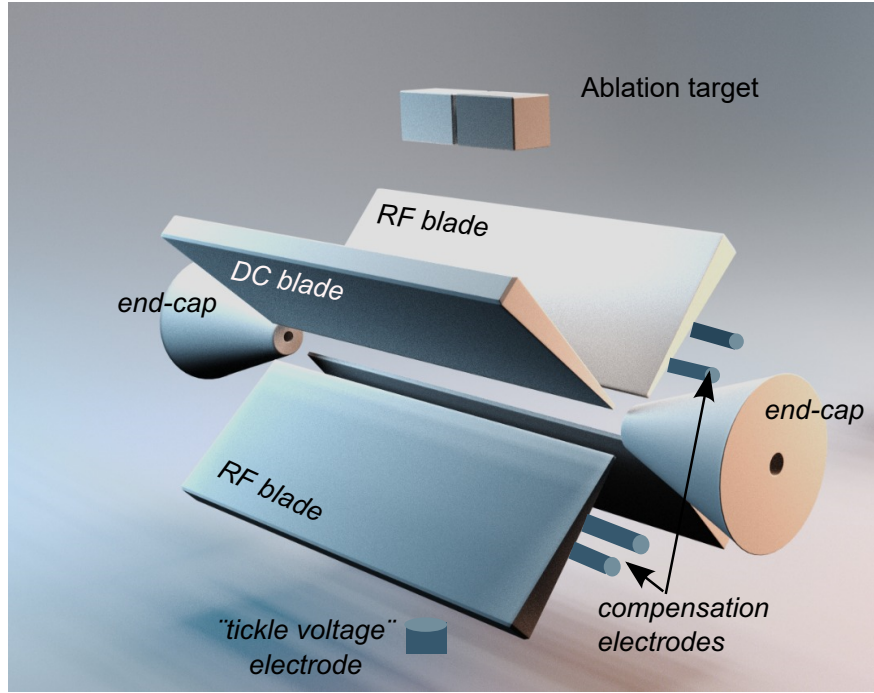


Figure 4.1: Schematic image of the linear Paul trap.

The ion trap consists of two pairs of opposite blade-shaped electrodes, one held at a fixed DC voltage (“DC blade”) and one held at an RF voltage (“RF blade”). Additionally, two tip electrodes (“end-caps”) are situated at each side of the trap. Two pairs of “compensation electrodes” are implemented to shift the radial ion position either in the horizontal or vertical direction. An external electrode “tickle-voltage electrode” located at the trap bottom allows the application of a variable controlled RF voltage. Two ablation targets are located at the top.

4.2 Vacuum vessel

The ultra high vacuum (UHV) vessel containing the trap is a stainless steel spherical octagon, with two big (100 mm radius) and eight smaller (40 mm radius) flanges. To enable vacuum pumping and pressure analysis, a non-evaporation getter (NEG) and an ion getter pump are installed in the west flange of the trap, see Figure 4.2. We estimate that the pressure in the vacuum chamber is approximately $(1.4 \pm 0.2) \times 10^{-10}$ mbar in normal operation conditions (Sec.7.2). In order to reduce magnetic field fluctuations, the trap chamber is mounted inside a magnetic field shield (Sec.4.3). As illustrated in Fig.4.2, a pair of concentric permanent magnet holders situated in the west and east viewports of the chamber define the magnetic quantization field (Section 4.3) along the z-axis of the trap. In order to trap, cool and excite the ions, the center of the trap is optically accessible from three different sides:

- Parallel to the quantization field following the z-axis of the trap: used to send the photoionization lasers (422 nm, 394 nm and 375 nm) and the clock lasers (729 nm, 267.4 nm and 267 nm).

- In the vertical plane at an angle of 45° to the trap axis: used to send the cooling, repumping and detection lasers (397 nm, 854 nm and 866 nm) and the 729 nm laser.
- In the horizontal plane orthogonal to the quantization axis: dedicated to fluorescence collection and for the clock lasers (729 nm and 267.4 nm).

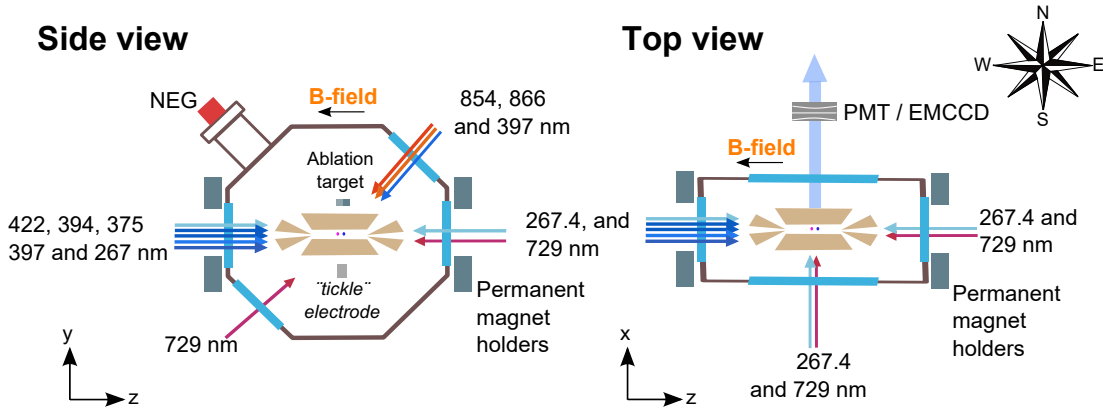


Figure 4.2: Schematic of the Side view and Top view of the vacuum chamber.

The trap is mounted in the middle of a stainless-steel octagon. The different lasers and imaging directions are illustrated with respect to the cardinal directions (indicated by the compass rose). The magnetic quantization field (B-field) (Section 4.3), along the z-axis of the trap, is provided by a pair of concentric permanent magnet holders, situated in the west and east viewports of the chamber. A non-evaporative getter (NEG) and an ion getter (not shown) provide vacuum pumping and analysis. The ablation targets and the "tickle" voltage electrode are situated above and below the trap along the y-axis respectively. The fluorescence emitted by the ion is detected by a photomultiplier tube (PMT) and an electron multiplying charge-coupled device (EMCCD) camera through the northern viewport.

The fluorescence emitted by the ions during experiments is filtered through a bandpass filter (381 nm - 399 nm), split and detected by a photomultiplier tube (PMT)¹ and an electron multiplying charge-coupled device (EMCCD)².

4.3 Magnetic field stabilization

In order to define the quantization axis, a weak magnetic field ($\sim 3-4$ G) is applied. As described in Michael Guggemos thesis, the quantization axis in our setup was originally defined by a pair of coils situated at the west and east viewports of the chamber. The 220 turn coils are designed to generate a field of 4 G at the position of the ion. The magnetic-field stability of the coils was good enough for precision experiments, exhibiting drifts of about ± 1.19 nG/s over two-hours periods. The limiting factor for achieving long coherence times was the magnetic-field noise coming from the current driver of the coils. We decided to exchange the coils by a pair of concentric permanent magnet holders designed by Martin Meraner [89] which improved the coherence

¹Sens-Tech P₂₅PC

²Andor iXon DV885JCs-VP

times by a factor of 7. The pair of concentric magnets generate a field of (3.07872 ± 0.00001) G with a drift of (-0.06 ± 0.01) nG/s over a period of 10 days with fluctuations on an hour scale on the order of ± 2 nG/s. A full characterization of the daily magnetic field variations is described in Section 5.2.1.

As it is carefully described in Cornelius Hempel thesis [52] the mains electricity at 50 Hz alternating current (AC) used to power devices in the laboratory produces spurious AC magnetic fields that also affect the energy levels of the ion. As it is described in his thesis, depending on the probing scheme this noise can be greatly mitigated through the use of a *line trigger*. A time trigger is a device that generates a TTL signal synchronous with the power-line frequency at a phase selected such that the coherent operations happen only in the quiet periods of the cycle. However, in order to perform the absolute frequency measurement of the Ca^+ transition we need to probe 6 different transitions which would be consequently affected differently by the magnetic field noise. In order to reduce the effect of this noise we choose to implement an approach designed by Johannes Franke and described in his Master thesis [90]. The method consist of the implementation of a pair of coils that can generate a time-dependent magnetic field that cancels out the magnetic field noise generated by the 50 Hz alternating current.

4.4 Laser system

The necessary lasers for trapping and manipulation of single ions can be divided into three groups:

- Ablation loading and photoionization
- Doppler cooling and state detection
- Spectroscopy

Since we work with two different ion species ($^{40}\text{Ca}^+$ and $^{27}\text{Al}^+$), two sets of lasers are necessary. Fig.3.1 and Tab 4.1 illustrate the relevant energy levels and necessary lasers for the calcium ion experiments and Fig 3.3 and Tab.4.2 illustrate the ones necessary for the aluminum ion experiments. As explained in Sec 2.4, sympathetic cooling (SC) and quantum logic spectroscopy (QLS) are implemented for cooling and state detection of $^{27}\text{Al}^+$. The photoionization, Doppler cooling and detection lasers are all external cavity diode lasers (ECDLs) and are frequency locked to a wavelength meter (WLM)³.

Operation	Laser wavelength
Ablation and photoinization	532 nm pulsed, 375 nm and 422 nm
Doppler cooling and state detection	397 nm, 866 nm, 854 nm and 850 nm
Spectroscopy	729 nm

Table 4.1: Overview of the laser wavelengths necessary for loading, cooling, state detection and spectroscopy of $^{40}\text{Ca}^+$ ion .

³HighFinesse WS U/2

Operation	Laser wavelength
Ablation and photoionization	532 nm pulsed, 375 nm and 394 nm
Spectroscopy	267.4 nm and 267 nm

Table 4.2: Overview of the laser wavelengths necessary for loading, cooling, state detection and spectroscopy of $^{27}\text{Al}^+$ ion.

Ablation loading and photoionization

In our system ions are generated via ablation loading. This method has proven to avoid temperature variations and reduce contamination of the trap blades and the vacuum as has previously been observed with resistive oven sources [91, 92]. Our ablation loading and photoionization setup has previously been described in detail [55, 69]. As illustrated in Figure. 4.3, two ablation targets⁴ are located 26 mm above the trap, one of pure aluminum and the second of an alloy (30% Ca and 70% Al). A single pulse at 532 nm, from a frequency-doubled laser⁵ operating at a fundamental wavelength of 1064 nm, triggered via a TTL signal, is fired at one of the targets. The emitted pulses have a maximum energy of up to 400 μJ and a pulse width of 2 ns. A configuration of a half wave plate (HWP) and a polarized beam splitter (PBS) is implemented to attenuate the ablation pulses intensity by approximately 10 %. In order to select between the two targets a second HWP is located in front of a calcite beam displacer⁶ which permits to select between two polarization-dependent paths. Both atom species are ionized in a two-step photoionization process [52, 93], as illustrated in Figure. 3.1 and Figure. 3.3. In both schemes, the first stage facilitates isotope selectivity by means of an ECDL⁷ laser at a wavelength of 422.79 nm for calcium and 394 nm for aluminum. The second stage is performed with a free-running diode laser⁸ at 375 nm, for both species. The three laser beams are overlapped and coupled into a single-mode (SM) fiber and sent to the center of the trap through the end-caps. The photoionization laser beams can all be blocked by a TTL controlled shutter located in front of the fiber coupler.

⁴Konik industries

⁵Coherent Flare 532

⁶Thorlabs BD40

⁷Toptica DL pro

⁸Toptica iBeam smart

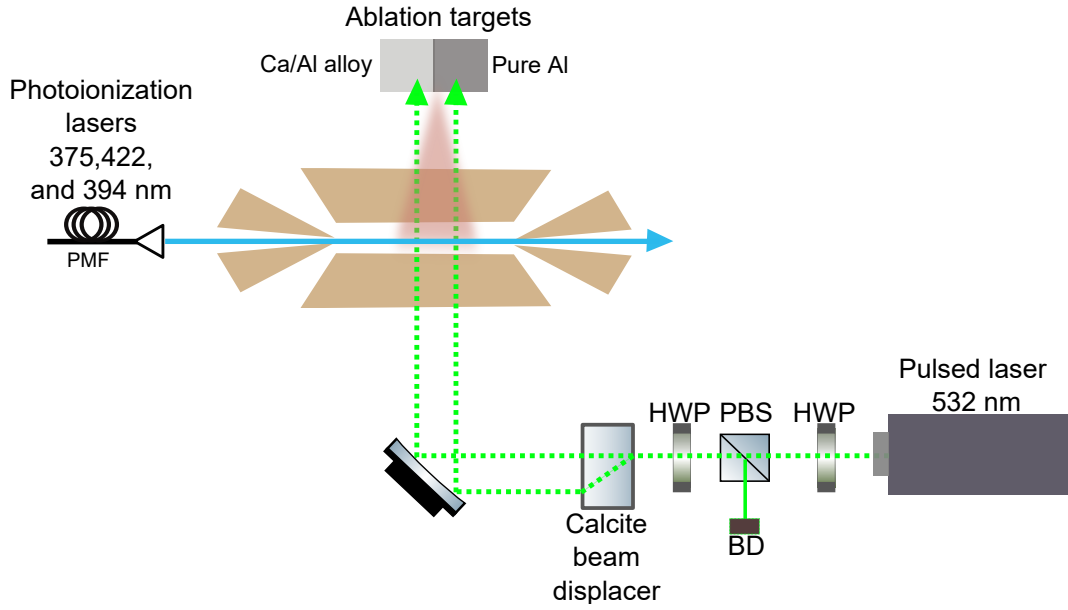


Figure 4.3: Schematic of the ablation and photoionization setup.

A single pulse at 532 nm, with a duration of 2 ns and a pulse energy of $100 \mu\text{J}$ is fired at one of the ablation targets (either the Ca/Al alloy or to the pure Ca) situated above the trap. The first half-wave plate (HWP) in combination with a polarizing beam splitter (PBS) and a beam dump (BD) are used to attenuate the pulses. The second HWP together with a calcite beam displacer are used to select the target to ablate. The photoionization laser beams are overlapped and coupled into a single-mode (SM) fiber and sent to the center of the trap through the end-caps.

4.4.1 Fluorescence and state detection

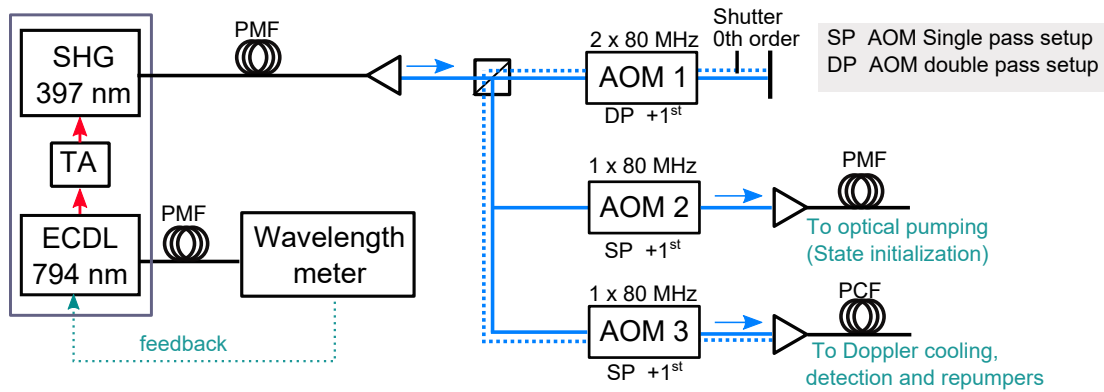


Figure 4.4: Schematic of the 397 nm setup.

Light at 397 nm is sent through a polarization-maintaining fiber (PMF) to the breadboard and is split into three beam paths: AOM 1 and AOM 3 provide light for Doppler cooling and detection, AOM 1 and AOM 2 for optical pumping, a third path (dashed line) is controlled by a mechanical shutter that allows the non-diffracted 0th order light to be sent to the trap as well. A fraction of the fundamental light at 794 nm is used to lock the laser to the WLM. Modified figure from [69].

As illustrated in Figure. 3.1, the strong $S_{1/2} \rightarrow P_{1/2}$ dipole transition in $^{40}\text{Ca}^+$ is used for laser cooling, state detection and optical pumping. As shown in Figure. 4.4, the

397 nm laser light is generated by a frequency-doubled [ECDL](#)⁹ with a fundamental wavelength at 794 nm. A fraction of the fundamental light is used to stabilize the laser frequency to the [WLM](#). The remaining light is amplified in a tapered amplifier ([TA](#)) and then frequency doubled by a nonlinear crystal. The light at 397 nm is sent to a separate breadboard attached to the optical table, through a polarization-maintaining fiber ([PMF](#)) and split into three beam paths controlled by acoustic-optic modulators ([AOMs](#)):

- AOM 1 and AOM 3 provide light for Doppler cooling
- AOM 1 and AOM 2 are used for optical pumping
- a mechanical shutter allows the non-diffracted beam path of AOM 1 to be sent to the trap to help re-crystallize melted ion crystals.

The implementation of consecutive [AOMs](#) has the supplementary advantage to further suppress unwanted light when the [AOMs](#) are switched off.

4.4.2 Pumping lasers

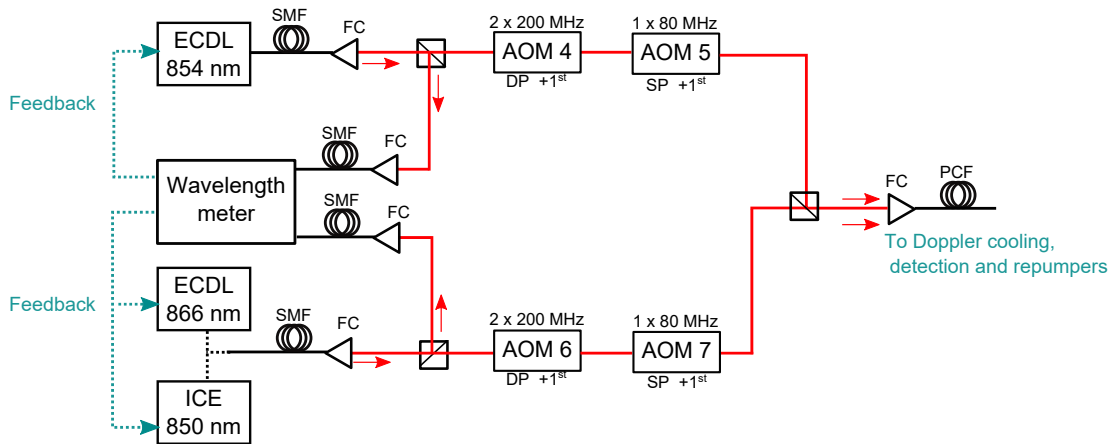


Figure 4.5: Repumpers laser setup.

The same setup is implemented for 854 nm, 850 nm and 866 nm lasers. A fraction of the light is sent to lock the laser to the [WLM](#). One [AOM](#) in double pass configuration and a second one in single-pass, shift the light by 400 + 80 MHz and suppress any unwanted light when the [AOM](#) are switched off. The same path can be used either for the laser at 866 nm and the one at 850 nm. Modified figure from [69].

As presented in Figure. 3.1, the $3D_{3/2}$ state can be pumped out by means of lasers either resonant with the $3D_{3/2} \rightarrow 4P_{1/2}$ (866 nm) or the $3D_{3/2} \rightarrow 4P_{3/2}$ (850 nm). The $3D_{5/2}$ state can be pumped out by a laser resonant with the $3D_{5/2} \rightarrow 4P_{3/2}$ (854 nm). The 866 nm and 854 nm lasers are both [ECDLs](#)¹⁰ and the 850 nm a tunable Titanium Sapphire [Ti:Sa](#)¹¹. All lasers are controlled following the same optical setup shown in Figure 4.5: A fraction of the light is sent to lock the laser with the [WLM](#) while the rest of the light is controlled by two consecutive [AOMs](#): one in double pass configuration and the second in single-pass. The repumper's light paths overlap with the 397 nm path and are sent through a photonic crystal fiber ([PCF](#)) to the trap.

⁹Toptica-SHGpro

¹⁰2 x Toptica DLpro

¹¹SolsTiS 140105

4.4.3 Spectroscopy lasers

A key ingredient of any optical atomic clock is the spectroscopy laser: the light used to drive the atomic transition and the atomic states being driven must be highly coherent.

As previously described in Section 2.4.3, quantum logic spectroscopy (QLS) with $^{40}\text{Ca}^+$ and $^{27}\text{Al}^+$ ions requires a set of three ultra-stable narrow-linewidth laser systems. The clock transitions of the $^{40}\text{Ca}^+$ and the $^{27}\text{Al}^+$ ion have a natural linewidth of $2\pi \cdot 139$ mHz and $2\pi \cdot 7.6$ mHz respectively. A third laser is necessary to drive the intercombination line of the $^{27}\text{Al}^+$ which has a natural linewidth of $2\pi \cdot 520$ Hz. The three laser setups were previously described in the works of Michael Guggemos and Cornelius Hempel [69, 52]. In this section, a schematic overview with a condensed summary of the key elements for each laser is presented. Each laser setup has three main sections illustrated with different colors in the schematics:

- I Frequency stabilization (in blue).
- II Frequency measurement (in orange).
- III Light preparation and distribution to the trap access (in red).

To carry the light over longer distances in each of the laser setups we use PMF fibers whose optical-path length is stabilized by means of the fiber noise cancellation method (FNC). The method is described in detail in the section: [Fiber noise cancellation](#).

I-Frequency stabilization

Each laser is phase-stabilized to an external high-finesse cavity via a Pound-Drever-Hall (PDH) locking scheme [13]. The frequency stabilization setup is housed inside a wooden box specially designed to shield RF and acoustic noise. The design and construction are described in detail in [69]. The light is carried to the box through an optical path-length stabilized PMF by means of the fiber noise cancellation (FNC) method. At the output of the fiber, light passes an optical isolator (FI), that ensures the suppression of possible unwanted back-reflections. The FI is followed by a Glan-Thompson polarizer (GTP) that matches the polarization of incoming light to the windows and crystals of the electric optic modulator EOM used to phase-modulate the laser frequency. The light is then finally coupled into the cavity (TEM₀₀ mode). The light reflected from the cavity is detected on a PD and mixed with the EOM frequency and generates the PDH error signal fed into a PID controller that acts on different feedback elements depending on the laser system. A CCD camera located after the cavity is used to monitor the cavity mode. The light intensity sent to the cavity is stabilized: a PD detects the transmitted power and sends the value to a PID controller that regulates the RF power of the AOM located before the fiber input.

II-Frequency measurement

The three laser frequencies are constantly monitored by a wavelength meter (WLM)¹² in conjunction with an 8-channel mechanical switch. The WLM has a precision of around 2 MHz and is calibrated every 5 mins to the light of the 729 nm laser when it is referenced to the clock transition of the $^{40}\text{Ca}^+$.

The frequency of the lasers can also be measured with a fiber-based optical-frequency comb¹³ (FC). The FC setup has been previously described in detail [69, 86]. The FC

¹²HighFinesse WS U/2

¹³Menlo Systems FC 1500-250-WG

has 20 MHz carrier envelope offset frequency (f_{CEO}) and a 250 MHz repetition rate frequency (f_{REP}). In normal operation they are both locked to a 10 MHz signal from a GNSS disciplined passive hydrogen maser¹⁴ with a fractional instability of $\sim 9 \cdot 10^{-15}$ in 1 hour. The setup is described in more detail in Section. 4.7. The repetition rate f_{REP} can also be locked to the ultra-stable 729 nm laser.

III-Light preparation and distribution

The lasers' light is distributed to the various optical access paths of the trap via PMFs. Each distribution setup follows the same configuration: an AOM set in double pass configuration is used to tune the laser in resonance with any desired transition of the Zeeman split manifold of the $^{40}\text{Ca}^+$ or $^{27}\text{Al}^+$ ion and a second AOM in single pass configuration is used to facilitate or block accordingly the passage of light to the respective viewport of the trap.

Fiber noise cancellation

Light carried by fibers over long distances suffers from fiber noise. This effect originates from the modulation of the refractive index of the fiber core, induced by acoustic and temperature changes in the fiber path. In order to suppress this noise, a fiber noise cancellation (FNC) [94] scheme is implemented on all the fibers used for the spectroscopy lasers. A beat note between the laser light at the fiber input and the light reflected from the flat-polished (FC-PC) end of the fiber is detected on a PD. This signal controls a home-built voltage-controlled oscillator (VCO) phase-locked loop that steers the signal of an AOM located before the fiber input, suppressing frequency variations originating in the fiber path.

Ultra-stable 729 nm laser system

The laser system, located in laboratory 1 of IQOQI, has been described in detail in previous works [52, 53]. The setup illustrated in Figure. 4.6, is composed of a diode-pumped Nd:YVO₄ laser at 532 nm¹⁵ that pumps a titanium-doped sapphire (Ti:Sa) crystal inside a modified dye laser¹⁶. The Ti:Sa laser is locked to a high-finesse cavity (with a finesse $\mathcal{F} \approx 400000$), equipped with an intra-cavity EOM, via a three-fold laser lock. The system provides a short-term linewidth of 1-10 Hz and is used in regular operation, in laboratory 1, for the coherent manipulation of long strings of $^{40}\text{Ca}^+$ ions [95, 96, 97]. In order to correct for long-term cavity drifts (≈ 50 mHz/s) Ramsey experiments (Sec.2.4.2) are performed with the $^{40}\text{Ca}^+$ ion every 2-5 minutes. The cavity drift is continuously compensated via AOM 8, assuring that the laser is on resonance with the ion. As a test of the system's performance, the frequency of the laser is compared with another similar laser setup located at a university laboratory [59, 88]. A 400 m optical-path length stabilized PMF brings the light to laboratory 1 where beat measurements are regularly performed to evaluate the performance of both systems [98]. The light is sent to laboratory 2 via a 10 m optical-path length PMF. The stable light seeds a tapered amplifier TA¹⁷ with a maximum power output of 560 mW and is distributed to the rest of the experimental setup. The light is split into two main branches: one for performing frequency measurements and the other for preparing and sending the light to the ion trap.

¹⁴pHmaser 1009

¹⁵Coherent Verdi V-10

¹⁶Coherent model 899

¹⁷Toptica TA 100

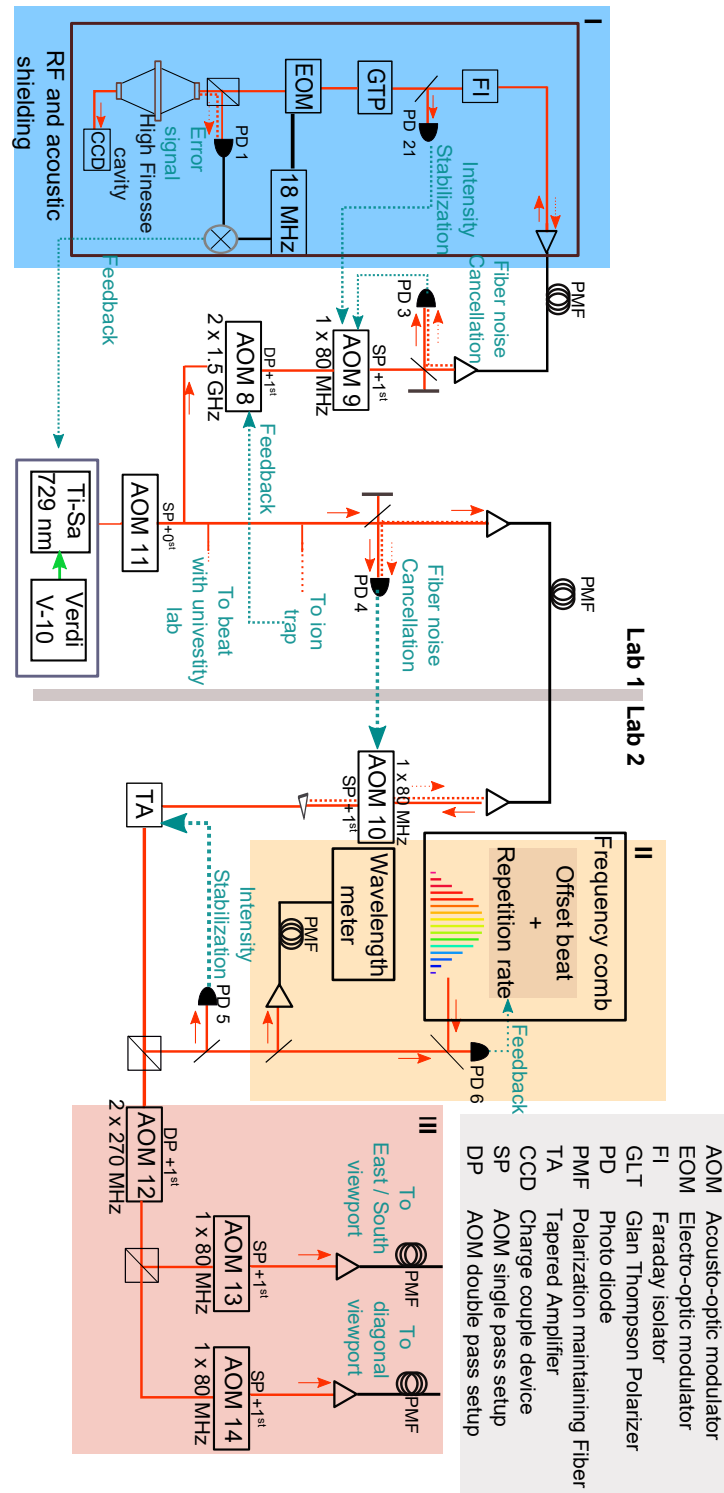


Figure 4.6: Schematic overview of the 729 nm laser setup.

The setup is separated in three main sections: I Frequency stabilization (in blue), II Frequency measurement (in orange) and III Light preparation and distribution (in red). The frequency stabilization setup is located in Lab 1, the light is carried to Lab 2 via an optical path length stabilized PMF.

A fraction of the light from the first branch is used to calibrate the WLM. The rest of the light is used to perform a beat-note measurement with the frequency comb. The signal detected at PD 6 is then fed back to an intracavity EOM that stabilizes the repetition rate frequency (f_{REP}) of the comb.

The second branch is split in two: part of the light is sent to either the East or the South viewport and the second part to the diagonal viewport (see Figure. 4.2). AOM 12 is used to tune the laser with the transitions of the $^{40}\text{Ca}^+$ while AOMs 13 and 14 allow or block the passage of the light to the respective PMF that carry the light to the different viewports.

Ultra-stable 267 nm laser system

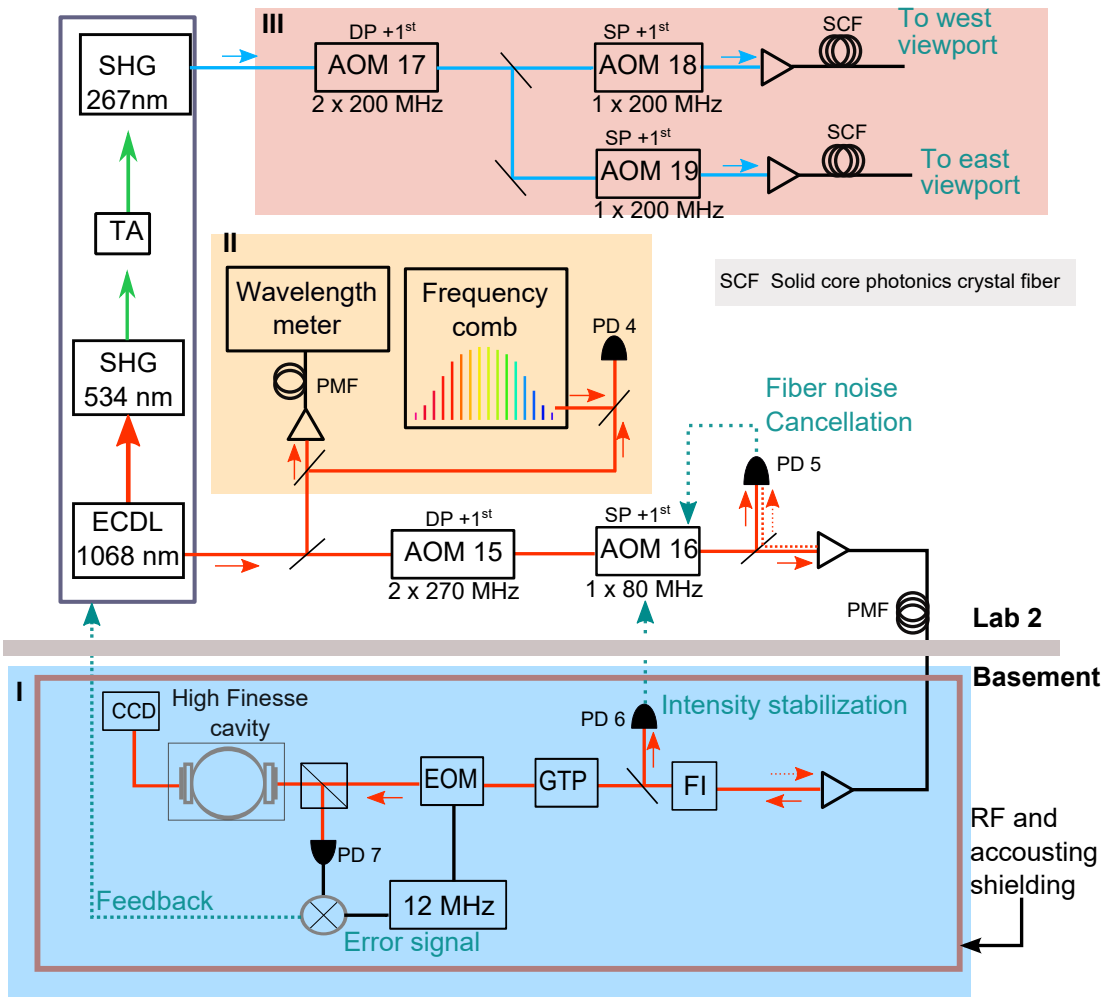


Figure 4.7: Schematic overview of the 267 nm laser setup.

The setup is separated into three main sections: I Frequency stabilization (in blue), II Frequency measurement (in orange) and III Light preparation and distribution (in red).

The laser setup, illustrated in Fig. 4.7 has been described in previous works [69, 70]. The setup consists of a frequency quadrupled ECDL¹⁸ diode laser. The fundamental laser light at 1068 nm is locked to an external high-finesse cavity¹⁹ ($\mathcal{F} \approx 340000$)

¹⁸Toptica DL TA FHG pro

¹⁹ATF 6300 spherical cavity

located in a basement under the laboratory. The PDH error signal generated in PD 11 is used to feed the fast analog linewidth control (FALC) of the laser in two branches: a slow locking branch that feeds back on the piezo controller and a fast one that feeds back on the laser-diode current. The system provides a short-term linewidth of 1-10 Hz. Long term cavity drifts (≈ 46 mHz/s) are compensated daily via AOM 15. The fundamental light frequency is measured with the WLM and the frequency comb. The quadrupled light at 267 nm is split into two branches: one that is directed to the west viewport and the other to the east viewport. The frequency sent to the ion is tuned via AOM 17 while AOMs 18 and 19 are used to allow or block the light that is sent to solid-core photonic crystal fibers that carry the light to the ion. These custom-made fibers²⁰ have the advantage of avoiding power losses induced by color-center formation in the UV [99].

Ultra stable 267.4 nm laser system

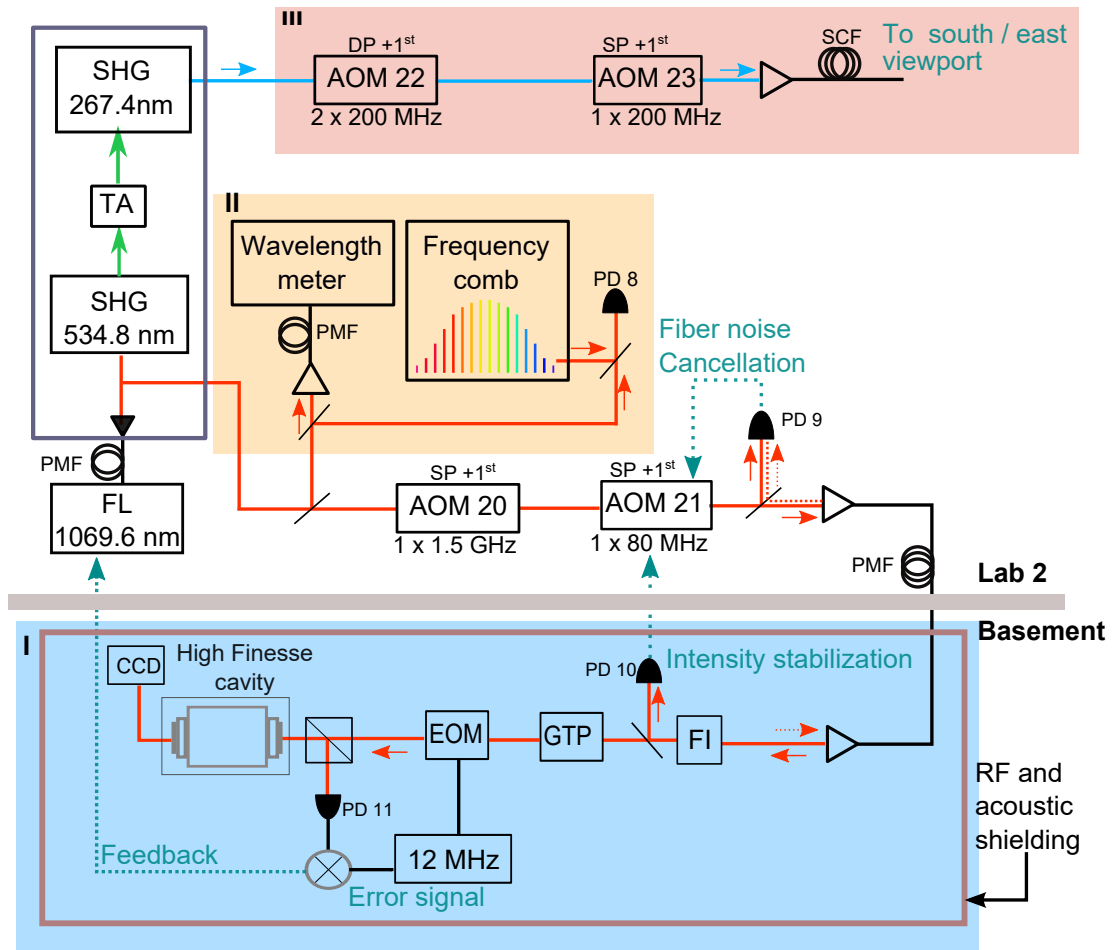


Figure 4.8: Schematic overview of the 267.4 nm laser setup.

The setup is separated into three main sections: I Frequency stabilization (in blue), II Frequency measurement (in orange) and III Light preparation and distribution (in red).

The laser setup, almost identical to the one for the 267 nm laser has been also described in the works [69, 70]. The setup, illustrated in Figure. 4.8 consists of a frequency

²⁰NKTphotonics LMA-10-UV-FUD

quadrupled²¹ fiber laser²². The fundamental light at 1069.6 nm is locked to an external high-finesse cavity²³ ($\mathcal{F} \approx 405000$) located in a basement. In this case, the PDH error signal generated in PD 11 feeds a homemade PID controller with two branches: the slow part feeds back on the piezo of the laser and the fast part feeds back on a low-noise voltage controlled oscillator (VCO) that drives the frequency of the fiber AOM inside of the laser. The system provides a short-term linewidth of 1-10 Hz. Long term cavity drifts (≈ 100 mHz/s) are compensated daily via AOM 20. Following the same setup as for the 267 nm laser the fundamental light is measured with a WLM and the FC. The quadrupled light at 267.4 nm is sent to the south or east viewports. The frequency sent to the ion is tuned via AOM 22 while AOM 23 is used to allow or block the light sent via a solid core photonic fiber to the ion.

4.5 Fluorescence and state detection

The ion crystal fluorescence is used in our experiments for two main purposes: state detection and thermometry.

To detect the internal state of the $^{40}\text{Ca}^+$ ion we employ the electron shelving technique [100, 101]. Laser excitation on the strong $S_{1/2} \leftrightarrow P_{1/2}$ dipole transition combined with repumping light on the $D_{3/2} \leftrightarrow P_{1/2}$ transition (see Fig. 3.1) is used to differentiate the state of the valence electron of the calcium ion: while the valence electron is in the so called "bright" $S_{1/2}$ state millions of photons per second are scattered. However, while the ion is in the "dark" $D_{5/2}$ state, no light is scattered.

To determine the internal energy or "temperature" of the $^{40}\text{Ca}^+$ ion, we implement Doppler cooling thermometry measurements [102]. The technique is described in detail in Section 7.3. In simple terms, it is based on determination of the fluorescence scattering-rate variations as a function of the ion's internal energy.

The fluorescence emitted by the $^{40}\text{Ca}^+$ ion crystal is detected using a similar setup as the one described in Cornelius Hempel's thesis [52]. A 5-lens objective²⁴ with an effective focal length of 66.8 mm and a pupil diameter of 34 mm collects and guides the light through a variable slit²⁵ and through a band-pass filter²⁶ (transmission between 381 nm and 399 nm). The fluorescence is then split and detected using both a photomultiplier tube (PMT) and an electron multiplying charge-couple device (EMCCD) camera (see Fig. 4.2).

The detection and manipulation of the internal state of the $^{27}\text{Al}^+$ ion cannot be performed using the same state-dependent fluorescence technique. The dipole-allowed transition $^1S_0 \leftrightarrow ^1P_1$ that could be used for these purposes has a wavelength of 167 nm, making its operation technically more challenging. Moreover, the transition has a large linewidth (≈ 220 MHz). Doppler cooling on this transition would lead to minimum temperatures that are an order of magnitude above the ones reached with Sr^+ , Hg^+ , Yb^+ or Ca^+ ions [4]. To overcome these difficulties, the calcium ion is used to cool down and detect the state of the aluminum ion via sympathetic cooling and quantum logic spectroscopy (see Section. 2.4.3 and 2.4).

²¹Toptica FHG standalone

²²Menlo Systems orange one

²³ATF6020 notched cavity

²⁴custom made by Silloptics

²⁵Owis Spault 40

²⁶Semrock SEM-FF_{01-390/18-25}

4.5.1 PMT detection

The **PMT**²⁷ is used for capturing a large solid angle fraction of all the emitted photons by the trapped ion(s). The overall detection efficiency of our setup, including all optical elements is $(0.28 \pm 0.01)\%$. For a single Doppler cooled $^{40}\text{Ca}^+$ we measure a bright count rate of (107 ± 7) kcounts/s and a dark count rate of (17.5 ± 2.3) kcounts/s due to scattered light at 397 nm. To process the detected **PMT** pulses, two different methods are implemented:

- The number of **PMT** pulses detected during a given interval are recorded by a Ni daq (National Instruments data acquisition system) counter triggered by a **TTL** pulse.
- A time stamp is assigned and recorded to every **PMT** pulse detected by the **PMT** using a time tagger²⁸.

The first method is implemented in regular operations to detect the quantum state of the $^{40}\text{Ca}^+$ ion(s) at the end of an experimental sequence. The detection time windows are usually on the order of milliseconds and each sequence is repeated N times (cycles). From these measurements, two-photon count distributions can be identified in a histogram: one corresponding to the bright and the other to the dark state of the ion(s).

The second method is implemented to detect the atom's fluorescence during the process of laser Doppler cooling. During thermometric measurements the time at which each emitted photon arrives to the detector is recorded allowing a better time resolution to observe evolution of fluorescence rate.

These techniques are very effective when working with a single ion. However, difficulties arise when they are implemented for many ions. For experiments with many ions it becomes more delicate to differentiate the count distribution corresponding to each ion leading to state discrimination errors [52]. For the specific case of the aluminum ion, for which there is no available "detection"-transition it is not possible to detect the presence of the ion by using only **PMT** detection schemes. The ion is indirectly detected through the observation of the $^{40}\text{Ca}^+$ ion for which is necessary to spatially resolve the fluorescence of the ion.

4.5.2 Camera

To spatially resolve the ion(s) fluorescence distribution, an **EMCCD** camera²⁹ is employed. The camera has a quantum efficiency of $\approx 37\%$ at 397 nm, a pixel size of $8 \mu\text{m} \times 8 \mu\text{m}$ and the magnification of the imaging system is about ~ 27 . It has the advantage that it allows not only to spatially resolve but also to record the temporal evolution of the position of the ions in the trap. The camera is controlled via a home-made program³⁰ that can be linked with TrICS, our main experimental control program (see Section. 4.6). The camera offers five different acquisition modes: single-scan, video, accumulative, kinetics and fast kinetics. They are all briefly illustrated and explained in Figure. 4.9. The single, video and accumulative acquisition mode are used to record experimental events happening in real time. The kinetics and fast kinetics modes are implemented to record the temporal evolution of physical processes.

²⁷Sens-Tech P25PC quantum efficiency of $\approx 27\%$ at 397 nm

²⁸ID900

²⁹Andor iXon DV885JCs-VP

³⁰Written in Python 3.6 by Daniel Heinrich

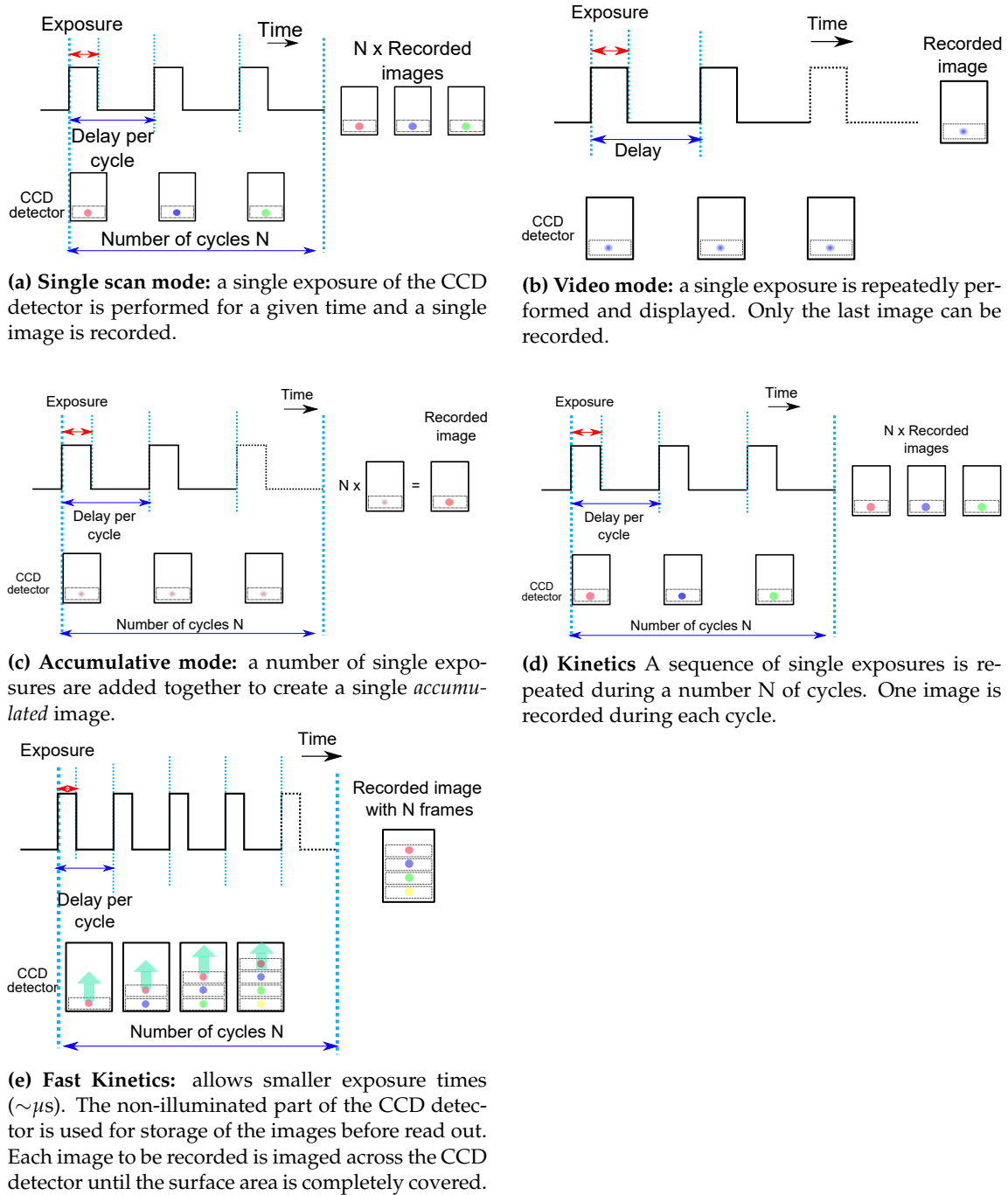


Figure 4.9: Camera acquisition modes: (a) single, (b) video and (c) accumulative are used to record experimental events happening in real time. (d) Kinetics and (e) fast kinetics are implemented to record the temporal evolution of physical processes.

4.6 Experimental Control

The experimental control system has been previously described in the thesis of Michael Guggemos [69]. As illustrated in Figure. 4.10 the "brain" of the experiment is at the *Control PC*. All the components of the experiment are linked and can be manipulated through this main computer via an in-house designed program called Trapped Ion Control Software *TrICS*, described in more detail in Daniel Heinrich thesis [86].

The diagram illustrates the experimental setup for the trapped ion quantum simulator. The central component is the **Control PC** (red box), which manages the system. It is connected to several other components:

- WLM PC** (red box): Contains a **Python Server**. It connects to the **Control PC** via **TCP/IP**. It also connects to a **WLM** (black box) via **USB** and **RS 232**, and to **Diode lasers** (pink box) via **DC**.
- Frequency comb PC** (red box): Contains a **Python Server**. It connects to the **Control PC** via **TCP/IP**. It also connects to a **Frequency comb** (black box) via **TCP/IP**. The **Frequency comb** connects to a **GNSS receiver** (black box) and a **MASER** (black box). The **GNSS receiver** also connects to a **Trap electrodes** (pink box) via **DC**.
- USB PC** (red box): Contains a **Python Server**. It connects to the **Control PC** via **TCP/IP**. It also connects to a **Time Tagger** (black box) via **USB** and **DC**. The **Time Tagger** connects to a **PMT** (blue box) via **TTL**.
- Control PC** (red box): Contains **TrICS LabView Matlab**, a **Python Server**, and **NI DIO-32 HS**. It connects to a **Signal Generators** (black box) via **GPIO**. The **Signal Generators** connect to **Tickle Voltage** and **Trap RF** (pink boxes) via **RF**. The **Control PC** also connects to an **EMCCD** (blue box) via **Andor Bus** and to a **PMT** (blue box) via **TTL**. The **PMT** connects to a **Time Tagger** (black box) via **TTL**. The **Control PC** connects to a **DDS rack** (black box) via **Bus**. The **DDS rack** connects to **AOMs** (orange box) via **RF**. The **AOMs** connect to **Cooling and pumping lasers** (dashed box) and **Spectroscopy Lasers** (dashed box). The **Control PC** also connects to a **Pulse Box** (green box) via **TCP/IP**. The **Pulse Box** connects to **Ablation laser** (pink box) via **TTL** and **RF + TTL**. The **Pulse Box** also connects to the **EMCCD** via **TTL** and to the **Signal Generators** via **TTL**.

The core of the experiment is the control PC (red square): all components of the experiment are linked and can be manipulated through this main computer. Three other PCs (red square) are used to control: the wavelength-meter, the frequency comb and any external device via USB. The Control PC commands the Pulse Box (green square) through a home made software: **TrICS** (Trapped Ion Control System). The pulse box provides timing control between all the components via TTL pulses and RF signals according to user-programmed sequences. The elements interacting directly with the ion are marked in purple. The data is acquired via the **PMT** and the **EMCCD** camera. The entire system can be operated remotely.

4.7 GNSS-link

In order to perform absolute frequency measurements, we have implemented a method based on Global Navigation Satellites Systems **GNSS**, such as the USA's NAVSTAR Global Position System (**GPS**) or the European system Galileo. This method allows us to remotely characterize our clock frequency with respect to the international realization of the second by simply receiving the signals transmitted from the satellites [103]. This method has the advantage of being simpler and cheaper to implement than other techniques such as optical fiber links or two-way satellite time and frequency transfer (TWSTFT). For this reason it is commonly used by most metrology institutes and laboratories as a way to compare their atomic frequency standards.

We implemented a similar scheme to the one described in the thesis of Thorsten Feldman [104] and in the paper by Julia Leute et al. [36]. A schematic of the experimental setup is illustrated in figure.4.11. The **GPS** consists presently of a constellation of 31 satellites in orbit that can provide geolocation and time information to **GNSS** receivers anywhere on Earth. On board of each **GNSS** satellite, an atomic clock (caesium or rubidium) is operated. The satellites continuously transmit signals that carry information about their position and the offset of their internal clock with respect to a common time system. These signals can be decoded by means of a **GNSS** receiver. The receiver is also connected to a flywheel oscillator, in our case a passive hydrogen **maser**. From this information the relative time difference between the satellite's clock and the local clock is estimated. By means of a frequency comb, the frequency of the **maser** is compared to the frequency of the ion's clock transition. We can perform four measurements: two comparing the frequency references (maser) with the frequency of the transition of the ion (Al^+ , Ca^+) and two comparing the frequency reference (maser) to the IGST (timescale of the International GNSS Service). The characterization of the link and measurements are described in detail in Sec.5.1.3. This section is devoted to describe three new elements that were added to the experimental setup to establish the **GNSS** link: a **GNSS** antenna, a **GNSS** receiver and a passive hydrogen **maser**.

4.7.1 GNSS Antenna and cable

As illustrated in Figure. 4.11, the antenna was installed on the roof of the **IQOQI**. A 50 m cable connects the antenna with the **GNSS** receiver located, at the -1 floor of the building, inside the laboratory. The receiver is then connected to the frequency comb and the **maser**. Inside of the laboratory the temperature is stabilized by the air condition, however, both the antenna and the cable are exposed to environmental temperature variations. Outdoor temperature variations can introduce frequency offsets by introducing long-term variations in the receiver hardware delays. These effects become even more considerable during frequency-comparison campaigns spanning over several days or weeks. The temperature stability of the outdoor equipment plays a central role in the whole stability of the **GNSS** link. Following the reviewed technical guidelines for the development of **GNSS** receiver hardware [105], the antenna and antenna cables should tolerate diurnal temperature changes. Innsbruck has maximal diurnal temperature range of about 20°.

Typically, Dorne-Margolin choke ring antennas [106] are implemented for precision measurements. They are composed of three to five concentric ring structures and have been known to provide the most consistent performance. The sensitivity of this type of antennas has been tested for the range of temperature variations in Innsbruck

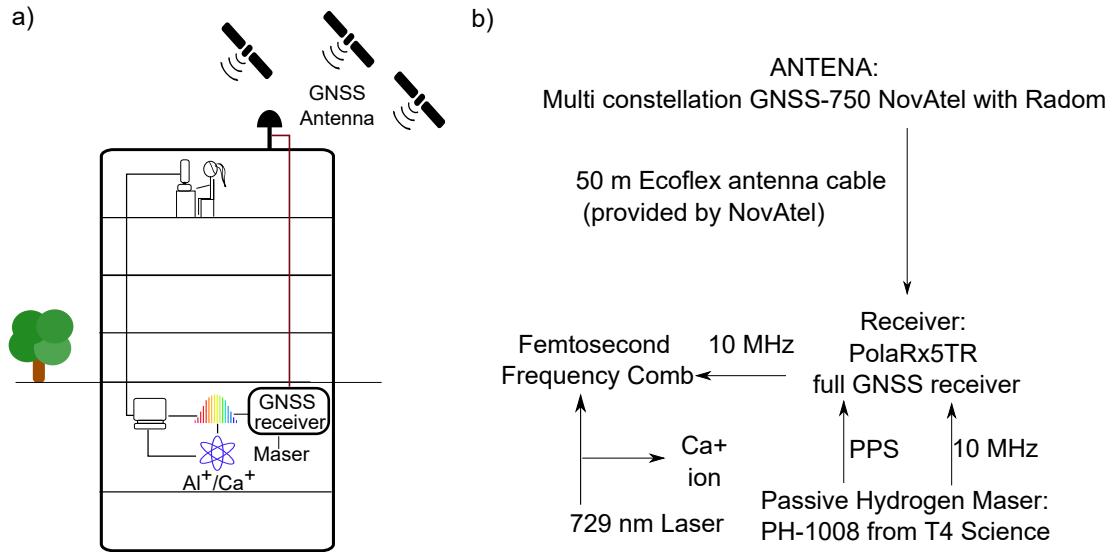


Figure 4.11: Schematic cartoon of the GNSS link hardware. A GNSS antenna was installed in the roof of IQOQI. The antenna is connected to a GNSS receiver located in the laboratory (at the -1 floor) via a thermally isolated cable. The receiver is linked to both the frequency comb and the passive hydrogen maser. All the elements are connected to the Control PC and can be remotely manipulated.

[107]. The carrier phases measured with these types of antennas showed maximum diurnal variations of about 40 ps and the code measurements up to 2 ns.

We installed a NovaAtel GNSS750 antenna composed of an ultra-wideband Dorne-Margolin element that assures an operating range from -55°C to 80°C . This antenna offers also the advantage to be multi-constellation, which means that it can be implemented to detect signals from a variety of satellite constellations such as GPS, GLONASS, GALILEO and BEIDOU. The antenna is located at the roof of the IQOQI in an unobstructed area separated from reflective objects and covered by a protective radome.

4.7.2 GNSS receiver

The operation of GNSS receivers is described in [104], here a summary of the main necessary elements is given.

As previously described on board of each satellite atomic clocks are operated. The clocks on these satellites have a nominal output frequency of $f_0 = 10.23\text{ MHz}$. This frequency is multiplied by 154 and 120 to generate two microwave frequencies $f_1 = 1575.42\text{ MHz}$ and $f_2 = 1227.60\text{ MHz}$. These are the two-emitted frequencies on the so-called L1 and L2 bands. Each frequency is used to transmit particular information suited for certain applications. Before being transmitted these two carrier frequencies are phase modulated with pseudo-random noise codes denominated PRN-codes. These codes are specific to each satellite and used for tracking and identifying the satellite by means of a GNSS receiver. A 50 bits per second binary code denominated as "navigation message" is superimposed and contains information about the state of the individual satellite as well as of the constellation as a whole, the so-called ephemeris data or satellites' position, information about the ionosphere and the offset of the satellites' clock with respect to the GPS time.

The GNSS receiver decodes the information received from the satellites. As described in [104] the signal reception and demodulation is done via a correlation process. In simple terms, a local copy of the PRN-code generated by the receiver internal oscillator is compared with the received satellite PRN-code. As explained by Thomas Feldmann in his thesis [104]: "The PRN-code copy is electronically shifted in time and multiplied with the incoming satellite signal. If the received satellite PRN code which is hidden in the noise, and the replica signal coincide the result of the multiplication, called the correlation function, is at a stable maximum and the receiver's tracking loops can lock to the satellite." Via the correlation process and with the help of the navigation message encoded the receiver calculates the apparent signal propagation time between the satellite and the receiver. The information decoded with the receiver is used to calibrate the frequency of a passive hydrogen maser with respect to the satellite's clocks.

As illustrated in Figure 4.11, we installed a Multi-frequency GNSS time and frequency transfer receiver PolaRx5TR developed by Septentrio. A square pulse per second (PPS) and a 10 MHz signal from the hydrogen maser are connected to the receiver. This receiver is designed to measure and compensate for the delay between the PPS input, from the maser, and the internal time reference. It offers the advantage to allow a constant and easy generation of the Receiver Independent Exchange Format (RINEX) data necessary for the evaluation of the GNSS link data. The RINEX files generated contain raw satellite navigation system data. This data can be post-processed to generate more accurate results by means of better models of the atmospheric conditions at the time of the measurement. The data from our receiver is processed with the help of PTB with the NRCan-PPP software, see Chapter 5.



Figure 4.12: Photography of passive hydrogen maser VCH-1008.

4.7.3 Maser

Ideally to properly characterize the performance of an optical clock via a frequency comparison it is necessary to reach statistical uncertainties in the 10^{-16} range and below. However, GNSS links between distant clocks reach instabilities of 10^{-15} at 1 day averaging time [108]. A continuous operation for several days is required in order to attain the desired uncertainties. In order to circumvent this challenge, a hydrogen maser is used as a flywheel oscillator between the GPS receiver and the optical clocks. The very reliable and continuous frequency oscillation of the maser is used in combination with numerical approaches to estimate the uncertainties resulting from the discontinuous availability of the optical clock data.

A hydrogen **maser** (Microwave amplification by stimulated emission of radiation), as indicated by its name, uses the hyperfine ground-state transition at 1420.405 MHz of dissociated atomic hydrogen gas in a microwave cavity. In an active maser the cavity oscillates by itself delivering a signal whose frequency is mainly determined by the atomic transition. Active hydrogen **masers** are more complex and more expensive but have better short-term and long-term frequency stability. In a passive hydrogen maser the cavity is fed by an external 1420.405 MHz interrogation signal to lock a quartz oscillator frequency to the atomic line. This allows the design of masers to be simpler, lighter and cheaper however degrading their accuracy and stability compared to the active masers.

We installed in our system a passive hydrogen maser VCH-1008 from the company T4 Science shown in Figure 4.12. It has a weight of 33 kg and size of 53x46x20 cm. The maser has 7 outputs: 2 at 5 MHz, 2 at 10 MHz, 1 at 100 MHz, 1 at 1 MHz, and 1 at 2.048 MHz. A touch screen display allows to monitor the status of the device and to adjust the output frequency generated by a digital synthesizer code. The relative value of the output frequency f_{out} can be change by steps of $10^{-15} \times f_{out}$ in a range of $\pm 10^{-10} \times f_{out}$. In the following sections the frequency drift of the maser is determined to be of about 0.4 Hz per day.

Chapter 5

Absolute frequency measurement of the $4s\ ^2S_{1/2} \leftrightarrow 3d\ ^2D_{5/2}\ ^{40}\text{Ca}^+$ clock transition

“There are no eternal facts,
as there are no absolute truths”
Friedrich Nietzsche
Human, All too human(1878)

Since its first measurement in 2009 by our group [76], the absolute frequency of the $4s\ ^2S_{1/2} \leftrightarrow 3d\ ^2D_{5/2}\ ^{40}\text{Ca}^+$ clock transition has been reported 4 more times: by the group of K. Hayasaka at the National Institute of Information and Communications (NICT) in Japan [109] and by the group of K. Gao at the Wuhan Institute of Physics and Mathematics (WIPM) [110, 26, 111]. However, as can be seen in Figure 5.1, the earlier published results (between 2009 and 2012) disagree with the latest measurements (between 2013 and 2017). In this chapter I describe and present the results of a new campaign to measure the absolute frequency of the $4s\ ^2S_{1/2} \leftrightarrow 3d\ ^2D_{5/2}\ ^{40}\text{Ca}^+$ clock transition with respect to the coordinated universal time UTC at PTB by means of a GNSS link using the Precise Point Positioning (PPP) technique. The campaign was held during 10 days from the 16th to the 25th of June 2021. After the evaluation of the systematic shift the transition frequency is measured as $(411\,042\,129\,776\,401.2 \pm 0.6)$ Hz with a fractional uncertainty of 1.4×10^{-15} . This value is in agreement with the latest measurements from the K. Gao group. The first section of the chapter is devoted to the frequency measurement of the clock transition via the GNSS link. The second part is centered around the description of the methods used for the evaluation of the systematic shifts. Finally, a third section summarizes the results of the absolute frequency measurement.

5.1 Absolute frequency measurement of the clock transition via GNSS link using the PPP technique

As stated by D.B Sullivan et al [112]: “It is impossible to measure purely only one oscillator: any frequency measurement involves two oscillators”. Frequency measurements are always relative to a reference, which ideally performs better than the oscillator that we wish to characterize. With that in mind, an absolute frequency measurement consists of measuring the frequency of a source with respect to a primary frequency standard. Our goal is to measure the frequency of the $4s\ ^2S_{1/2} \leftrightarrow 3d\ ^2D_{5/2}\ ^{40}\text{Ca}^+$ calcium ion transition with respect to the SI second. We want to compare our clock’s performance with respect to the clocks at the Physikalisch-Technische Bundesanstalt

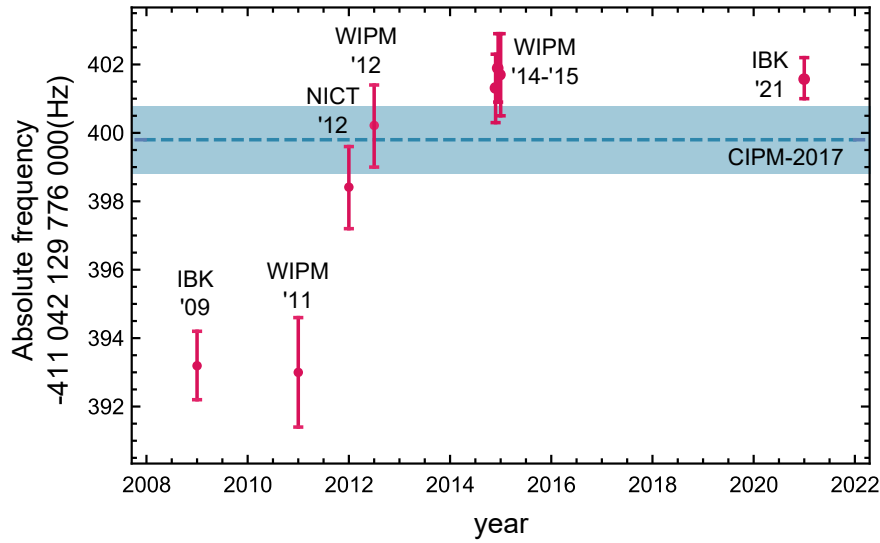


Figure 5.1: Overview of absolute frequency measurements of the $^{40}\text{Ca}^+$ clock transition.

The measurement result from our campaign (IBK '21) is in agreement with the latest measurements of the Wuhan group (WIPM '12 and WIPM '14-'15) [26, 111]. They are however in disagreement with the three first measurements performed between 2009 and 2012 [76, 109, 110]. As a reference the recommended frequency and uncertainty by the CIPM (International Committee for Weights and Measures) in 2017 is shown in light blue.

(PTB) implemented for the realization of the coordinated universal time UTC(PTB). Given that PTB is located at approximately 800 km from our laboratory in Innsbruck, we have established a Global Navigation Satellite System GNSS link to compare both frequencies. What this means in simple terms is that we have implemented a chain of relative frequency comparisons, taking advantage of the satellite's atomic clocks, to characterize our clock frequency with respect to the primary standards located at PTB. The chain is composed of the following steps: the calcium's clock transition is measured with respect to a flywheel oscillator, in our case a passive hydrogen maser. The maser's frequency is then measured with respect to the GNSS satellite's atomic clock frequency, whose frequency's is determined with respect to the UTC(PTB).

I will give a brief clarification of some time and frequency metrology conventions [112]:

- **The nominal frequency (ν_0)** refers to an ideal frequency with zero uncertainty. It corresponds to the frequency of the reference with respect to which a measurement is performed.
- **The fractional frequency offset (y)** is the frequency difference between the nominal frequency ν_0 and the output frequency ν_1 . It is more commonly expressed as a fractional frequency offset which corresponds to the frequency offset divided by the nominal frequency. The fractional frequency offset at an instant t is measured as:

$$y(t) = \frac{\nu_1 - \nu_0}{\nu_0}. \quad (5.1)$$

- **The time offset (x)** corresponds to the measurable time difference between a pair of clocks or a clock and a primary reference. The measurement result is usually reported in fractions of a second, such as milliseconds, microseconds, or

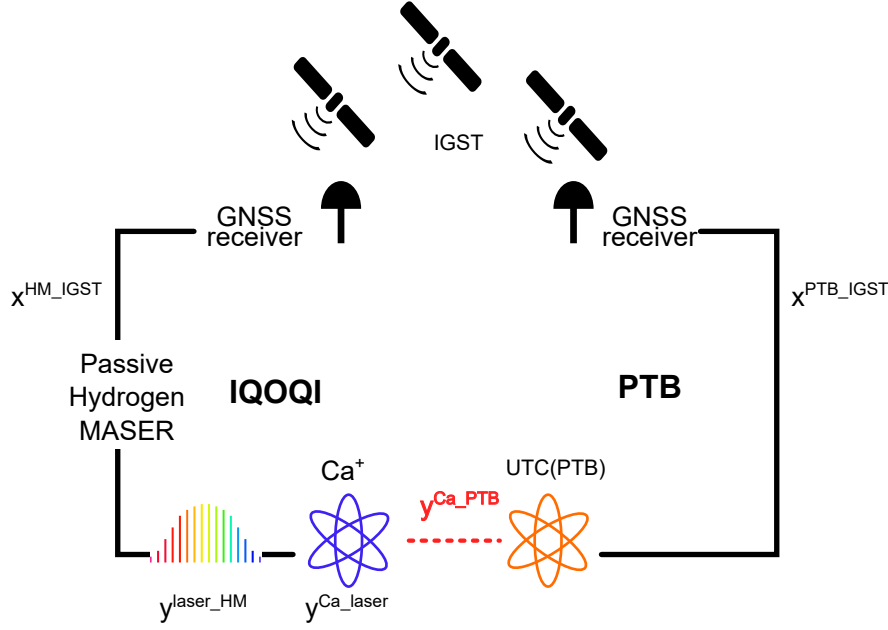


Figure 5.2: Schematic illustration of the GNSS link. In order to compare the calcium clock transition with respect to the UTC(PTB) ($y^{\text{Ca_PTB}}$) 4 measurement sets are necessary: the relative frequency difference between the calcium ion transition and the laser $y^{\text{Ca_laser}}$, the relative frequency difference between the laser and the maser ($y^{\text{laser_HM}}$), the relative phase difference between the maser and the IGST ($x^{\text{HM_IGST}}$) and the relative phase difference between the UTC(PTB) and the IGST ($x^{\text{PTB_IGST}}$).

nanoseconds. The average fractional frequency over a period τ can be extracted by measuring the time offset of an oscillator with respect to a reference source over that period:

$$y(t) = \frac{x(t + \tau) - x(t)}{\tau} \quad (5.2)$$

As illustrated in Figure 5.2, the following steps are necessary in order to compare our frequency source respect to the UTC(PTB):

- The calcium clock transition is probed by means of laser light at 729 nm locked to a high finesse cavity ($y^{\text{Ca_laser}}$).
- The probe light is measured using a femtosecond frequency comb referenced to a passive hydrogen maser ($y^{\text{laser_HM}}$). From the combination of this data set with the previous one we obtain the transition frequency of the calcium ion with respect to the hydrogen maser ($y^{\text{Ca_HM}}$).
- By means of the GNSS link, as described in Section 4.7 we extract the time offset of the hydrogen maser with respect to the time reference emitted by the satellites denominated as the International GNSS Service Time IGST ($x^{\text{HM_IGST}}$). This data set is compared to the time offset of the UTC(PTB) with respect to the IGST ($x^{\text{PTB_IGST}}$) from which we extract the time offset between our maser and the UTC(PTB) ($x^{\text{HM_PTB}}$) and consequently by applying Eq. 5.1 the fractional frequency offset between both sources ($y^{\text{HM-PTB}}$).

- We combine the clock frequency measurements relative to the hydrogen maser with the measurements of the maser relative to the UTC(PTB) and obtain the clock frequency with respect to the UTC(PTB) ($y^{\text{Ca_PTB}}$):

$$y^{\text{Ca_PTB}} = y^{\text{Ca_HM}} + y^{\text{HM_PTB}}. \quad (5.3)$$

In the following subsections, I describe each one of these steps. First, the scheme implemented to probe the calcium ion clock transition by means of the laser is described in Section 5.1.1. The combination of this data set with the measurement of the laser frequency by means of the frequency comb referenced to the passive hydrogen maser is described in Section 5.1.2, followed by a description of the maser characterization with respect to the UTC(PTB) by means of a GNSS link in Section 5.1.3. Finally, in Section 5.1.4, the data sets are combined to obtain the calcium clock transition frequency with respect to the UTC(PTB).

5.1.1 Probing scheme of the $4s\ ^2S_{1/2} \leftrightarrow 3d\ ^2D_{5/2}$ $^{40}\text{Ca}^+$ clock transition

To measure the clock transition, we probe three pairs of Zeeman transitions:

$$\begin{aligned} |S_{1/2}, m_s = \pm 1/2\rangle &\leftrightarrow |D_{5/2}, m_D = \pm 1/2\rangle, \\ |S_{1/2}, m_s = \pm 1/2\rangle &\leftrightarrow |D_{5/2}, m_D = \pm 3/2\rangle, \\ |S_{1/2}, m_s = \pm 1/2\rangle &\leftrightarrow |D_{5/2}, m_D = \pm 5/2\rangle, \end{aligned} \quad (5.4)$$

illustrated in Figure 5.3, by Ramsey phase experiments (see Section 2.4.2). As illustrated in the figure and described in more detail in Section 5.2, the dominant shifts caused by the linear Zeeman shift, the electric-quadrupole shift and the tensor part of the Stark shift cancel out when averaging over all frequency measurements of these six transitions. To infer the center frequency, we perform two sets of Ramsey experiments: the first set ($f_1, f_2, f_3, f_4, f_5, f_6$) probes each transition in order with a fixed phase on ϕ_2 and the second set ($f'_1, f'_2, f'_3, f'_4, f'_5, f'_6$) probe the same transitions in reversed order with a phase ϕ_2' at 180° respect to ϕ_2 . From these measurements, the magnetic field strength, the second order Zeeman shift and the laser frequency relative to the ion are inferred. This information is fed back to the frequency of AOM 12 (see Figure 4.4.3) to compensate for slow drifts of the reference cavity and magnetic field.

Each probing cycle consists of 5 ms of Doppler cooling on the $S_{1/2} \leftrightarrow P_{1/2}$ transition at a wavelength of 397 nm, repumping at 866 nm to counter decay into the $D_{3/2}$ level and repumping at 854 nm to clear out population from the $D_{5/2}$ level. State initialization is done by optical pumping into the $|S_{1/2}, m_s = \pm 1/2\rangle$ level, using two different methods consecutively: one using circularly polarized light at 397 nm to drive a $\sigma \pm$ transition between $S_{1/2}$ and $P_{1/2}$ followed by the second one using the narrowband laser at 729 nm to selectively couple the $|S_{1/2}, m_s = \pm 1/2\rangle$ level to the $D_{5/2}$ manifold, from where it is pumped out using light at 854 nm. In both pumping cycles, repumper light at 866 nm ensures that decays to the $D_{3/2}$ state are returned to the pumping cycle. Optical pumping is followed by the probing pulses at 729 nm and finalized by the 5 ms ion state detection (see Section 4.5). The transitions are probed through the diagonal viewport (see Figure 4.2), which means that there is an angle of 45° between the laser beam wave vector and the magnetic field vector. The polarization of the 729 nm laser beam is adjusted to obtain a similar coupling strength for all 6 transitions [50]. The experiments were done with a waiting time τ_R of 5000 μs and a π pulse length of approximately 200 μs for each probed transition. Every cycle is repeated 100 times for each individual frequency measurement yielding a total

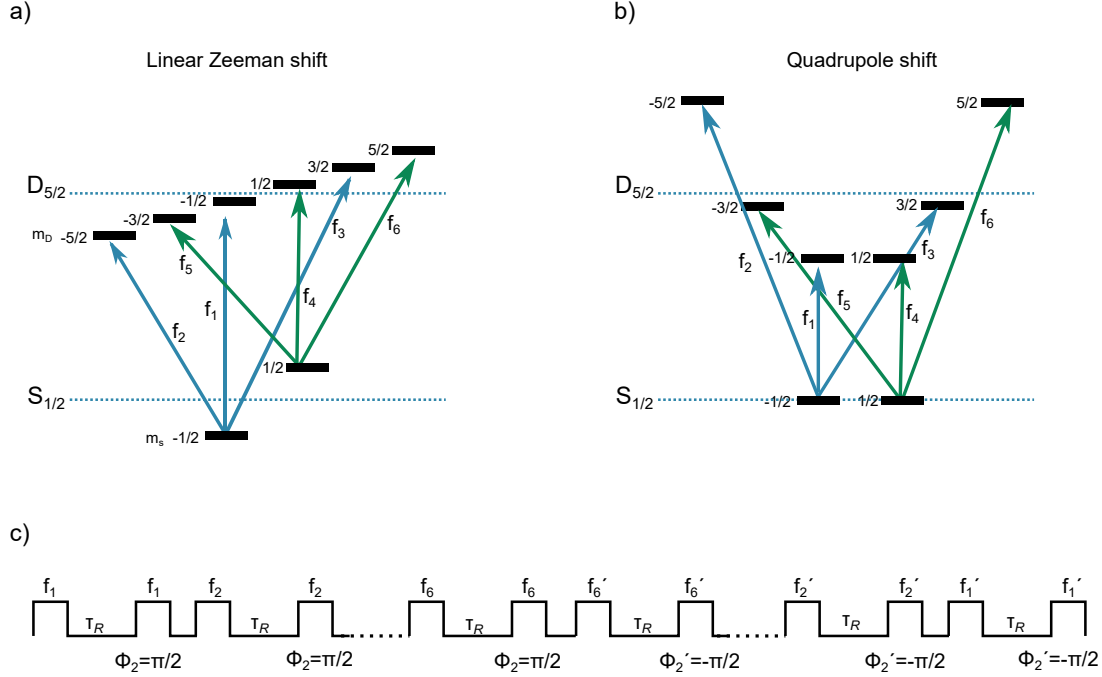


Figure 5.3: Probing scheme to cancel the linear Zeeman shift and quadrupole shift of the $4s\ ^2S_{1/2} \leftrightarrow 3d\ ^2D_{5/2}$ $^{40}\text{Ca}^+$ clock transition.

Transitions $f_1, f_2, f_3, f_4, f_5, f_6$ are probed in order to cancel the a) Zeeman shift and the b) Quadrupole shift. c) Each transition is probed twice, the second set of frequencies $f'_1, f'_2, f'_3, f'_4, f'_5, f'_6$ is probed in reverse order with a relative phase of the second pulse switched by 90° .

time of 30 s. All the data is recorded, specifying the corresponding time tag of the measurement in a file that contains the excitation probability of each measured point, the frequency of each transition as well as the estimated deviation, the magnetic field strength, the waiting time τ_R and the laser frequency relative to the ion.

5.1.2 Frequency measurement of the calcium clock transition referenced to the passive hydrogen maser ($y^{\text{Ca-HM}}$)

The laser frequency is measured via an optical beat note with the light of the frequency comb (see Section 4.4.3). Every second, the repetition rate (f_{REP}), the carrier envelop offset (f_{CEO}) and the beat frequency (f_{beat}) are recorded with their respective time tag. From these measurements the frequency of the laser f_{CW} is determined using:

$$f_{\text{CW}} = n f_{\text{REP}} \pm 2 f_{\text{CEO}} \pm f_{\text{beat}}, \quad (5.5)$$

where the mode number value n and the sign of the f_{CEO} and the f_{REP} , are determined following the approach described in [70], and re-estimated for each individual measurement. All "Out of lock" events where any of the recorded frequencies deviate by more than 3 times the standard deviation from the resulting mean value are discarded. As illustrated in Figure 4.6 the beat note is detected on PD 6 and measured using a frequency counter. A decay in the signal to noise ratio of the beat signal can cause cycle slips. Cycle slips are discontinuities of an integer number of cycles in the measured frequency and can induced errors. To detect cycle-slips, the signal is split in two sections, one of which is attenuated by 3 dB. This method ensures that if there is a drop in the signal to noise ratio that could generate a cycle slip the frequency measured

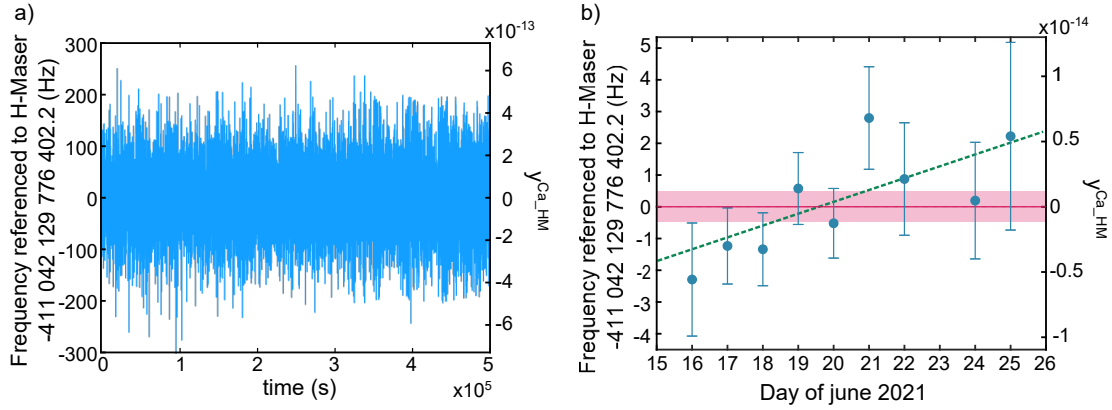


Figure 5.4: Total frequency measurements referenced to the hydrogen maser from the June 2021 campaign. The clock transition frequency is measured combining the ion trap data with the readings from the frequency comb referenced to a hydrogen maser. a) Total frequency measurement data as a function of probing time. b) Mean frequency measurements per day during the campaign. The total mean frequency (411 042 129 776 402.2 Hz) and a statistical error of (± 0.6 Hz) are indicated by the pink center line and the shaded area respectively. The measurements show a drift of about 0.4 Hz/day illustrated by the dashed green line. A scale showing the fractional frequency offset ($y_{\text{Ca-HM}}$) is given on the right side of both plots.

by both counters is going to differ. Following the approach described in [113]: all data points for which the counted signals disagree by more than 8 times the medium absolute deviation (MAD) are discarded. This value proves to be robust in the sense that small variations of the threshold did not affect the amount of detected cycle-slips significantly.

The measurements of the laser frequency with the comb are combined with the deviations of the laser relative to the ion extracted from the Ramsey phase experiments over the 6 transitions (see Section 5.1.1). The valid points measured with the frequency comb during the time window in which the the ion data is taken are averaged. The data extracted directly with the ion is then combined with the frequency comb data. The clock transition frequency measured with the frequency comb referenced to the hydrogen maser during the June 2021 campaign are summarized in Figure. 5.4. A total of 16821 combined measurements with an acquisition time of 30 s each are shown in Figure. 5.4.a. The data was taken over 10 days from the 16th to the 25th of June. Figure 5.4.b shows the average frequency measured every day. The data taken during the 23th of June had to be discarded due to the presence of unwanted light at 422 nm that was not turned off after reloading ions leading to undesired AC stark shifts. During the 10 days campaign we have observed a slow drift of the frequency of about 0.4 Hz per day, illustrated by the green dashed line in the figure. This drift matches with the expected drift of the passive hydrogen maser which is discussed in more detail in the following section. The solid pink line correspond to a Gaussian fit with a statistical error of (± 0.6) Hz. From these measurements, the frequency of the clock transition, referenced to the hydrogen maser, without corrections for systematic shifts, was determined to be $(411\,042\,129\,777\,402.1 \pm 0.6)$ Hz.

5.1.3 Frequency measurement of the passive hydrogen maser frequency respect to the UTC(PTB) ($y^{PHM-UTC(PTB)}$) via a GNSS link using the PPP technique

The passive hydrogen maser frequency was calibrated via a GNSS link referenced to the UTC(PTB) using the Natural Resources Canada Precise Point Positioning (PPP) data-processing technique [114].

Precise Point Positioning PPP technique

The Precise Point Positioning technique (PPP) was originally developed as a global navigation satellite post processing method to facilitate the determination of position with sub-centimeter precision [115], as the name implies. As described in Section 4.7, GPS satellites continuously transmit signals that carry information about their individual status as well as of the whole constellation. This information is encoded in the "Navigation message". It includes the satellites' positions or ephemeris data, the satellites' clock offset with respect to the common reference timescale GPS time and data to estimate delays due to variations of the space weather conditions in the ionosphere. This information is received and demodulated by the GNSS receiver [116]. With this knowledge, the receiver can calculate the apparent signal propagation time between the satellite and the receiver and from that, the range between them. All the information is recorded, usually in 30 s intervals, in the Receiver Independent Exchange Format (RINEX). There are two types of RINEX files: the so-called "observation" data contains measurements from all GNSS systems while the "navigation" files contain information regarding only GPS and GLONASS. These files gather all the information necessary for the application of post-processing methods such as the PPP technique for high precision positioning applications or for time and frequency comparison. This technique uses not only the information from the individual receiver but also the one collected by the International GNSS Service (IGS). The IGS is a voluntary federation of about 200 universities, agencies and research institutions that work together to gather RINEX observation and navigation data from more than 100 countries [117]. With this information, the GNSS receiver is operated as part of a network, allowing the user to calculate and correct for signal delays and access precise information about the satellite's ephemeris and clock. A detailed explanation of this technique can be found in the thesis of Thorsten Feldman [104]. To calibrate the frequency of our passive hydrogen maser, we worked in collaboration with Dr. Andreas Bauch and Thomas Polewka in the Dissemination of time group from the Time and Frequency department at PTB. The RINEX files were processed using the Natural Resources Canada (NRCAN) Precise Positioning data processing technique. This online navigation tool uses the information derived from the IGS network to calculate the precise user position and time delay extracted from the corresponding RINEX files.

Calibration of the frequency of the passive hydrogen maser with respect to UTC(PTB)

As described previously in Section 4.7 the GNSS receiver is referenced to the 10 MHz and the PPS signal from the passive hydrogen maser. The receiver decodes the signal from the GNSS satellites and generates the RINEX files. Using the NRCAN Precise Positioning software, the time delay between the maser and the satellites' clocks is estimated ($x^{HM-IGST}$). A similar setup located at PTB estimates the time delay between the satellites' clocks and the UTC(PTB) ($x^{PTB-IGST}$). Combining the two data sets, the time delay of the hydrogen maser with respect to the UTC(PTB) is estimated (x^{Ca-PTB}).

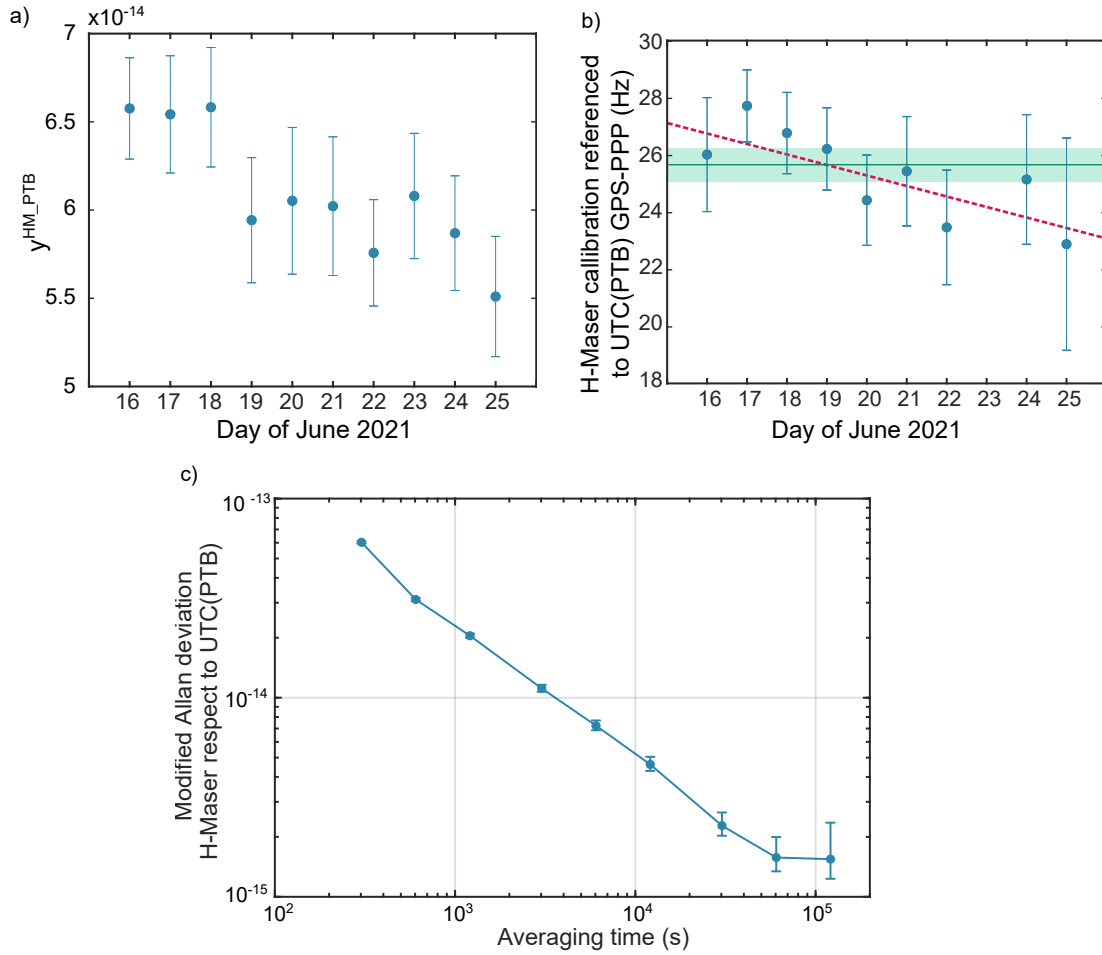


Figure 5.5: Calibration of the hydrogen maser respect to UTC(PTB).

The frequency comparison is done using the PPP data-processing technique. a) Relative frequency offset average per day. b) Combining these measurements together with the ion data and frequency comb data we determine the average frequency offset per day of the H-maser during the measurement campaign. The mean frequency of the totality of the data and the standard uncertainties are indicated with a green line and shaded area respectively. The corrections do not yet include an estimation of the gravitational shift that originates from the difference of altitude between our clock and the time reference. The pink dashed line corresponds to a drift of about 0.4 Hz/day. c) Modified Allan Deviation plot of the instability of the frequency comparison.

From these measurements, applying Eq. 5.1, we calculated the relative frequency offset of the passive hydrogen maser with respect to the UTC(PTB) ($y^{\text{HM_PTB}}$). The data is recorded every 30 s and processed in 5 min batches. Figure 5.5 a) shows the average relative frequency offset per day. Combining these measurements together with the ion data and frequency comb data, we calibrated the frequency offset of the hydrogen maser respect to the UTC(PTB). The daily averaged results are presented in Figure 5.5 b). The measurements show a mean frequency offset of the maser respect to the UTC(PTB) of (25.6 ± 0.6) Hz. It is important to notice, at this point, that our data analysis does not yet include an estimation of the gravitational shift that originates from the difference of altitude between our clock and the clocks at PTB. The characterization of this shift is presented in Section 5.1.4. The analysis of these measurements confirms the slow maser drift of 0.4 Hz per day, illustrated by the pink dotted line in the figure, previously observed in Section 5.1.2. The Modified Allan deviation plot in the inset c) shows that for the total measurement campaign, an instability of $1.5 \cdot 10^{-15}$ is achieved. The magnitude of the standard deviation of the daily mean value is $3.5 \cdot 10^{-15}$. It has been previously demonstrated that frequency comparisons using the PPP technique can achieve lower statistical uncertainties, on the order of a few 10^{-16} [11, 36]. However, as is carefully described in Julia Leute's PhD thesis [118], the final uncertainty is mainly limited by the instability of the flywheel oscillator. In order to improve the daily instability of the link the passive hydrogen maser should be replaced by a more stable source such as an active hydrogen maser.

5.1.4 Frequency measurement referenced to UTC(PTB) ($y^{\text{Ca_PTB}}$)

The final step consists in combining the results from the frequency measurement relative to the hydrogen maser ($y^{\text{Ca_HM}}$) with the characterization of the hydrogen maser with respect to the UTC(PTB) ($y^{\text{HM_PTB}}$), to finally obtain the frequency of the calcium clock transition respect to the UTC(PTB) ($y^{\text{Ca_PTB}}$). We followed a similar approach as the one presented in the previous subsections: the valid points measured with the frequency comb and the ion trap during the time window used for the PPP analysis are averaged and combined with the calibrated maser data. The results are summarized in Figure 5.6. Panel a) shows the average frequency measured every day. The total mean is 411 042 129 776 428.7 Hz, with a statistical uncertainty of 0.6 Hz, represented by the purple shaded region in the plot. The error bars in the plot represent the daily statistical uncertainty, limited mainly by out-of-lock events. b) shows the modified Allan deviation plot of the total measurement campaign. As observed in the previous section, the instability reaches a minimum at low 10^{-15} values at an averaging time of 10^5 . A logarithmic fit of the modified Allan deviation data with respect to the averaging time shows a stability close to $6.83 \times 10^{-13} \tau^{-1/2}$ revealing the presence of white frequency noise most likely originating from the hydrogen maser. This confirms our previous statement that our uncertainty is mainly limited by the instability of the passive hydrogen maser. From these measurements, the frequency of the clock transition, referenced to the UTC(PTB), without corrections for systematic shifts, is determined to be $(411\,042\,129\,776\,428.7 \pm 0.6)$ Hz.

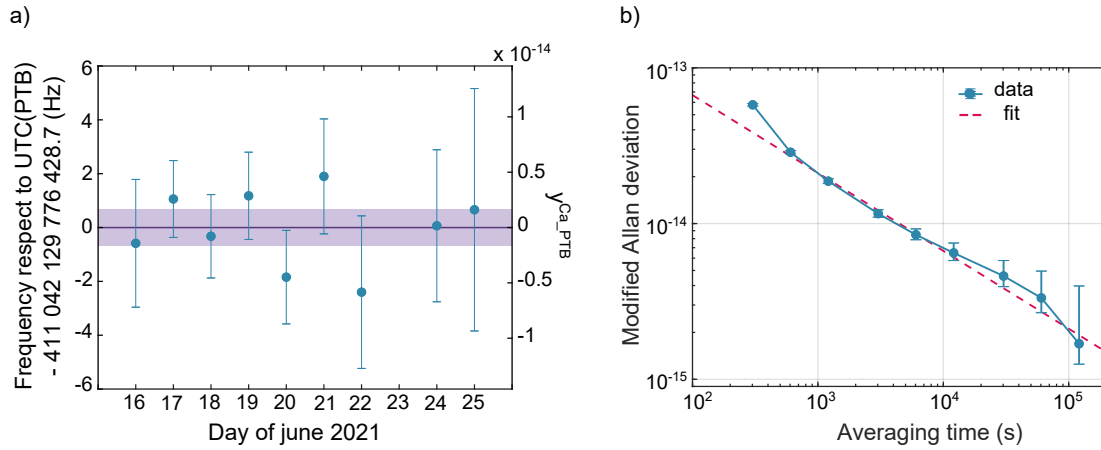


Figure 5.6: Total frequency measurements referenced to UTC(PTB). a) Mean daily frequency deviation from the total average at 411 042 129 776 428.7 Hz with an uncertainty of 0.6 Hz, represented by the purple shaded area. The fractional frequency deviation is given on the right side. b) Modified Allan deviation plot of the frequency comparison. The data points are presented in blue. The dotted pink line is a fit that follows $\sigma_y(\tau) = (6.8 \pm 0.1) \times 10^{-13} \tau^{-1/2}$.

Gravitational Red Shift

As it was described in detail in Section 3.3.2, the gravitational red shift for a clock at rest on the Earth's surface can be calculated with [83]:

$$\frac{\Delta\nu_{\text{GR}}}{\nu_0} = \frac{gH}{c^2} \quad (5.6)$$

where g is the gravity acceleration and H is the height of the clock respect to the zero potential. To determine H for our clock measurements we implemented the GNSS/geoid approach [119] using the EGG2015 geoid model and the GPS coordinates obtained with the antenna and the receiver. To perform the calculations we used the online products provided by the International Service for the Geoid [120]. To these calculations we added the measurement of the height difference between the antenna (located on the roof) and the ion trap (located in the -1 floor) using a laser distance sensor. We estimate that the height of the clock above the geoid is $H = (579 \pm 1)$ m, assuming a conservative error of 1 m. The gravitational red shift is equal to: $(\Delta\nu_{\text{GR}} = 25.95 \pm 0.05)$ Hz. The shift and uncertainty of the UTC(PTB) with respect to the TAI and of the TAI with respect to the TT can be found in the report of the BIPM [84, 121].

Effect	Clock shift (Hz)	Error (mHz)	Fractional error
Gravitational	25.95	50	1×10^{-16}
UTC(PTB) referenced to TAI	-0.04	120	2.9×10^{-16}
TAI referenced to TT(SI)	-0.08	0.06	1.4×10^{-16}
Systematic shift of the GNSS link	25.83	130	3.2×10^{-16}

5.1.5 Frequency comparison between two $^{40}\text{Ca}^+$ clocks

To determine the stability of our spectroscopic measurements independently from the hydrogen maser we performed a frequency comparison between our $^{40}\text{Ca}^+$ clock and a similar clock located in a neighboring laboratory. As illustrated in Figure 4.6, our laboratory (lab 2) is located next to another laboratory (lab 1) that hosts a similar setup dedicated to experiments with calcium ion chains [52]. As shown in the figure, both experimental setups share the 729 nm laser. In order to investigate the stability of both setups, we probed a symmetric pair of Zeeman transitions: $|S_{1/2}, m_s = \pm 1/2\rangle \leftrightarrow |D_{5/2}, m_D = \pm 5/2\rangle$ by Ramsey experiments each with 4 different phases. We followed a similar scheme as the one described in Section 5.1.1, though with the difference that we probed 4 different phases with the second pulse ϕ_2 ($0, \pi/2, \pi, 3\pi/2$) in order to keep track of any contrast variation due to magnetic field noise. The experiments were done with a waiting time τ_R of 5000 μs and a π pulse length of approximately 200 μs for each transition. Since a full error budget evaluation of the second experimental setup was not available, our measurements were aimed at evaluating the stability of the frequency difference between the 729 nm laser and the ion transition. For a continuous data set over 30 hours, the Allan deviation of the frequency difference between the two traps was evaluated. The results are plotted in Figure 5.7. The individual contribution of each clock to the stability can be considered equivalent, so in order to get the stability for a single clock, the Allan deviation is divided by $\sqrt{2}$. A fit to the measured data reveals that the single clock stability is close to $8.7 \times 10^{-14} \tau^{-1/2}$. The Allan deviation as a function of the averaging time τ obtainable with Ramsey experiments can be calculated using [122],

$$\sigma_y(\tau) = \sqrt{\bar{p}(1-\bar{p})} \frac{\Delta\omega_0}{p_{\max} - p_{\min}} \frac{1}{2\pi\nu_0} \sqrt{\frac{t_c}{\tau}} \quad (5.7)$$

where the first factor describes the quantum projection noise for the interrogation and the second factor is inversely proportional to the slope of the obtainable error signal. $p_{\max}$ and $p_{\min}$ are the maximum and minimum excitation probabilities near the central Ramsey fringe, $\bar{p} = \frac{p_{\max} + p_{\min}}{2}$ is the average excitation probability. $\Delta\omega_0$ corresponds to the frequency difference between resonance and the first minimum of the Ramsey fringe and t_c to the time duration of each individual cycle including the dead time and the probing time. Finally ν_0 is the center frequency of the atomic resonance. The theoretical trend calculated and illustrated as a solid green line in the Figure 5.7 is approximately $7.4 \times 10^{-14} \tau^{-1/2}$. The small deviation of the fitted trend from the theory prediction might be caused by the parameters of the servo algorithm that stabilizes the laser frequency to the single-ion signal and that eliminates errors due to laser frequency drift or by some external yet to be defined noise sources. However, these results allows us to confirm that our spectroscopy measurements are mostly limited by quantum projection noise (QPN).

5.2 Evaluation of systematic shifts and uncertainties

So what Time is it really? How (un)certain are we?

The previous section was centered around the determination of the level of precision of our measurement, in simple terms on determining how good we are at always measuring the same frequency with our clock. The following section is focused on the estimation of the accuracy, or how close we are to the "real" frequency of oscillation of our clock transition. Chapter 3 describes in detail how the environment surrounding

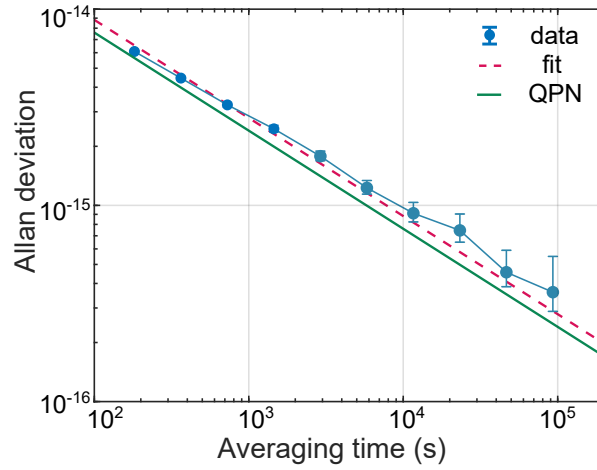


Figure 5.7: Standard Allan deviation plot of the frequency comparison of two $^{40}\text{Ca}^+$ clock divided by $\sqrt{2}$. The data points are presented in blue. The dotted red line is a fit that follows $\sigma_y(\tau) = 8.7 \times 10^{-14} \tau^{-1/2}$. The green solid line is theory calculation using Eq. 5.7 that follows $\sigma_y(\tau) = 7.4 \times 10^{-14} \tau^{-1/2}$.

the ion perturbs the frequency of the clock transition. In this section we verify experimentally that the systematic shifts are well-understood and controlled. The level at which we can estimate each one of these shifts limits the uncertainty of our measurement and our capability to answer to the questions: what time is it really? and how (un)certain are we?

5.2.1 Linear Zeeman shift, second order Zeeman shift and quadrupole shift

The linear Zeeman shift, the second order Zeeman shift and the quadrupole shift are the three most dominant shifts of the calcium clock transition. As described in Chapter 3, the linear and second order Zeeman shift result from the interaction of the ion with the magnetic field B which defines the quantization axis, while the quadrupole shift results from the interaction with the static electric field gradient caused by the DC-trapping fields applied to the end-cap electrodes. Due to the Zeeman effect, both fine structure states ($S_{1/2}$ and $D_{5/2}$) split into $2j+1$ Zeeman levels m_i and m_j respectively. Following the selection rules for an electric quadrupole transition ($\Delta m = 0, \pm 1, \pm 2$), a total of 10 transitions ($f_{m_i \rightarrow m_j}$) can be probed. Figure 5.8 illustrates how these transitions are affected by the linear Zeeman shift and the quadrupole shift. In the following subsections each one of these shifts will be addressed independently. However, to measure the clock transition, it is easier to study their joint effect on the transitions $f_{m_i \rightarrow m_j}$ using the following equation:

$$f_{m_i \rightarrow m_j} = f_0 + \frac{\mu_B B}{h} (m_j g_D - m_i g_S) + K_{m_j} \frac{(\mu_B B)^2}{h^2 \nu_{FS}} + \delta_q(m_j), \quad (5.8)$$

where f_0 is the bare frequency unperturbed by magnetic or electric fields, μ_B is the Bohr magneton, g_D and g_S the Landé g -factors of the $D_{5/2}$ and $S_{1/2}$ states, K_{m_j} a constant dependent on the magnetic sublevel m_j , ν_{FS} the fine structure splitting and $\delta_q(m_j)$ the quadrupole shift also dependent on the magnetic sublevel m_j . The second and third elements refer to the linear and second order Zeeman shifts, and the fourth refers to the quadrupole shift. As illustrated in Figure 5.8 a), due to the linear Zeeman shift,

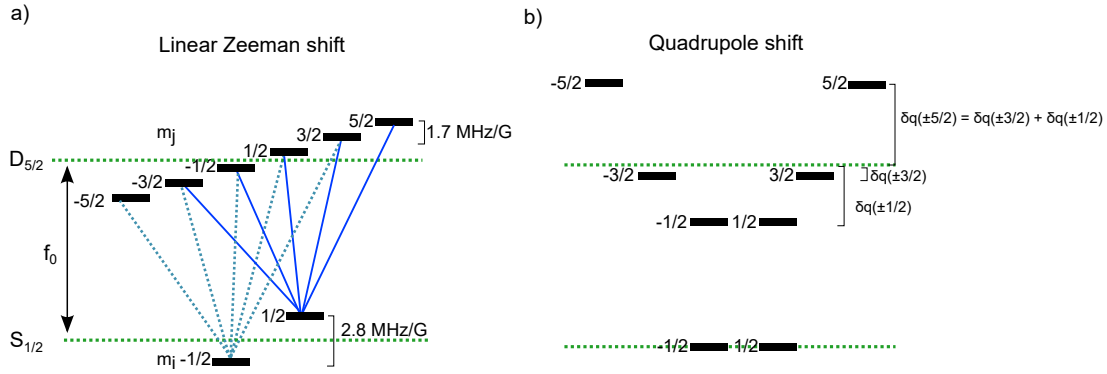


Figure 5.8: Linear Zeeman shift and quadrupole shift.

a) Due to the Zeeman effect the $D_{5/2}$ and the $S_{1/2}$ levels split into 6 and 2 sub-levels, respectively. Following the selection rules, a total of 10 transitions can be probed. b) The sub-transitions of the the $D_{5/2}$ level are also shifted by the interaction with the electric field gradient. The quadrupole shift for $m_j = \pm 5/2$ is equal to the combined shifts of $m_j = \pm 3/2$ and $m_j = \pm 1/2$.

the sublevels m_j and m_i are symmetric with respect to the line center. This allows us to cancel the linear dependence on the magnetic field by probing and averaging over symmetric Zeeman transitions pairs. Figure 5.8 b) shows how the quadrupole shift for $m_j = \pm 5/2$ is equal to the combined shifts of $m_j = \pm 3/2$ and $m_j = \pm 1/2$. The quadrupole shift can then be canceled by probing any set of three transitions containing these three magnetic sublevels. Following these two ideas we designed our probing scheme, described in Section 5.1.1 and illustrated in Figure 5.3. Six different transitions are probed and defined as:

$$\begin{aligned}
 f_1 &: f_{-1/2 \rightarrow -1/2}, \\
 f_2 &: f_{-1/2 \rightarrow -5/2}, \\
 f_3 &: f_{-1/2 \rightarrow 3/2}, \\
 f_4 &: f_{1/2 \rightarrow 1/2}, \\
 f_5 &: f_{1/2 \rightarrow -3/2}, \\
 f_6 &: f_{1/2 \rightarrow 5/2}.
 \end{aligned} \tag{5.9}$$

By probing these 6 transitions we can not only cancel for both the linear Zeeman effect and the quadrupole shift, but we can also estimate the magnetic field B , the Landé g -factor $g_{5/2}$ of the $D_{5/2}$ state, the second order Zeeman shift, the quadrupole shift $\delta_q(m_j)$ and then determine the bare frequency f_0 . To perform these calculations we use two systems of equations (sets I and II) where we define:

$$f_{ij} = f_i - f_j, \tag{5.10}$$

as the frequency difference between two of these 6 transitions,

$$\delta_q(i, j) = \delta_q(i) - \delta_q(j), \tag{5.11}$$

the difference between their respective quadrupole shift and

$$K_{ij} = K_i - K_j \tag{5.12}$$

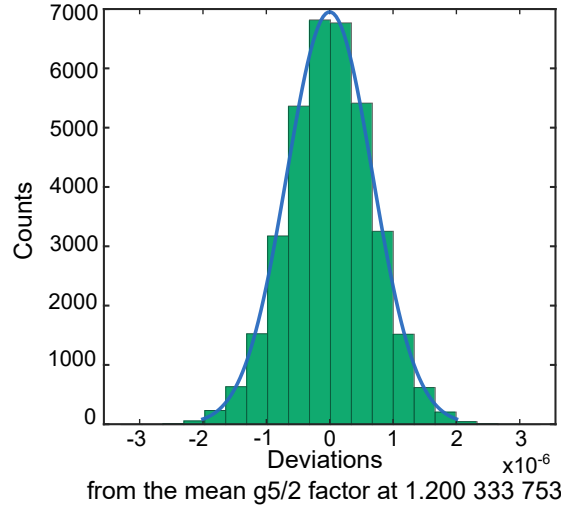


Figure 5.9: Measurements $g_{5/2}$ factor. Solving the system of equations 5.2.1 and 5.2.1 for our 10 days measurement campaign we get a result equal to 1.200 333 753 with a statistical uncertainty of $\pm 3 \times 10^{-9}$.

the difference between their second order Zeeman shift constants. Set I corresponds to the frequency differences $\{f_{12}, f_{13}, f_{41}\}$ and has the following system of equations:

$$\begin{aligned} f_{12} &= K_{12} \frac{(\mu_B B)^2}{h^2 \nu_{FS}} + 2g_{5/2} \frac{\mu_B B}{h} + \delta_q(1, 2), \\ f_{31} &= K_{31} \frac{(\mu_B B)^2}{h^2 \nu_{FS}} + 2g_{5/2} \frac{\mu_B B}{h} + \delta_q(3, 1), \\ f_{41} &= (g_{5/2} - g_{1/2}) \frac{\mu_B B}{h}. \end{aligned} \quad (5.13)$$

Set II correspond to the frequency differences $\{f_{45}, f_{64}, f_{41}\}$ and has the following system of equations:

$$\begin{aligned} f_{64} &= K_{64} \frac{(\mu_B B)^2}{h^2 \nu_{FS}} + 2g_{5/2} \frac{\mu_B B}{h} + \delta_q(6, 4), \\ f_{45} &= K_{45} \frac{(\mu_B B)^2}{h^2 \nu_{FS}} + 2g_{5/2} \frac{\mu_B B}{h} + \delta_q(4, 5), \\ f_{41} &= (g_{5/2} - g_{1/2}) \frac{\mu_B B}{h} \end{aligned} \quad (5.14)$$

The following subsections are devoted to the individual calculation of the Landé $g_{5/2}$ -factor of the $D_{5/2}$ level, the magnetic field variations, the first and second order Zeeman shifts and the quadrupole shift.

Landé $g_{5/2}$ -factor of the $D_{5/2}$ level

Using the spectroscopy data taken during the campaign and solving the two previously described system of equations, we extracted the Landé $g_{5/2}$ -factor of the $D_{5/2}$ level. The $g_{1/2}$ -factor of the $S_{1/2}$ has been previously measured by Tammaseo et. al. [85] to be $g_{1/2} = 2.002\,256\,64 \pm 9 \times 10^{-8}$. As illustrated in Figure 5.9, the obtained data follows a Gaussian distribution. From these measurements we get a result equal to

$g_{5/2} = 1.200\,333\,753$ with a statistical uncertainty of $\pm 3 \times 10^{-9}$. These results are consistent with the measurements previously done by Chwalla et. al [76] where the $g_{5/2}$ was determined to be equal to 1.200 334 0(3).

Magnetic field

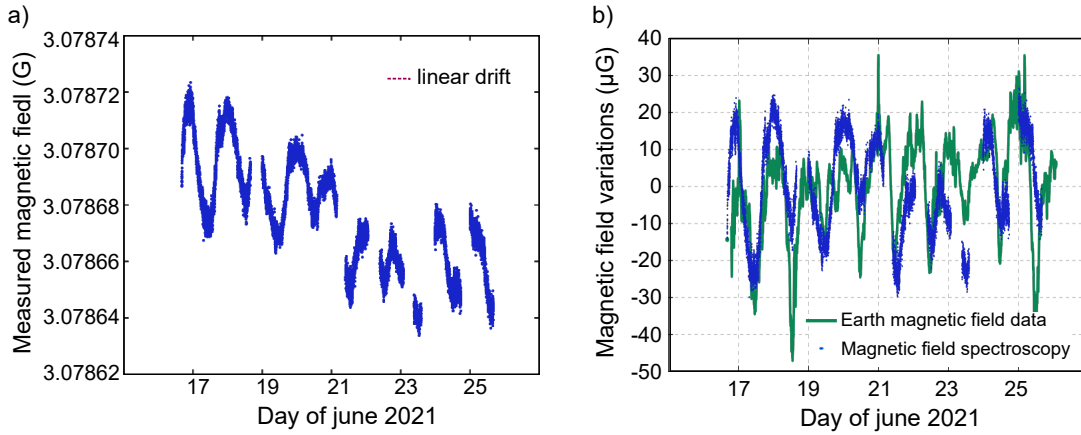


Figure 5.10: Magnetic field variations.

a) The weak field applied to define the quantization axis has a combination of a slow drift (-0.06 ± 2 nG/s) and a daily semi-sinusoidal variation. b) The magnetic field measured variations without the slow drift are compared to the variations of the Earth magnetic field data [123]. The daily magnetic field fluctuations as measured by the ion, seem to follow closely the variations of the earth magnetic field. These results are surprising since we expected that the μ -metal shield would protect the ion from these external magnetic field variations.

The variations of the magnetic field during the measurements are extracted using the same method described for the determination of the g -factor. As illustrated in Figure 5.10 a) we observe a slow linear drift of (-0.06 ± 2) nG/s that probably originates from temperature variations near the permanent magnets. Additional to this slow drift, a daily semi-periodic variation is also observed. To better understand these variations, Figure 5.10 b) shows the magnetic field measurements without the slow drift. We compared these variations with data of the earth magnetic field fluctuations in the same direction of the quantization axis of our setup. This data was measured at the Department of Earth and Environmental Sciences from the Ludwig-Maximilians Universität (LMU) it can be obtained at the official website of the International Real-time Magnetic Observatory Network (INTERMAGNET [123]). As can be seen in the plot, the daily magnetic field fluctuations as measured by the ion, seem to follow closely the variations of the earth magnetic field. These results are surprising since we expected that the μ -metal shield would protect the ion from these external magnetic field variations. More efforts are currently being done to fully characterize the origin of these magnetic field variations. Since the variations in magnetic field are not normal-distributed, in order to obtain the uncertainty in the determination of the magnetic field it is necessary to determine the combined standard uncertainty (for more details see Appendix B). From equations 5.2.1 and 5.2.1 the combined standard uncertainty

of the magnetic field ΔB can be derived to be:

$$\Delta B = \sqrt{\left(\frac{1}{\mu_B(\overline{g}_{5/2} - g_{1/2})}\right)^2 \Delta f_{41}^2 + \left(\frac{\overline{f}_{41}}{\mu_B(\overline{g}_{5/2} - g_{1/2})^2}\right)^2 \Delta g_{5/2}^2} \quad (5.15)$$

where $\overline{g}_{5/2}$ is the Landé g-factor. For these calculations we used the value measured in [76], $\overline{f}_{41}$ the mean frequency difference of the transitions 4 and 1, $\Delta g_{5/2}$ and Δf_{41} are their respective uncertainties. As previously described in Section 5.1.5 the spectroscopy measurements are mainly limited by quantum projection noise, so the uncertainty of the frequency difference is equal to ± 3.2 Hz for each individual measurement set and equal to ± 0.028 Hz for the entire data set. The uncertainty of each individual magnetic field data point in Figure 5.10 is equal to $3.0 \mu\text{G}$ and the uncertainty for the total magnetic field measurement is equal to 26 nG .

The presence of an orthogonal component of the oscillating-magnetic field arising from the trap-induced RF current could potentially induce errors in the determination of the magnetic field perceived by the ion. This field induces AC Zeeman shifts of the Zeeman sublevels that can be estimated using [124]:

$$\Delta_{AC\text{Zeeman}} = \left[\frac{1}{2} \frac{\omega_z^2}{\omega_z^2 - \Omega^2} \frac{\langle B_{\perp}^2 \rangle}{B_0^2} \right] m\omega_z, \quad (5.16)$$

where $\omega_z = g_i \mu_B B / \hbar$ is dependent of the Landé g-factor g_i of each energy level. The magnitude of this field was previously determined in the work of Michael Guggemos [69] and measured to be of $B_{\perp} = (9.7 \pm 1.2) \mu\text{G}/\text{W}$. This shift cancels out completely when averaging over the 6 symmetric transitions. However, the influence of AC magnetic fields, if bigger, could lead to uncertainties in the determination of the Landé g-factor in experiments using Paul traps. Following that idea, we are currently working on a more detailed characterization of these fields through the measurement of the coupling strength of two-photon transitions mediated by the sidebands generated by the AC magnetic field.

Cancellation of the linear Zeeman shift

As previously described, the linear Zeeman shift for each $f_{m_i \rightarrow m_j}$ with respect to the center transition (f_0) can be calculated with:

$$\Delta \nu_{linZ(S,D)} = \frac{\mu_B}{h} (g_{5/2} m_j - g_{1/2} m_i) B. \quad (5.17)$$

Given the magnetic field applied to define the quantization axis ($\approx 3 \text{ G}$) the frequency difference between adjacent Zeeman levels is about 1.7 MHz/G for the excited state and 2.8 MHz/G for the ground state. As was previously described and illustrated in Figure 5.8 a), the Zeeman levels for both states are symmetric with respect to the line center, which allows us to completely cancel the linear dependence on the magnetic field by probing and averaging over the 6 transitions defined at the beginning of this section. The implementation of the symmetric two-phase Ramsey probing scheme described in Section 5.1.1, where each transition is probed twice, each time with a switched phase with respect to their first pulse, allows us to cancel linear magnetic field variations during the probing time. The scheme does not completely cancel the shift in the presence of higher order magnetic field variations. However, it considerably minimizes its effect: magnetic field variations on the order of 2 nG/s^2 would

be necessary to observe shifts on the order of 1 mHz. From the measurements of the magnetic field described in Section 5.2.1, the maximum quadratic variation measured is on the order of 0.002 nG/s² which corresponds to a linear Zeeman shift of 1 μ Hz.

Effect	Clock shift (mHz)	Error (mHz)	Fractional error
Linear Zeeman	0	0.001	2×10^{-18}

Second Order Zeeman shift

In the presence of the magnetic field, the D_{5/2} Zeeman sublevels with a magnetic quantum number $|m_j| \leq 3/2$ couple to the D_{3/2} level, inducing a higher-order contribution to the Zeeman effect. As described in Section 3.1.2 this quadratic component can be calculated using second-order perturbation theory [24] :

$$\Delta\nu_{quadZ(S,D)} = K \frac{(\mu_B B)^2}{h^2 \nu_{FS}}, \quad (5.18)$$

where ν_{FS} is the fine structure splitting¹ and K is a constant dependent of the magnetic sublevel such that:

$$\begin{aligned} K &= \frac{6}{25} \quad \text{for } M_J = \pm \frac{1}{2}, \\ K &= \frac{4}{25} \quad \text{for } M_J = \pm \frac{3}{2}, \\ K &= 0 \quad \text{for } M_J = \pm \frac{5}{2}. \end{aligned} \quad (5.19)$$

These shifts are not symmetric around the baseline at zero magnetic field so they cannot be easily canceled through the implementation of a probing scheme. The second order Zeeman shift is one of the largest shifts that affects the frequency of the calcium clock transition. However, the contribution of this shift can be estimated with very high precision, given that its uncertainty is mainly limited by the determination of the magnetic field. As described in Section 5.2.1, during the measurement campaign, the uncertainty in the determination of the magnetic field (ΔB) is equal to 25 nG. Using Equation 5.18 we derived the combined standard uncertainty of the determination of the second order Zeeman shift:

$$\Delta_{quadZ} = \sqrt{\left(\frac{2(\mu_B^2 B) \Delta B}{6h^2 \nu_{FS}} \right)^2 (2K_{1/2}^2 + 2K_{3/2}^2 + 2K_{5/2}^2)}. \quad (5.20)$$

The second order Zeeman shift during the measurement campaign is equal to $(1.36055690 \pm 1 \times 10^{-8})$ Hz.

Effect	Clock shift (Hz)	Error (mHz)	Fractional error
Second Order Zeeman	1.360 556 90	1×10^{-5}	2.4×10^{-23}

¹ $\nu_{FS} = 1.819$ THz

Cancellation of the Quadrupole shift

The quadrupole shift originates from the coupling of the electric quadrupole moment of the $D_{5/2}$ state with the electric field gradient caused by the DC trapping field, generated by voltages on the end cap electrodes or by the presence of spurious electric field gradients from patch potentials. As described in Section 3.2.1, the quadrupole shift of the Zeeman sublevel $|D_j, m_j\rangle$ can be calculated using [79]:

$$\delta_q(m_j) = \frac{1}{4} \frac{dE_z}{dz} \Theta(D, j) \frac{(j(j+1) - 3m_j^2)}{j(2j-1)} (3\cos^2\beta - 1), \quad (5.21)$$

where dE_z/dz is the electric field gradient along the potential's symmetry axis z , $\Theta(D, j)$ the strength of the quadrupole moment, β the angle between the potential's symmetry axis $\vec{z}$ and the magnetic field vector $\vec{B}$. As previously illustrated in Figure 5.3 and described in Section 5.2.1, the quadrupole shift can be canceled by probing any set of three transitions that combine the Zeeman sublevels $\pm 5/2$, $\pm 3/2$ and $\pm 1/2$. Following a similar approach as for the cancellation of the linear Zeeman shift, our two-phase symmetric Ramsey probing scheme ensures that the shift is completely canceled even if the electric field gradient drifts continuously during the measurements. However, as is the case with the Zeeman shift, the probing scheme does not ensure that the shift is canceled in the presence of higher order variations. In order to determine possible variations of the electric field gradient during the measurement, we extracted the quadrupole shift from the two system of equations. From these measurements, no visible higher order variations are observed, only a very slow linear drift equal to $(0.1 \pm 0.3) \mu\text{Hz/s}$. From these results we can confirm that during the measurement campaign the quadrupole shift is completely canceled.

5.2.2 Shifts caused by ion motion

Chapter 2 describes in detail the different components of the ion motion in a Paul trap. Three kinds of motion are distinguished: secular motion, micromotion and excess micromotion. The secular motion can be described as the oscillation of the ion assuming that it is trapped in a pseudo-potential. The micromotion corresponds to the modulated oscillation generated by the interaction of the ion with the RF field of the trap. Finally, the excess micromotion is generated by static electric stray fields that push the ion away from the RF null position, increasing its interaction with the RF field of the trap. The oscillation of the ion induces two kinds of shifts on the ion's clock transition: quadratic Stark shifts and time dilation also known as second order Doppler shifts. Quadratic Stark shifts are generated when the ion is exposed to oscillating electric fields (for more details, see Section 3.2.2) and second-order Doppler shifts are caused by the difference between the atom's transition frequency in its frame of reference and the probing laser in the "laboratory frame" (for more details see Section 3.3.1). In order to minimize the effect of these shifts, two parameters need to be considered: the temperature of the ion and the compensation of the excess micromotion. The shifts generated by both the secular and micromotion are linked to how well we can cool down the ion. Additionally, the mitigation of the shifts originates from the excess micromotion is limited by how well we can compensate the stray fields and push back the ion to the RF null position. However, as I will explain in detail in the following subsections, for certain ion species such as calcium and strontium, these shifts can also be minimized by simply applying the right trap frequency.

Quadratic Stark shifts

Due to the Stark effect, when an ion is exposed to an oscillating field E , it experiences a frequency shift of the magnetic sublevels m_j of the clock transition. This shift can be estimated using the following relation [24, 71]:

$$\Delta\nu_{Stark} = -\frac{\langle E^2 \rangle}{2h} \left(\alpha_0 + \frac{1}{2}\alpha_2(3\cos^2\phi - 1) \times \frac{(3m_j^2 - j(j+1))}{j(2j-1)} \right) \quad (5.22)$$

where α_0 and α_2 are respectively, the scalar and tensor polarizabilities of the level considered and ϕ the angle between the electric field direction and the quantization axis. The tensor polarizability of $^2S_{1/2}$ is zero. The remaining tensor shift from $^2D_{5/2}$ has the same dependence of the Zeeman sublevel m_j as the quadrupole shift (see Equation 5.20). The tensor shift is canceled through the implementation of the 6 transitions probing scheme described in Section 5.1.1. The quadratic Stark shift is reduced to:

$$\Delta\nu_{Stark} = -\frac{\Delta\alpha_0}{2h} \langle E^2 \rangle, \quad (5.23)$$

where $\Delta\alpha_0 = \alpha_0(D_{5/2}) - \alpha_0(S_{1/2})$.

Second-order Doppler shift

As it was described in detail in Section 3.3.1, the motion of the ion in the trap generates a relativistic Doppler shift that reduces the center frequency ν_0 measured in the laboratory frame as a function of the atom's velocity v . The shift can be calculated using [4]:

$$\frac{\Delta\nu_D}{\nu_0} = \frac{\langle v_{||} \rangle}{c} - \frac{\langle v^2 \rangle}{2c^2} + \frac{\langle v_{||} \rangle^2}{c^2} + O(v/c)^3 \quad (5.24)$$

where c is the speed of light and $v_{||}$ is the atom's velocity along the probe laser beam direction which averages down to zero for long trapping duration ($\langle v_{||} \rangle = 0$). For trapped ion clocks the shift is reduced to the so called second-order Doppler shift:

$$\Delta\nu_{D2} = -\frac{\langle v^2 \rangle}{2c^2}. \quad (5.25)$$

Shifts related to the temperature of the ion

The thermal secular motion of the ion has two main effects that lead to shifts: on one hand it causes a second-order Doppler shift and on the other hand it produces an average displacement from the RF null position. When the ion is displaced from the trap center it interacts with the RF field of the trap, consequently causing a micromotion-induced Stark shift and second order Doppler shift. These three shifts are solely dependent on the ion's temperature T . The relation between the ion's temperature, its mean square velocity and the electric field E is described in detail in Section 3.2.2. The total second-order Doppler shift for both the secular motion ($\Delta\nu_{D2,s}$) and the micromotion ($\Delta\nu_{D2,\mu}$) can be determined using [24]:

$$\frac{\Delta\nu_{D2,s}}{\nu_0} = \frac{\Delta\nu_{D2,\mu}}{\nu_0} = -\frac{3kT}{2mc^2}, \quad (5.26)$$

where k is the Boltzmann constant and m the mass of the ion. The scalar Stark shift can be determined using [24]:

$$\frac{\Delta\nu_{\text{scalar},\mu}}{\nu_0} = \frac{-3kT}{2} \frac{\Delta\alpha_0}{\hbar\omega_0} \left(\frac{m\Omega^2}{e^2} \right), \quad (5.27)$$

where $\omega_0 = 2\pi\nu_0$ is the clock transition frequency in rad/s and Ω the trap drive frequency. The sum of both shifts link to the micromotion $\frac{\Delta\nu_{D2}}{\nu_0}$ and $\frac{\Delta\nu_{\text{scalar}}}{\nu_0}$ gives the micromotion shift related to the thermal motion of the ion:

$$\frac{\Delta\nu_{\text{thermal},\mu}}{\nu_0} = \frac{-3kT}{2mc^2} \left[1 + \frac{\Delta\alpha_0}{\hbar\omega_0} \left(\frac{m\Omega c}{e} \right)^2 \right]. \quad (5.28)$$

From this equation, it is clear that for ions with a negative value of $\Delta\alpha_0$ such as $^{40}\text{Ca}^+$ and $^{88}\text{Sr}^+$ the shift is equal to zero when the trap frequency is equal to:

$$\Omega_{\text{magic}} = \frac{e}{mc} \sqrt{\frac{\hbar\omega_0}{\Delta\alpha_0}}. \quad (5.29)$$

The exact "magic" RF drive frequency and the differential scalar polarizability were measured by the Wuhan group [27] to be $\Omega_{\text{magic}} = 2\pi \times (24.801 \pm 0.002)$ MHz and $\Delta\alpha_0 = (-7.2677 \pm 0.0021) \times 10^{-40} \text{ Jm}^2\text{V}^{-2}$. During our measurement campaign, the trap frequency was set to $\Omega = 2\pi \times 32$ MHz. Since the used frequency is close to the magic frequency the thermal frequency shift is considerably reduced. In order to extract the temperature of the ion we evaluated the phonon distribution $\bar{n}_i$ in each direction i measuring the excited state population after applying a π pulse on the carrier $p[\Delta = 0]$ and using the same pulse length on the first motional sideband $p[\Delta = -\omega_i]$:

$$\bar{n}_i = \frac{1}{\eta_i^2} \left(\frac{p[\Delta = -\omega_i]}{p[\Delta = 0]} \right) \quad (5.30)$$

where η_i corresponds to the Lamb-dicke parameter in each direction i . During the measurements only one of the radial modes was cooled down to the ground state. We measured a temperature on the remaining motional modes equal to $T = (1.6 \pm 0.4)$ mK. This temperature generates a micromotion-thermal shift equal to $\Delta\nu_{\text{thermal},\mu} = (2 \pm 1)$ mHz, where the uncertainty on the combined shifts accounts for the contribution of each shift calculated separately. The second order Doppler shift corresponding to the secular motion of the ion is equal to: $\Delta\nu_{D2,s} = (-2.2 \pm 0.5)$ mHz.

Effect	Clock shift (mHz)	Error (mHz)	Fractional error
Combined thermal micromotion	2	1	2.4×10^{-18}
Second order Doppler secular motion	-2.2	0.5	1.2×10^{-18}

Shifts related to the excess micromotion

Uncompensated static electric stray fields push the ion away from the RF null position, adding another contribution to the second order Doppler and micromotion induced Stark shifts. The effects of these fields are minimized by shifting the ion position back to the RF null with two pairs of compensation electrodes located on each side of the

trap (see Section 4.1). The magnitude of the excess micromotion, in the limit of low modulation, β_i is determined from the intensity ratio of the micromotion sideband to the carrier of one the Zeeman transitions [80]:

$$R_i = \frac{J_1(\beta_i)^2}{J_0(\beta_i)^2} = \frac{\Omega_{SB}^2}{\Omega_{car}^2} = \frac{\beta_i^2}{4}, \quad (5.31)$$

where J_n are Bessel functions of order n that relate the micromotion strength to the modulation index β_i and Ω_{car} and Ω_{SB} correspond to the Rabi frequency of the carrier and the micromotional sideband. The voltage in the compensation electrodes is set to minimize the sum of the micromotion sideband intensity ratios $\sum_{x,y,z} R_i$. The mean square electric field perceived by the ion due to the excess micromotion can be estimated with [24]:

$$\langle E^2(t) \rangle = 2 \left(\frac{m\Omega^2 c}{e\omega_0} \right)^2 \sum_{x,y,z} R_i. \quad (5.32)$$

Using Equation 5.23 the scalar Stark shift generated by the excess micromotion is estimated with:

$$\frac{\Delta\nu_{\text{scalar,Excess}}}{\nu_0} = -\frac{\Delta\alpha_0}{\hbar\omega_0} \left(\frac{m\Omega^2 c}{e\omega_0} \right)^2 \sum_{x,y,z} R_i. \quad (5.33)$$

The relation between the coupling ratio and mean square velocity can be estimated using:

$$R_i = \left(\frac{\omega_0}{\Omega} \right)^2 \frac{\langle v^2 \rangle}{2c^2} \cos^2 \theta_i, \quad (5.34)$$

where θ_i is the angle between the unitary vector in the direction of propagation of the laser beam and the direction of the oscillation i . From this equation the second order Doppler shift can be estimated using 5.25:

$$\frac{\Delta\nu_{D2,Excess}}{\nu_0} = -\left(\frac{\Omega}{\omega_0} \right)^2 \sum_{x,y,z} R_i. \quad (5.35)$$

The sum of both shifts related to the excess micromotion $\frac{\Delta\nu_{\text{scalar,Ex}}}{\nu_0}$ and $\frac{\Delta\nu_{D2,Excess}}{\nu_0}$ can be calculated with:

$$\frac{\Delta\nu_{\text{Excess}}}{\nu_0} = \left(\frac{\Omega}{\omega_0} \right)^2 \left[1 + \frac{\Delta\alpha_0}{\hbar\omega_0} \left(\frac{m\Omega c}{e} \right)^2 \right] \sum_{x,y,z} R_i. \quad (5.36)$$

In the same way as for Equation 5.28, the combined shift is also equal to zero independently of the strength of the excess micromotion at the "magic" RF drive frequency Ω_{magic} obtained with the Equation 5.29. However, as described, during our measurements the trap drive frequency was set at $\Omega = 2\pi \times 32$ MHz. As for the thermal shifts, the closeness of this value to the "magic frequency" considerably minimizes the excess micromotion shift but does not fully cancel it. The excess micromotion is minimized with the compensation electrodes such that $\sum_{x,y,z} R_i = (7 \pm 3) \times 10^{-5}$. With the minimization of the micromotion the quadratic Stark shift is $\Delta\nu_{\text{scalar,Excess}} = (0.3 \pm 0.1)$ mHz and the second order Doppler shift is $\Delta\nu_{D2,Excess} = (-0.18 \pm 0.08)$ mHz. The combined excess micromotion shift is equal to $\Delta\nu_{\text{Excess}} = (0.1 \pm 0.2)$ mHz. The uncertainty of the combined shifts accounts for the contribution of each shift calculated separately.

Effect	Clock shift (mHz)	Error (mHz)	Fractional error
Combined excess micromotion	0.1	0.2	4.8×10^{-19}

5.2.3 Black body radiation shift

As it was described in detail in Section 3.2.2, the thermal electromagnetic radiation surrounding the ion shifts the energy of the two clock states by off-resonant coupling to other energy levels. The mean-squared electric field emitted by a black body at an average environmental temperature T can be estimated using [81]:

$$\langle E^2(t) \rangle = ((831.9 \text{ V/m})^2 \left(\frac{T(\text{K})}{300} \right)^4. \quad (5.37)$$

Using Equation 5.23, the generated shift can be approximated as a quadratic Stark shift of the form [82]:

$$\Delta\nu_{BBR} = -\frac{1}{2h} \langle E^2(t) \rangle \Delta\alpha_0 (1 + \eta) \quad (5.38)$$

where $\Delta\alpha_0$ is the differential scalar polarizability, previously defined in Section 5.2.2 and η is small dynamic correction due to the frequency distribution of the black body radiation field. The stability and accuracy of the environmental temperature measurement limits the uncertainty of the black body radiation shift [110]. The temperature generated at the trap as a function of the RF power was determined using the 4-point method. A detailed description of these measurements can be found in Michael Guggemos thesis [69]. At the input power of 1 W the trap heats up approximately by (1.4 ± 0.5) K, while the environmental temperature of the laboratory, constantly monitored, remains constant at (294 ± 2) K. Assuming a uniform temperature distribution and a conservative 2 K uncertainty in the determination of the temperature, the black body radiation shift is equal to $\Delta\nu_{BBR} = (355 \pm 10)$ mHz.

Effect	Clock shift (mHz)	Error (mHz)	Fractional error
Black Body Radiation	355	10	2.4×10^{-17}

5.2.4 Stark shift caused by laser light

Another source of AC quadratic Stark shifts on the clock transition comes from the electromagnetic radiation of the lasers necessary for cooling, optical pumping and probing. In a Ramsey experiment, ideally all laser are switched off during the waiting time and only the 729 nm laser is activated during the two probing pulses. However, since this cannot be done perfectly, the residual light fields can cause AC Stark shifts.

As described in Section 3.2.2, the Stark shift of an energy level by a light detuned from a dipole transition as a function of the optical intensity I can be estimated with [24]:

$$\Delta E_{AC}(\lambda) = -\frac{\Delta\alpha_{AC}(\lambda)}{2hc\epsilon_0} I. \quad (5.39)$$

where the frequency dependent polarizability $\Delta\alpha_{AC}$ is composed of the contributions from the off-resonant coupling of the dipole transitions to the levels of the clock transition [125]. The intensity I is estimated by measuring the optical power P of the laser and using $I = \frac{P}{a}$ where a is the estimated beam surface area.

For the case of a quadrupole transition the Stark shift can be calculated with:

$$\delta_{\text{Stark}_{\text{quadrupole}}} = \pm \frac{\Omega^2}{4\Delta} \quad (5.40)$$

where Ω is the Rabi frequency. During the probing pulses, these stray fields induce a phase shift of the Ramsey pulses and during the waiting time, if present, they can generate a frequency offset of the measured clock transition. For each one of the light sources we estimated the possible shifts and simulated their effects during the probing pulse and the waiting time. The results are summarized in Table 5.1.

Cooling and repumping lasers: 397 nm, 854 nm and 866 nm

The shift of these lasers, if present, most likely originates from zeroth-order leaking light. As described in Section 4.4 the optical path for each of these lasers is composed of a double pass and a single pass AOM assuring, when necessary, a combined attenuation of approximately 80 dB. The dominant shift for the 397 nm laser is generated by off-resonant coupling light to the cooling transition ($S_{1/2} \leftrightarrow P_{1/2}$). For both the 854 nm and 866 nm the dominant shift is generated by off-resonant coupling to the $D_{5/2} \leftrightarrow P_{3/2}$ transition. To characterize any possible leaking light we carefully measured the intensity of each laser beam in front of the fiber that goes to trap in the "off" condition. We measured powers that are equal to or lower than 0.1 nW which are limited by the resolution of our power meter. If we assume that only 1% of that unfocused light is coupled to the fiber and reaches the trap, we can estimate that any possible AC Stark shift generated by leaking light of the cooling and repumping lasers is going to be below 1 mHz.

Probing laser 729 nm

During the probing pulse, the 729 nm laser light contributes to the AC Stark shift by off-resonantly coupling to the Zeeman levels of the $S_{1/2} \leftrightarrow D_{5/2}$ as well as to the $S_{1/2} \leftrightarrow P_{1/2}$, $S_{1/2} \leftrightarrow P_{3/2}$ and $D_{5/2} \leftrightarrow P_{3/2}$ transitions. This can happen either by the light resonant to the probed transition or by 0th order leaking light detuned by the corresponding single and double pass AOM frequencies. The shift generated by off resonant coupling with the Zeeman levels can be estimated as a function of the detuning Δ and the coupling strength Ω with respect to the probed transition using Equation 5.40. As described in Section 5.1.1, the 729 nm probing beam was adjusted to obtain a similar coupling strength for the $\Delta m = 0, \pm 1, \pm 2$ transitions of approximately $\Omega = 2 \times \pi 1.250$ kHz. By probing 6 symmetric transitions with a similar coupling strength, the shift generated by the "on-resonance" probing pulses light cancels out. The shift corresponding to the 0th order leaking light is also minimized although not completely canceled; a conservative estimate is calculated considering the extra detuning of 620 MHz and a beam power of 0.1 nW. The shift generated by the off resonant coupling to the $S_{1/2} \leftrightarrow P_{1/2}$, $S_{1/2} \leftrightarrow P_{3/2}$ and $D_{5/2} \leftrightarrow P_{3/2}$ levels can be estimated using Equation 2.38. As for the other shifts, the calculations for both probing time and waiting time are summarized in table 5.1.

5.2.5 Summary of Clock systematics

Table 5.2 summarizes the evaluation of the systematic shifts and uncertainties for the clock measurement. The total shift considering only the spectroscopic measurements is (1.724 ± 10) Hz. Our measurements are mainly limited by the determination of the

Radiation	Shift wait time (mHz)	Shift probing (mHz)	Clock shift (mHz)	Error (mHz)
397 nm	< 1	< 0.03	< 1	< 1
866 nm	< 1	< 0.03	< 1	< 1
854 nm	< 1	< 0.03	< 1	< 1
729 nm	< 0.1	6	6	< 0.1
Total	3	6	9	2

Table 5.1: AC Stark shifts from cooling, repumping and probing lasers. A conservative estimation of the shift and respective error for each of the lasers considering their effect during the probing pulses and the waiting time.

black body radiation shift. To improve the precision of this measurement it is necessary to refine the determination of the environmental temperature. The group of K.Gao [26] uses a thermal imaging camera through a MgF_2 camera window to estimate the temperature at the Kelvin level and propose the implementation of temperature stabilized boxes with chillers that could reduce the uncertainty to the 10^{-18} level [126]. Other groups have implemented cryogenic chambers, greatly reducing both the shift and the uncertainty [127, 128]. The implementation of such techniques in the development of new optical ion trap experiments with calcium ions could help us push the uncertainty further down. This work was focused on the implementation of a GNSS link to do an absolute frequency comparison respect to the UTC(PTB). The next section gives a complete summary of the total uncertainty budget during the measurement campaign.

5.3 Conclusion: absolute frequency measurement

The measurements presented in this chapter are summarized in table 5.3. The uncertainty in the determination of the total systematic shift for the spectroscopy evaluation, abbreviated as " $\text{syst}_{\text{link}}$ ", is equal to 0.01 Hz. The uncertainty in the determination of the total systematic shift due to the GNSS link, abbreviated as " $\text{syst}_{\text{link}}$ ", is equal to 0.13 Hz. Finally the statistical uncertainty of our measurements, abbreviated as " stat " is equal to 0.6 Hz. The absolute frequency of the $4s\ ^2S_{1/2} \leftrightarrow 3d\ ^2D_{5/2}$ $^{40}\text{Ca}^+$ transition with respect to the UTC(PTB) is measured to be:

$$411\,042\,129\,776\,401.2\ (0.6)_{\text{stat}}\ (0.01)_{\text{syst}_{\text{spect}}}\ (0.13)_{\text{syst}_{\text{link}}}\ \text{Hz}.$$

The uncertainty of 1.4×10^{-15} is mainly limited by the instability of the passive hydrogen maser. The stability of the link could be greatly improved by the implementation of a more stable source such as an active hydrogen maser. Nonetheless, the establishment of the GNSS link in our laboratory represents a major milestone: it offers the possibility to compare our ion clocks to primary and secondary frequency standards in the world. These comparisons are a fundamental tool to facilitate consistency checks of the performance and accuracy of our optical clocks [11]. Frequency comparison using fiber links have proven to outperform satellite-based links showing residual instabilities of few parts in 10^{19} [129, 130]. However, the implementation of fiber link connections between remote sites is still impractical in some geographical regions,

Effect	Clock shift (mHz)	Error (mHz)	Fractional error
Linear Zeeman	0	0.001	2×10^{-18}
Second order Zeeman	1360.55690	1×10^{-5}	2.4×10^{-23}
Combined AC Stark and second order Doppler due to thermal micromotion	2	1	2.4×10^{-18}
Second Order Doppler due to secular motion	-2.2	0.5	1.2×10^{-18}
Combined AC Stark and second order Doppler due to excess micromotion	0.1	0.2	4.8×10^{-19}
Black Body Radiation	355	10	2.4×10^{-17}
AC Stark shift (729 nm, 397 nm, 854 nm and 866 nm)	9	2	4.8×10^{-18}
Total	1724	10	2.4×10^{-17}

Table 5.2: Systematic shifts and error for the spectroscopy evaluation of the clock A summary of the most relevant shifts. A frequency offset of 1.724 Hz with an uncertainty of 10 mHz corresponding to the square root of the sum of the squared individual errors is obtained.

such as Innsbruck. Satellite links offer a simple solution that requires limited equipment. The implementation of a passive hydrogen maser, even if not ideal, represents also a more affordable and practical solution as a stable reference source to perform these frequency comparisons. As illustrated in Figure 5.1, our measurements are in agreement with the latest measurement of the K.Gao group but disagree with the first measurements performed by our group. The frequency difference between both historical measurements is still open for further analysis. A frequency comparison via GNSS link between our $^{40}\text{Ca}^+$ clocks and the ones by the group of K.Gao could potentially offer an even stronger final argument to this debate.

Effect	Shift (Hz)	Error (Hz)	Fractional error
Systematic shift spectroscopy	1.72	0.010	2.4×10^{-17}
Systematic shift GNSS link	25.83	0.13	3×10^{-16}
Total systematic	27.55	0.13	3×10^{-16}
Statistical results of the frequency referenced to the H-maser	411 042 129 776 428.7	0.6	1.4×10^{-15}
Absolute frequency	411 042 129 776 401.2	0.6	1.4×10^{-15}

Table 5.3: Systematic shifts and error for the absolute frequency via GNSS link The table gathers all the shifts with their respective errors described in the chapter. The transition frequency measurement during the 2021 campaign is 411 042 129 776 401.2 Hz with an uncertainty of 0.6 Hz.

Chapter 6

Quantum logic spectroscopy with a $^{40}\text{Ca}^+ / ^{27}\text{Al}^+$ mixed ion crystal

“Contrariwise, continued Tweedledee,
if it was so, it might be; and if it were so, it would be;
but as it isn’t, it ain’t. That is logic.”
Lewis Carroll
Through the Looking-Glass (1871)

The work presented here is published in:
New J. Phys. **21** 103003 (2019)

Single-ion frequency standards, similar to the $^{40}\text{Ca}^+$ ion clock presented in Chapter 5, based on Hg^+ , Sr^+ or Yb^+ have recently demonstrated uncertainties in the low 10^{-17} range or lower [131, 18, 132, 24]. These ion species offer the advantage that their relativistic shifts can be made small by laser-cooling the ions to sub-millikelvin temperatures and that their clock transition can be easily measured by means of the electron shelving technique, which enables the detection of an ion’s quantum state with an efficiency close to 100%. However, as it was demonstrated in chapters 3 and 5, these clocks require a careful evaluation of systematic frequency shifts such as electric quadrupole, ac-Stark or black body radiation-induced shifts. The uncertainty achieved with these clocks is limited by our capacity to either cancel or properly characterize these shifts.

From this perspective, as described in Section 3.4.2, the $^1\text{S}_0 \leftrightarrow ^3\text{P}_0$ transition in Al^+ seems to offer an interesting approach to this problem: an extremely narrow linewidth of about 8 mHz at 267.4 nm, which gives rise to a high Q factor of $\nu/\Delta\nu \approx 10^{17}$, with high immunity to perturbations by external fields. The transition has a low dc second-order Zeeman shift, a very small black-body radiation shift, and a negligibly small electric quadrupole shift. The total contribution of these shifts to the total systematic relative uncertainty of the clock has been reported with values below 10^{-18} [17]. It would appear that the intrinsic properties of the transition would minimize the effect of the environment on the ion. For this reason, several laboratories in the world are focusing their efforts on the construction and development of optical frequency standard based on $^{27}\text{Al}^+$ [58, 91, 133, 134]. The insensitivity of this clock to the environment makes it also an ideal candidate for the construction of a transportable optical clock with low fractional systematic uncertainties [135].

However, even if the aluminum ion seems to be the ideal candidate to build an ion clock there is a catch. Experiments with Al^+ are complicated by the fact that the dipole-allowed transition $^1\text{S}_0 \leftrightarrow ^1\text{P}_1$ that could be used for detecting the quantum

state of the ion via state-dependent fluorescence measurements and for preparing the ion in a desired initial state has a wavelength of 167 nm. This makes the operation of Al^+ clocks technically more challenging than other ion clocks. Moreover, its linewidth of about 220 MHz is rather large so that Doppler cooling on this transition would lead to minimum temperatures that are a magnitude above the ones reached when Doppler cooling other ion species such as Ca^+ , Sr^+ , Hg^+ or Yb^+ ions [136]. To circumvent the cooling difficulties, sympathetic cooling is implemented. As described in Section 2.4, an auxiliary ion that can be easily laser cooled, in our case Ca^+ , is stored in the trap together with the aluminum ion and is used to cool down the initially hot aluminum ion via the Coulomb interaction. The problem of detecting the quantum state of the aluminum ion is overcome by quantum logic spectroscopy [137], as described in Section 2.4.3, a technique that enables detecting the quantum state of a trapped atomic or molecular ion [58, 138, 139, 140, 141, 142] by transferring the information to a co-trapped ion that can be easily read out. The auxiliary ion or "logic" ion is then used to cool down the "spectroscopy" ion via sympathetic cooling and additionally allows the preparation and detection of the internal state of the "spectroscopy" via quantum logic spectroscopy.

In the present chapter I describe quantum logic experiments with a two-ion crystal composed of a $^{27}\text{Al}^+$ and a $^{40}\text{Ca}^+$ ion. The preliminary measurements of these experiments were first introduced in Michael Guggemos' thesis [69] and the final results were later published [70]. The first section presents the preparation of the mixed $^{40}\text{Ca}^+ - ^{27}\text{Al}^+$ ion crystal, followed in Section 6.3 by the quantum logic spectroscopy protocol. Section 6.4 describes the absolute frequency measurement of the $^1\text{S}_0 \leftrightarrow ^3\text{P}_1$ line in $^{27}\text{Al}^+$ by interleaving probing of this transition with probing of the $\text{S}_{1/2} \leftrightarrow \text{D}_{5/2}$ quadrupole transition in $^{40}\text{Ca}^+$, which is used as a frequency reference. Finally Section 6.6 presents the observation and first preliminary measurements of the $^1\text{S}_0 \leftrightarrow ^3\text{P}_0$ clock transition.

6.1 Trapping, cooling and motional state analysis of a two-ion $\text{Ca}^+ / \text{Al}^+$ crystal

Our experiments start by loading and Doppler-cooling a single Ca^+ ion into the trap. For these experiments a trap confinement was implemented such that the typical oscillation frequencies of a single Ca^+ were 820 kHz along the weak axial direction of the trap and approximately 1.5 MHz along the radial directions. The micromotion caused by residual electric stray fields is detected and compensated following the procedures described in Section 5.2.2. The $\text{Ca}^+ / \text{Al}^+$ ion crystal is created by loading an Al^+ ion via laser ablation as described in the reference [55]. As a way to confirm the composition of the ion crystal, the mass of the ions created in the trap is inferred using the "tickling" measurement technique: the fluorescence of the calcium ion is measured as a function of the frequency of a weak electric field applied to the "tickle electrode" (see Section 4.1) capable of exciting the in-phase collective motion of the crystal along its axis. The mixed ion crystal has typically a lifetime of several hours, limited by background gas collisions leading to ion loss or by chemical reactions giving rise to conversion of atomic ions to unwanted molecular ions such as AlH^+ . The formation of these unwanted molecular ions is monitored by the "tickling" measurement technique revealing an increase in the crystal mass.

The collective motion of the two-ion crystal in the trap, described in detail in Section 2.1.2, is composed of 6 different modes. As illustrated in Figure 2.2, there are two

motional modes along each axis, the "center of mass" (COM) mode where the velocities of the two ions are in the same direction and the "stretch" (STR) mode where they are in opposite directions. To investigate these modes we can implement the "tickling" technique or we can also perform measurements of the absorption side-band spectra on the quadrupole transition in Ca^+ , following the technique described in Section 4.4.1. Figure 6.1 shows part of an absorption spectrum, that spans over all six collective modes of motions. In the figure, the upper and lower vibrational sidebands can be seen next to the carrier transition at the center of the plot.

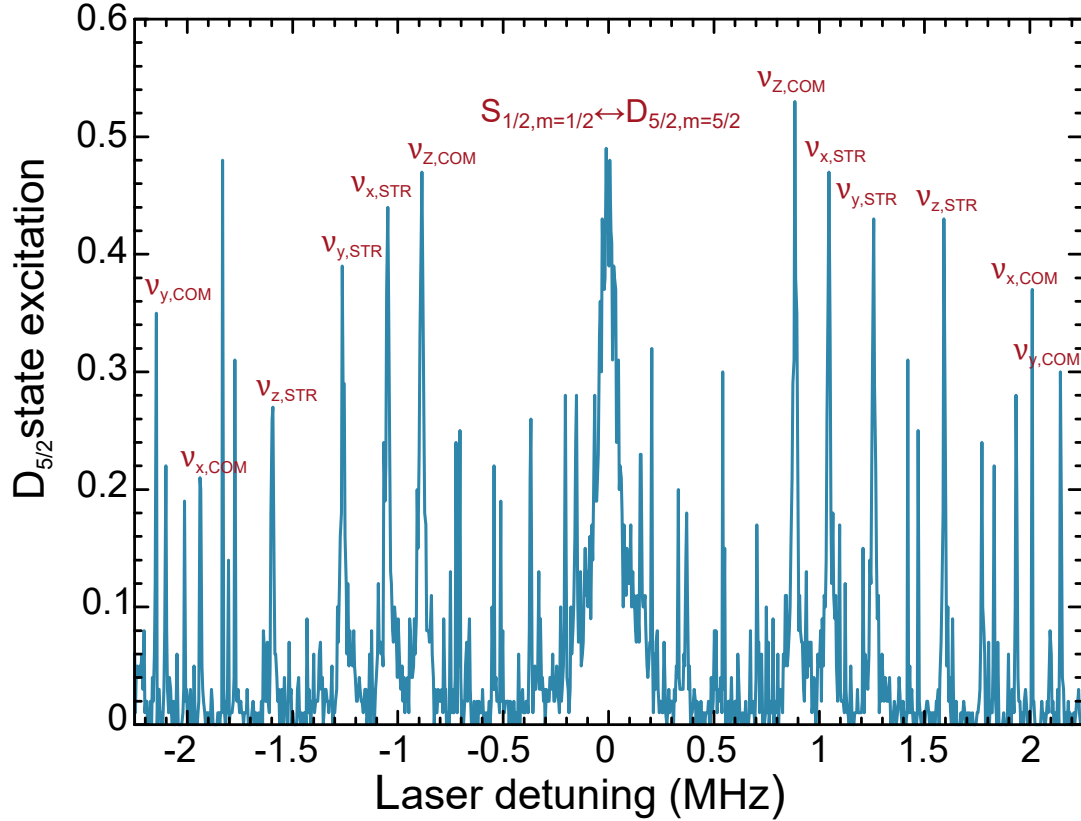


Figure 6.1: Excitation spectrum of a calcium ion probed at 729 nm in a mixed $\text{Ca}^+ / \text{Al}^+$ crystal at typical trapping condition. The center peak represents the $\text{Ca}^+ S_{1/2,mj=1/2} \leftrightarrow D_{5/2,mj=5/2}$ carrier transition with its red and blue motional sidebands of the mixed crystal symmetrically placed to the left and right respectively. The axial "center of mass" COM and "stretch" STR modes are visible at $\nu_{z,\text{COM}} = \pm 888$ kHz and $\nu_{z,\text{STR}} = \pm 1.596$ MHz respectively. The degeneracy of the radial potential is lifted by a dc-voltage applied to a pair of blade electrodes so that the radial modes are observed at approximately $\nu_{y,\text{STR}} = \pm 0.9$ MHz, $\nu_{x,\text{STR}} = \pm 1.1$ MHz, $\nu_{y,\text{COM}} = \pm 1.9$ MHz, and $\nu_{x,\text{COM}} = \pm 2.1$ MHz. Other peaks appearing correspond to second-order sidebands.

The quantum logic spectroscopy protocol introduced in Section 2.4.3 and described in the next section requires one of the collective vibrational modes of the crystal to be cooled to its ground state. Given our trap configuration the modes in the axial direction (z) are more likely to have lower heating rates. We measure a heating rate of the axial center mode ($\nu_{z,\text{COM}}$) of approximately 70 phonons/s and of 0.8 phonons/s for the stretch mode ($\nu_{z,\text{STR}}$). During our experiments, both vibrational modes are cooled to mean phonon numbers below 0.05 phonon by sideband cooling the calcium ion. This ensures the minimization of coupling strength fluctuations when resonantly

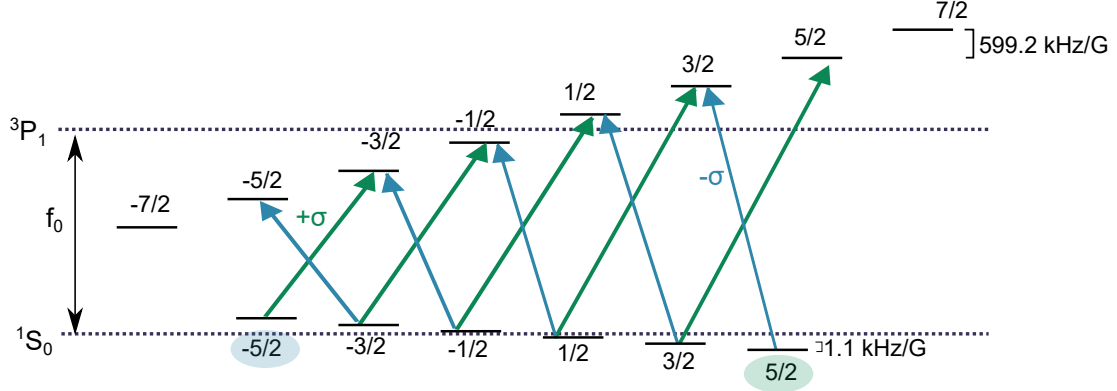


Figure 6.2: Energy sub-levels of the $^1\text{S}_0 \leftrightarrow ^3\text{P}_1$ intercombination line of the Al^+ due to linear Zeeman effect. The $^1\text{S}_0$ and $^3\text{P}_1$ levels split into 6 and 8 sub-levels respectively. The $m=\pm 5/2$ stretched Zeeman states of the $^1\text{S}_0$ level are populated using a series of carrier π -pulses with circular polarized light exciting the five $m \leftrightarrow m \pm 1$ Zeeman transitions that can be used for pumping the undesired Zeeman states. The polarization of the beam is inverted to go to $m=5/2$ (in green) or to $m=-5/2$ (in blue).

exciting sideband transitions in Al^+ or Ca^+ . The $\nu_{z,\text{STR}}$ mode was chosen, due to its lower heating rate, as a bus mode for the quantum state transfer.

6.2 Preparation of the Al^+ ion in a specific Zeeman ground state

As illustrated in Figure 6.2 due to the linear Zeeman effect (see Section 3.1) the $^1\text{S}_0$ splits into 6 energy sub-levels. To initialize the Al^+ ion in a pure electronic state we implemented optical pumping on the $^1\text{S}_0 \leftrightarrow ^3\text{P}_1$ intercombination line. As illustrated in Figure 4.2 there is only a single laser beam available for exciting the ion from a direction that is parallel to the quantization axis. The $m=\pm 5/2$ stretched Zeeman states of the $^1\text{S}_0$ level are populated using a series of carrier π -pulses with circular polarized light exciting the five $m \leftrightarrow m \pm 1$ Zeeman transitions that can be used for pumping the undesired Zeeman states. The polarization of the beam is inverted to go to $m=5/2$ (in green) or to $m=-5/2$ (in blue).

We also tested whether frequency-resolved optical pumping to the stretched states could be achieved by making the beam's polarization linear. The idea was to try to optically pump to any Zeeman state or to have the capability to rapidly switch between populating either one or the other stretched states by optical pumping without resetting the beam's polarization. Using the protocol described below we were able to excite all available $\sigma_+(\sigma_-)$ Zeeman transitions. We found, however, that the pumping worked less reliably as compared to the one by circularly polarized light. These difficulties can be attributed to coherent population trapping and ac-Stark shifts by the unwanted polarization components. As can be seen in Figure 6.2 adjacent Zeeman ground states have energy shifts of less than 10 kHz at a magnetic field of 4 G. We concluded that the more promising solution to perform the fast optical pumping to the stretched states is to add fast polarization control or a second laser beam with a different polarization to our experimental setup.

6.3 Quantum logic spectroscopy

The quantum logic spectroscopy scheme is described in Section 2.4.3, in the following section I will describe the experimental steps that we implement for quantum state initialization, excitation, and probing:

- I. *Logic ion initialization:* The ion crystal is prepared in the Lamb-Dicke regime by 5 ms of Doppler cooling on the $S_{1/2} \leftrightarrow P_{1/2}$ transition of Ca^+ at 397 nm. Light at 866 nm and 854 nm is used to optically pump out the metastable $D_{3/2}$ and $D_{5/2}$ states of the logic ion. A circularly polarized beam at 397 nm oriented in the direction of the quantization axis initializes the calcium ion in one of the $S_{1/2}$ ground states.
- II. *Spectroscopy ion initialization:* The Al^+ ion is optically pumped into either one of the two stretched $m_F = \pm 5/2$ Zeeman states of the 1S_0 ground state by exciting the $^1S_0, F = 5/2$ to $^3P_1, F = 7/2$ intercombination line with a circularly polarized beam at 267 nm counterpropagating to the circularly polarized beam at 397 nm. As described in the previous section a series of laser pulses driving the five $m_F \leftrightarrow m_{F'} \pm 1$ Zeeman transitions ($-5/2 \leq m_F < 5/2$) with pulse areas of π followed by a waiting time of 300 μs pushes the population towards the target state. This sequence of pulses is repeated 10 times in order to populate the stretched Zeeman state.
- III. *Ground-state cooling and logic ion preparation:* Both axial modes are sideband-cooled close to the ground state by two laser pulses on the quadrupole transition at 729 nm with a total duration of 7 ms. To minimise the average vibration quantum number of the stretch-mode used for the quantum logic state transfer, the COM-mode is cooled prior to cooling the stretch-mode. Finally, a carrier π -pulse transfers the Ca^+ ion into the $D_{5/2}$ state.
- IV. *Spectroscopy ion probing:* The desired carrier transition is probed by either a single pulse or in a Ramsey experiment by a pair of $\pi/2$ pulses separated by a waiting time.
- V. *Quantum state transfer:* For state mapping to the logic ion, a π -pulse of the upper motional sideband of the out-of-phase mode on the transition adds a phonon to the system if the previous carrier excitation was unsuccessful. The phonon is mapped to a change of the electronic state in Ca^+ by a consecutive π -pulse on the upper motional sideband of the same mode on the $S_{1/2} \leftrightarrow D_{5/2}$ transition, which returns the calcium ion to its electronic ground state. As a result, the calcium ion is found in $D_{5/2}$ if the aluminium ion was excited to the metastable state by the carrier excitation pulse of step (IV).
- VI. *Quantum state detection:* The quantum state of Ca^+ is measured via electron shelving.

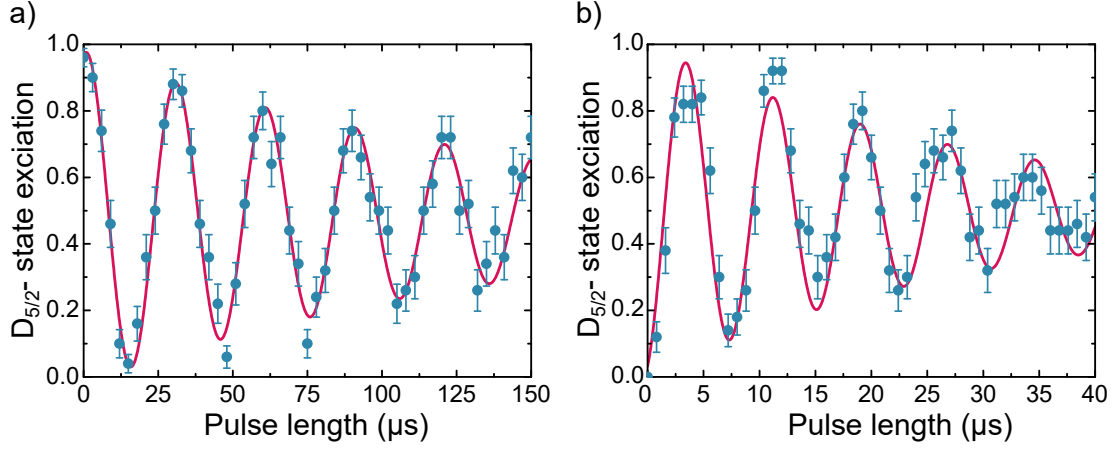


Figure 6.3: Rabi Oscillations on the blue sideband and Carrier transition of the intercombination line.

(a) Rabi oscillations on the blue sideband (z_{STR}) of the $(3s^2) \ ^1S_0, m_F = -5/2 \leftrightarrow (3s3p) \ ^3P_1, F = 7/2, m_F = -7/2$ transition detected by quantum logic spectroscopy. After $15 \mu\text{s}$ approximately 95% of the population is transferred to the excited state. The imperfections of this π -pulse give rise to the baseline in the Ramsey patterns. The fidelity is limited by high frequency noise of the laser and temperature fluctuations of the axial COM mode. The error bars are determined from quantum projection noise. An exponentially decaying sine function that includes a constant offset is fitted to the experimental data (pink curve). (b) Rabi oscillations on the carrier transition for identical parameters. The signal is obtained by adding a carrier excitation pulse of variable length to the pulse sequence prior to the blue-sideband π -pulse.

Figure 6.3 shows an application of this protocol that was used for recording Rabi oscillations on the blue sideband and the carrier transition of the $|^1S_0, F = 5/2, m_F = 5/2\rangle \leftrightarrow |^3P_1, F = 7/2, m_F = 7/2\rangle$ transition. Note, that in this case, we omit step (IV) and vary the duration for the sideband pulse in step (V). It demonstrates that π -pulses can be realised on the sideband with a fidelity of about 95 % and that the Al^+ ion can be coherently excited to the metastable state by a carrier π -pulse with a duration of about $4 \mu\text{s}$. On the carrier transition, the loss of contrast versus time is predominantly caused by high-frequency phase noise of the quadrupled diode laser system. This assumption is corroborated by the fact that the ratio γ/Ω between the damping rate γ of the oscillations and the carrier Rabi frequency Ω is not constant but increases with Ω in qualitative agreement with the measured spectral phase noise of the laser. On the sideband, the contrast loss is due to laser phase noise and loss of population from the upper state by spontaneous emission.

For a further investigation of the coherence time on the intercombination line, Ramsey experiments on the carrier transition were carried out using the quantum logic spectroscopy protocol for state read-out. Figure 6.4(a) shows the Ramsey signal as a function of laser detuning, whereas Fig. 6.4(b) shows the Ramsey contrast as a function of the waiting time between the $\pi/2$ -pulses. At short waiting times a Ramsey contrast of 0.81(1) is obtained which is limited by imperfect $\pi/2$ and state mapping pulses. At longer waiting times, the contrast decays exponentially with time, in agreement with the expected contrast loss caused by spontaneous decay of the 3P_1 state.

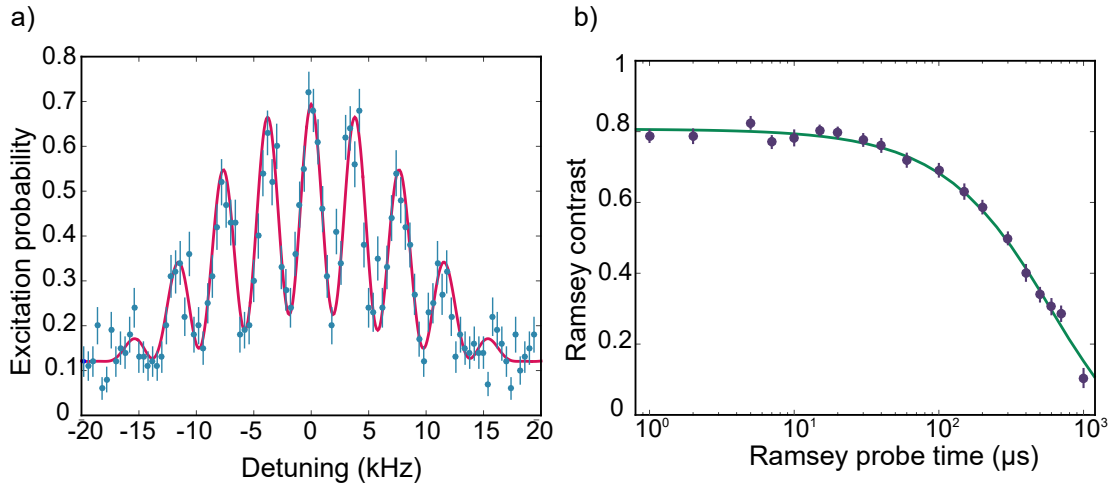


Figure 6.4: Ramsey experiments on the $^{27}\text{Al}^+$ carrier transition

$(3s^2) ^1S_0, m_F = -5/2 \leftrightarrow (3s3p) ^3P_1, F = 7/2, m_{F'} = -7/2$

(a) Measured excitation as a function of laser detuning (blue points) for Ramsey pulses of $50 \mu\text{s}$ duration and a waiting time of $200 \mu\text{s}$. The data is fitted by a numerical integration of the master equation describing the Ramsey experiment (solid line), including spontaneous decay of the 3P_1 level. The resulting excitation probability is adjusted for a frequency offset, an excitation baseline and a reduction in contrast. (b) Ramsey contrast versus waiting time on the same transition. Fitting an exponential decay curve to the data yields a contrast of $0.81(1)$ for very short Ramsey times and a decay time of $\tau = 598(20) \mu\text{s}$ that agrees within its error bar with twice the lifetime of the 3P_1 level.

6.4 Frequency measurement of the intercombination transition

Excitation of Al^+ ions on their $^1S_0 \leftrightarrow ^3P_1$ intercombination line at 267 nm by coherent laser pulses enables a set of useful tools necessary for the construction of our optical frequency standard. Given that the 3P_1 energy level of the $^{27}\text{Al}^+$ ion has a life time of about $300 \mu\text{s}$ [143], the $^1S_0 \leftrightarrow ^3P_1$ intercombination line can be used for initializing the ion in a pure electronic state by optical pumping, as described in Section 6.2. Even more importantly, the excitation of the intercombination line can be implemented for high-fidelity state detection after probing the Al^+ clock transition by repetitive quantum non-demolition measurements based on quantum logic spectroscopy [144]. Despite the importance of this transition, to our knowledge, a measurement of its frequency has only been reported in a conference abstract [145] and by our group [70].

In the following section I will describe the absolute frequency measurement of the $^1S_0 \leftrightarrow ^3P_1$ line. Following the steps described in the previous section 6.3 we performed quantum logic spectroscopy measurements with a two-ion crystal composed of $^{27}\text{Al}^+$ ion and a $^{40}\text{Ca}^+$ ion. The $S_{1/2} \leftrightarrow D_{5/2}$ quadrupole transition on $^{40}\text{Ca}^+$, previously measured in Chapter 5, was used for direct clock comparison. A similar experimental setup than the one used to measure the calcium clock transition is implemented: the frequency comb is applied to measure the transition frequency of the intercombination line in $^{27}\text{Al}^+$ by interleaving probing of the aluminum transition with probing of the $S_{1/2} \leftrightarrow D_{5/2}$ calcium clock transition. In addition we have also determined the g-factor of the $^3P_1, F=7/2$ level.

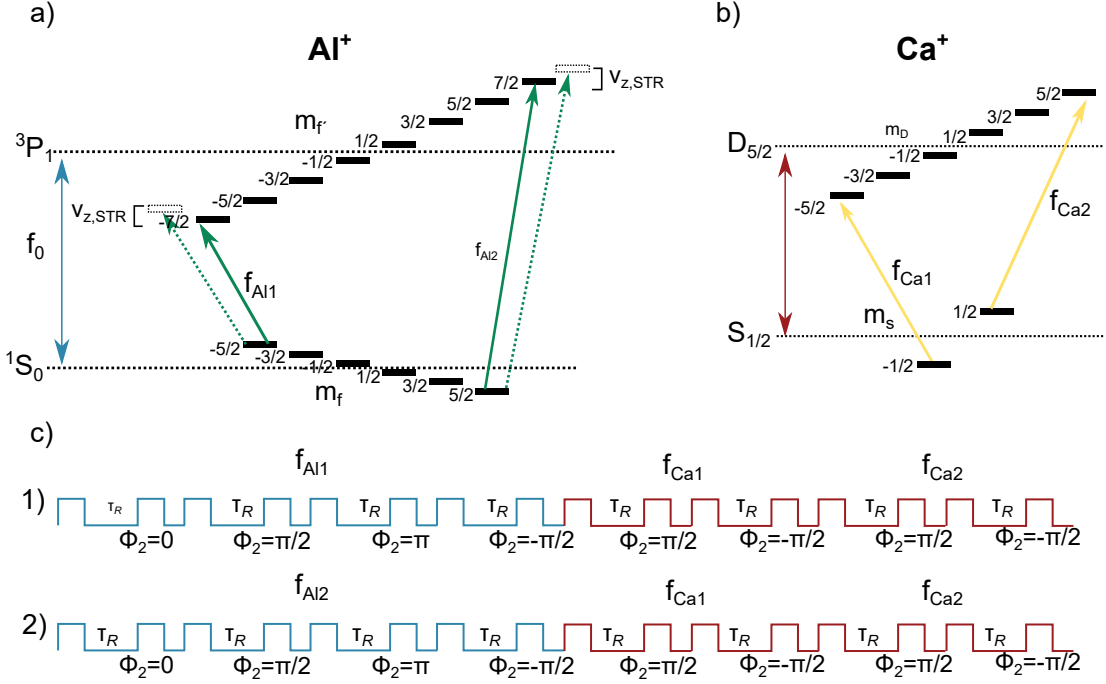


Figure 6.5: Probing scheme to measure the $^1\text{S}_0 \leftrightarrow ^3\text{P}_1$ intercombination transition on the Al^+ .

a) We interrogated the $\text{S}_{0,F=5/2,m_F=5/2} \leftrightarrow ^3\text{P}_{1,F=7/2,m_{F'}=7/2}$ and $\text{S}_{0,F=5/2,m_F=-5/2} \leftrightarrow ^3\text{P}_{1,F=7/2,m_{F'}=-7/2}$ Zeeman transitions of the aluminum ion (in green). The dashed arrow represent the transition of the blue side band stretched mode ($\nu_{z,\text{STR}}$) used for state mapping to the logic ion. b) The $\text{S}_{1/2,m_s=-1/2} \leftrightarrow \text{D}_{5/2,m_D=-5/2}$ and $\text{S}_{1/2,m_s=1/2} \leftrightarrow \text{D}_{5/2,m_D=5/2}$ transitions of the calcium ion (in yellow) are used to monitor the magnetic field variations and the laser field fluctuations. c) Each of the two transitions of the aluminium ion is probed with a Ramsey experiment (in blue) composed of $\pi/2$ -pulses of $50 \mu\text{s}$ duration separated by a waiting time of either 100 or $200 \mu\text{s}$ with the phase ϕ_2 of the second pulse shifted with respect to the first one by $0, \pm\pi/2$, and π . The measurements are interleaved with Ramsey experiments on the two calcium ion transitions (in red) with a waiting time of 2 ms with the phase of the second Ramsey pulse shifted by $\phi = \pm\pi/2$

6.4.1 Measurement results

We probe the Al^+ ion with Ramsey experiments following the steps described in Section 6.3. The fundamental frequency of the laser probing the transition is recorded with the frequency comb whose repetition rate is locked to the frequency of the ultrastable laser at 729 nm (see Figure 4.6). As illustrated in Figure 6.5, the frequency of the laser is monitored by Ramsey experiments on Ca^+ interleaved with experiments probing the Al^+ ion. In this way, the frequency of the intercombination line can be determined with respect to the $\text{S}_{1/2} \leftrightarrow \text{D}_{5/2}$ transition frequency of $^{40}\text{Ca}^+$. The comb measurements show that frequency fluctuations of the light probing the intercombination line in Al^+ are typically about 60 Hz over the course of fifteen minutes. We interrogated the $|^1\text{S}_0, F = 5/2, m_F = 5/2\rangle \leftrightarrow |^3\text{P}_1, F = 7/2, m_{F'} = 7/2\rangle$ and $|^1\text{S}_0, F = 5/2, m_F = -5/2\rangle \leftrightarrow |^3\text{P}_1, F = 7/2, m_{F'} = -7/2\rangle$ Zeeman transitions of the aluminum ion, illustrated in Figure 6.5, with Ramsey experiments (see Section 2.4.2) composed of $\pi/2$ -pulses of $50 \mu\text{s}$ duration separated by a waiting time of

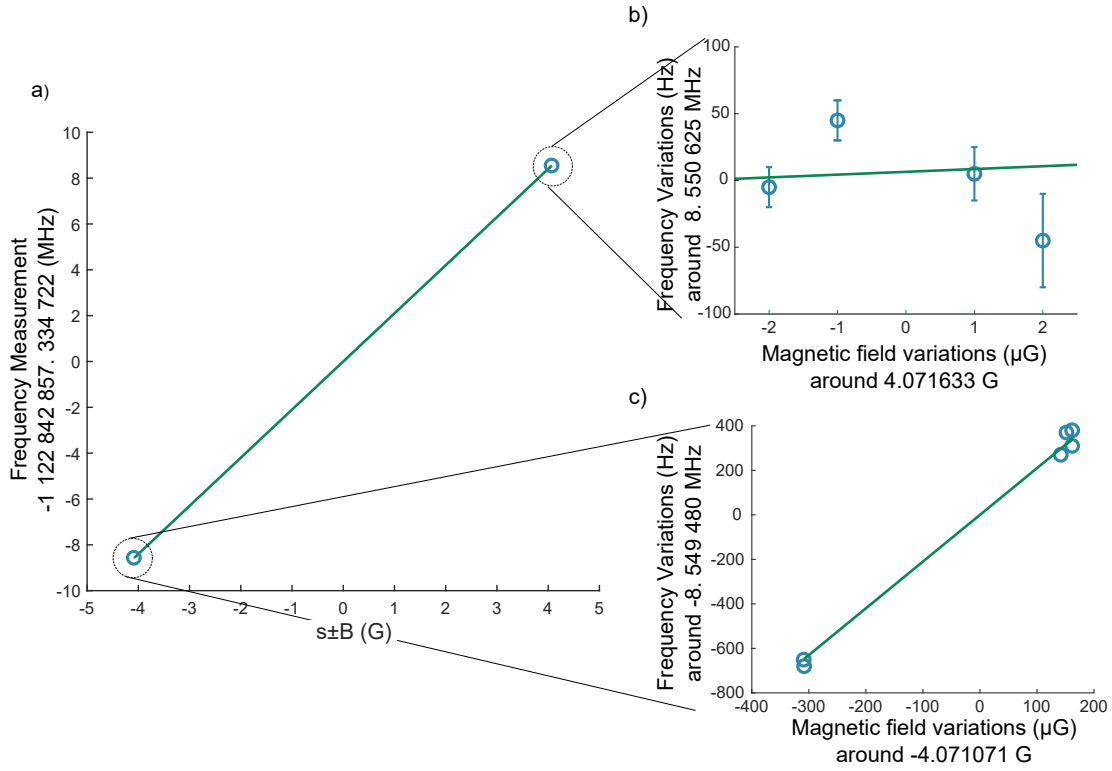


Figure 6.6: Evaluation of the $^1S_0, F = 5/2 \leftrightarrow ^3P_1, F = 7/2$ transition.

a) The 10 measured data sets are plotted as a function of $s\pm B$, where $s_{\pm} = \pm 1$ depending on which of the two stretched state transitions is probed. A linear fit is applied to the data to extract f_0 and the g-factor of the $^3P_1, F = 5/2$ state. b) and c) Are zoom-in plots to show in detail the individual data points on both extremes. This procedure yields a transition frequency at $B=0$ and $f_0 = 1\,122\,842\,857\,334\,711$ Hz with a statistical uncertainty of 36 Hz.

either 100 or 200 μs . The phase ϕ_2 of the second $\pi/2$ -pulse is shifted with respect to the first one by either 0, $\pm\pi/2$, or π , in order to extract both the laser-ion detuning and the contrast of the Ramsey fringe. Each measurement set is repeated 100 times. Next, another four sets of 100 cycles are carried out probing the two symmetric Zeeman $S_{1/2, m_s=-1/2} \leftrightarrow D_{5/2, m_D=-5/2}$ and $S_{1/2, m_s=1/2} \leftrightarrow D_{5/2, m_D=5/2}$ transitions of the calcium ion, with the phase of the second Ramsey pulse shifted by $\phi = \pm\pi/2$. From this second set we extract the detuning of the 729 nm laser from the atomic transition as well as the variations of the magnetic field. This cycle of eight different experiments was repeated fifty times for each of the aluminum Zeeman transitions, followed by a recalibration of experimental parameters. The absolute value of the transition frequency is obtained with respect to the transition frequency of the $S_{1/2} \leftrightarrow D_{5/2}$ transition frequency in $^{40}\text{Ca}^+$, determined in Chapter 5. Our evaluation of the $^1S_0, F = 5/2 \leftrightarrow ^3P_1, F = 7/2$ transition frequency is based on a total of 18 sets of measurements. The first 8 sets of measurements were taken in 2016 and are described in detail in Michael Guggemos thesis, the remaining 10 sets are presented in this thesis. For each set, the uncertainty of the measured average deviation of the laser frequency from the atomic transition is predominantly given by quantum projection noise. For the two probed transitions, the frequency f at non-zero magnetic field B can be calculated from the bare frequency unperturbed by magnetic or electric fields

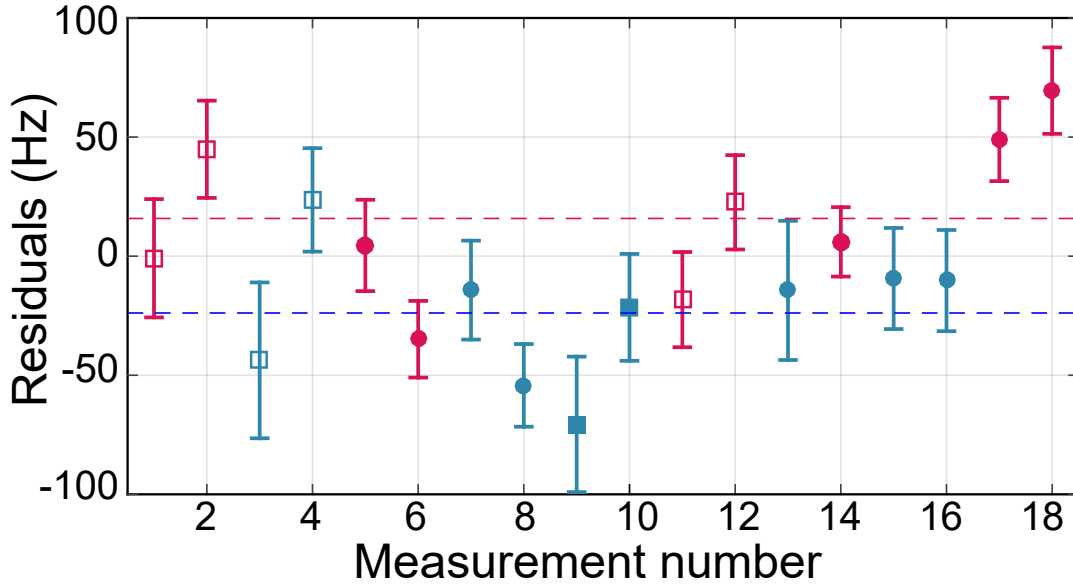


Figure 6.7: Residual of the 18 intercombination line frequency measurements from the linear fit. Data points 1-8 were taken with the frequency comb's repetition rate locked to a stable quartz oscillator. Data points 9-18 were recorded with a comb line locked to the frequency of the laser at 729 nm. Measurements of the $m_{f=5/2} \leftrightarrow m_{f'=-7/2}$ transition are denoted by squares, measurements of the $m_{f=-5/2} \leftrightarrow m_{f'=-7/2}$ are denoted with circles. The colour indicates whether the duration of the Ramsey experiments was 100 μs (blue) or 200 μs (pink). Dashed lines indicate the means of the residuals with the corresponding color.

f_0 using:

$$f = f_0 + \frac{\mu_B}{h} \left(\frac{7}{2} g_{3P_1, F=5/2} - \frac{5}{2} g_{1S_0} \right) s_{\pm} B, \quad (6.1)$$

where g_{1S_0} and $g_{3P_1, F=5/2}$ correspond to the Landé g -factor of the $1S_0$ and $3P_1, F = 5/2$ levels respectively, μ_B to the Bohr magneton, h to the Planck constant and $s_{\pm} = \pm 1$ depending on which of the two stretched state transitions is probed. For each measurement we determine the magnetic field strength, following a similar approach to the one described in Section 5.2.1, by measuring the frequency splitting of the two Zeeman transitions probed in Ca^+ with an uncertainty of about 1 μGauss .

As illustrated in Figure 6.6 we plot the measured frequency f_i as a function of $s_{\pm} B$ and fit a straight line to the data in order to extract the center frequency and the g -factor of the $3P_1, F = 5/2$ state. This procedure yields a transition frequency at $B=0$ of $f_0 = 1\,122\,842\,857\,334\,711$ Hz with a statistical uncertainty of 36 Hz. The residuals of the fit are shown in Figure 6.7 with error bars accounting for the standard deviation of the fifty measurements per data set and errors in the determination of the magnetic field. The scatter of the data points is somewhat bigger than what one would expect given the error bars of the individual data points. Moreover, the measurements with Ramsey waiting time durations of 200 μs yield a frequency estimate differing by $\delta\nu = 40$ Hz from the measurement based on Ramsey experiments of 100 μs duration. To evaluate the statistical significance of this finding, we test the null hypothesis H that the determined frequency is independent of the duration of the Ramsey experiment. Under this hypothesis, the difference $\Delta = 2/N \sum_{i=1}^{N/2} (X_i^{(200)} - X_i^{(100)})$ (with $\mathcal{N}(0, \sigma_r^2)$ -distributed Gaussian random variable $X_i^{(T)}$ describing the outcome of the i^{th} measurement with Ramsey duration T) is itself a Gaussian random variable with a distribution

given by $\mathcal{N}(0, \sigma^2)$ with $\sigma = \sqrt{4/N}\sigma_r = 17$ Hz. Then, the probability of finding a difference of δ or larger is given by $p = P(|\Delta| \geq |\delta| | H) = 1 - \text{erf}(\delta/(\sqrt{2}\sigma)) \approx 0.02$. This rather small p -value makes it seem unlikely that there was no systematic shift present in the experiment. However, no such shift was detected in subsequent control experiments probing the transition by alternating between Ramsey experiments of 100 and 200 μs duration.

From the variation of the magnetic-field-induced splitting $\Delta\nu/B = \frac{\mu_B}{h}(\frac{7}{2}g_{^3P_1, F'=7/2} - \frac{5}{2}g_{^1S_0}) = 2.100056(9)$ MHz/G and the knowledge of $g_{^1S_0}$ [68], we determine the Landé g -factor of the excited state to be $g_{^3P_1, F'=7/2} = 0.428132(2)$.

6.5 Evaluation of the systematic shifts and uncertainties

For the evaluation of the $^1S_0 \leftrightarrow ^3P_1$ transition frequency, both systematic frequency shifts in Al^+ and Ca^+ need to be taken into consideration. A very detailed description of the systematic frequency shifts for Ca^+ is presented in Chapter 5 and summarized in table 5.2. For the estimation of the error budget for the Al^+ we followed a similar approach to the one described for the Ca^+ . To avoid a repetitive description I will refer the reader in some sections to look at the previous chapter for more detail. The scatter of the frequency measurements shown in Fig. 6.7 suggests that an unexpected systematic shift might have been present when these measurements were taken. Even though it seems unlikely, the frequency shift of 40 Hz between the measurements taken with 100 μs (200 μs) Ramsey time could have been caused by an ac-Stark shift shifting the transition frequency during the $\pi/2$ -pulses. This effect would vanish in the limit of infinitely long Ramsey experiments and lead to a systematic shift of 85 Hz in the frequency measurement. As we cannot exclude the existence of such a shift, we added an uncertainty of 85 Hz to our error budget.

6.5.1 Quadrupole shift

Similar as for the Ca^+ the quadrupole shift, described in the Section 5.2.1, the shift for the Al^+ originates from a coupling of the electric quadrupole moment of the 3P_1 level with static electric field gradients in the trap. The dominant electric field gradient is caused by the quadrupolar static electric potential confining ions axially and by the electric field gradient of the co-trapped $^{40}\text{Ca}^+$ ion. These field gradients will shift the energy of the stretched $^3P_1, F = 7/2, m_F = \pm 7/2$ levels by:

$$\Delta E = \frac{1}{2\sqrt{30}} \langle nJ || Q_2 || nJ \rangle \frac{\partial^2 \Phi}{\partial z^2}. \quad (6.2)$$

Following the prescription of refs. [72, 134] for calculating the second derivative of the potential for a mixed ion crystal with 888 kHz axial in-phase oscillation frequency, one obtains a frequency shift of -7.4 Hz for the stretched Zeeman states ($\pm 7/2$) where we used the reduced matrix element $\langle nJ || Q_2 || nJ \rangle$ calculated in Ref. [72] for the estimation of the shift.

To estimate the quadrupole shift for the Ca^+ ion, we follow the procedure described in detail in Section 5.2.1. Using Equation 5.21 we estimate that the $m = 3/2$ Zeeman states are upshifted by 2.83 Hz.

6.5.2 Second order Zeeman shift

The fine-structure mixing effect of a non-zero magnetic field gives rise to a small second-order Zeeman shift of the $|^3\text{P}_1, F = 7/2, m_F = \pm 7/2\rangle$ states via a coupling to the $^3\text{P}_2$ states with the same magnetic quantum number. As it was described in detail in Section 3.1.2, using second order perturbation theory, the quadratic Zeeman shift, following [63, 146], can be approximated by:

$$\Delta E_{J,M}^{(2)Z} (^3\text{P}_1) = -\frac{1}{2} \zeta_{nLS} (B/B_{fs})^2 \quad (6.3)$$

where $B_{fs} \equiv \zeta_{nLS} J' / \mu'_B$ is the fine-structure crossover field, with $\mu'_B \equiv (g_s - g_J) \mu_B \cong \mu_B$, and $\zeta_{nLS} = 1.8591$ THz the coupling constant. For the $^3\text{P}_2$ - $^3\text{P}_1$ fine-structure splitting we have $L=1, S=1, J'=2$ and $B_{fs}=265.344 \times 10^4$ G. We calculate for the quadratic frequency shift of the $J=M=1$ level that $d^2\nu/dB^2 = -263.74$ mHz/G². For a magnetic field of approximately 4 G the systematic shift amounts to only -2.109(0.005) Hz. To estimate the second order Zeeman shift for the Ca^+ , we follow, in this case, the procedure described in Section 5.2.1. Using Equation 5.18 we estimate that a field of 4 G causes a frequency shift of the $\text{D}_{5/2, m=\pm 3/2}$ levels of 2.79 Hz.

6.5.3 Summary of systematic frequency shifts

The systematic frequency shifts discussed above are summarized in table 6.1. As it was described in Section 5 and summarized in table 5.2, other sources of frequency shifts such as black-body radiation, time-dilation shifts by excess micromotion or non-zero secular motion are expected to be no bigger than 1 Hz. Taking all the shifts into consideration leads to a correction of 24.5 Hz of the transition frequency and results in a measured transition frequency of $\nu_{\text{Al}} = 1122\,842\,857\,334\,736(93)$ Hz.

Effect	Ca shift (uncertainty) (Hz)	Al shift (uncertainty)(Hz)
$\text{S}_{1/2} \leftrightarrow \text{D}_{5/2}$ frequency	0 (4)	-
Electric quadrupole shift	2.7(0.1)	-7.4
2nd order Zeeman shift	2.8	-2.1
Ramsey probe time dependence	-	0 (85)
Statistics	-	0 (36)
Total shift	5.5 (4.0)	-9.5 (92)

Table 6.1: Systematic shifts and measurement uncertainties of the two transitions probed in Ca^+ and Al^+ For the determination of the inter-combination line frequency the systematic shifts of the calcium transition enter the error budget after having been multiplied by the frequency ratio $\nu_{\text{Al}}/\nu_{\text{Ca}}$.

Systematic frequency shifts also need to be considered for the determination of the $^3\text{P}_1$ state's g-factor. Electric quadrupole shifts and second-order Zeeman shifts do not affect the g-factor determination as they shift both stretched Zeeman states by the same amount. Ac-Zeeman and ac-Stark shifts, however, need to be considered. The ac-magnetic field generated by the ion trap drive at 32 MHz gives rise to a shift of the probed $|\text{S}_{1/2}, m = \pm 1/2\rangle \leftrightarrow |\text{D}_{5/2}, m = \pm 3/2\rangle$ Zeeman transitions in Ca^+ that mimics an additional dc-magnetic field of about 4 μG . For the dc-field of 4 G used in the experiment, this corresponds to a fractional error of 10^{-6} in the g-factor determination

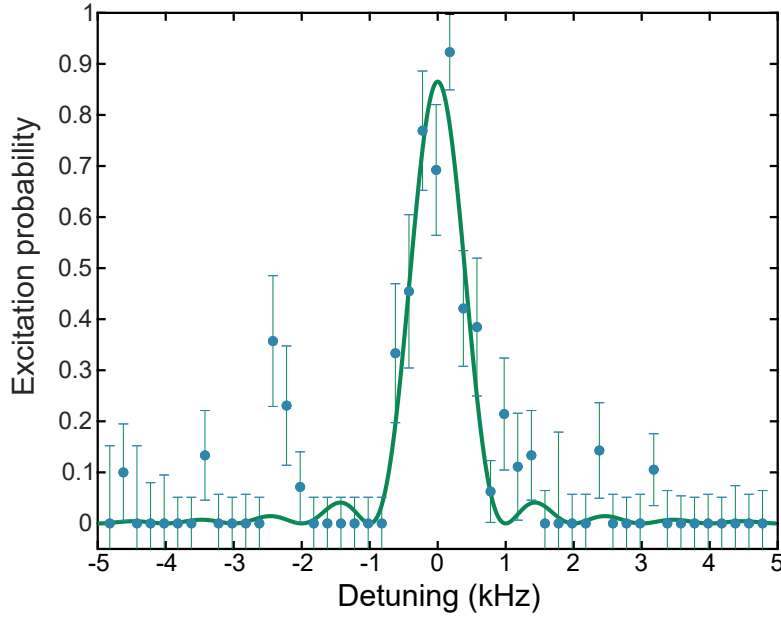


Figure 6.8: Excitation of the $|^1S_0, m_F = -5/2\rangle \leftrightarrow |^3P_0, m_{F'} = -3/2\rangle$ transition with a laser pulse of 1 ms duration. The excitation probability is inferred from measuring the probability of the ion to undergo a change of its electronic state from one experiment to the next. For probing the transition, the measurement protocol described in subsection 6.3 is modified by probing the clock transition instead of the intercombination line in step (IV) and repeating the quantum logic steps (V) and (VI) twice. In this way, errors arising from imperfect state mapping from Al^+ to Ca^+ are suppressed.

which is below our measurement uncertainty. In Al^+ , due to the smaller splitting of the Zeeman levels, the ac-magnetic field shift is even smaller. The static magnetic field gradient of $30 \mu\text{G}/\text{m}$ causes only a negligible magnetic field difference in the two ion locations and can thus be neglected. Ac-Stark shifts on the $^1S_0 \leftrightarrow ^3P_1$ transition that arise from off-resonant coupling to the axial out-of-phase sideband transitions or to $\Delta m = 0, \pm 1$ transitions induce fractional errors in the g-factor determination of well below 10^{-6} . Therefore, we conclude that systematic shifts do not alter the measured g-factor value of $g_{^3P_1, F'=7/2} = 0.428132(2)$.

6.6 Conclusion

We have successfully implemented sympathetic cooling and quantum logic spectroscopy to probe the $^{27}\text{Al}^+ \ ^1S_0 \leftrightarrow ^3P_1$ transition. We determine the intercombination line frequency to be equal to

$$1122842857334736(93) \text{ Hz},$$

and the Landé g-factor of the excited state to be

$$g_{^3P_1, F'=7/2} = 0.428132(2).$$

We have also probed the $^1S_0 \leftrightarrow ^3P_0$ clock transition. Figure 6.8 shows a spectrum of the $(m = -5/2) \leftrightarrow (m = -3/2)$ Zeeman transition with a probe-time limited

width of 1 kHz. Efforts to obtain spectrally narrower lines are hampered by two experimental shortcomings, namely frequency drifts of the frequency-quadrupled fibre laser probing the clock transition and creation of molecular ions by reaction of Al^+ with H_2 background gas molecules. Molecular ion creation limits the time for experiments probing the clock transition to about 15 minutes, which, in combination with long Al^+ reloading times [55], prevented us from investigating the clock transition more thoroughly. The following chapter is devoted to the development of experimental methods to further investigate the composition of the background gas in the chamber.

Chapter 7

Experimental characterization of trapped-ion kinetics due to background-gas collisions

"These motions were such as to satisfy me,
after frequently repeated observation,
that they arose neither from currents in the fluid,
nor from its gradual evaporation,
but belonged to the particle itself"
Robert Brown

Even if ultra-high vacuum conditions ($< 1 \times 10^{-10}$ mbar) are nowadays a given in many trapped-ion experiment, the interaction between remaining background-gas particles and the trapped ion plays an important role in day-to-day operations. As explained in the paper by Wineland et al. [42], "the effects of collisions can be separated in two classes: inelastic collisions that alter the internal state of the ion or even result in chemical reactions, and elastic collisions, which alter the kinetic energy of the ion". Depending on the kind of experiments carried out, the collision event, might not have at first sight any visible or noticeable effect on the measurement, but in many cases it might prompt the repetition of the data point or even the necessity to reload the ion(s). Experiments with strings of 51 ions report "melting" events, collisions that transfer enough energy to disrupt the ion string configuration, approximately every 30 s [147]. In the previous chapter, we reported the formation of molecular ions by reaction of Al^+ with background H_2 molecules during experiments probing the clock transition at a rate of 1 event every 15 minutes. Background gas collisions affect the frequency of atomic clocks due to two main effects [148]: The first one is due to the fact that the energy imparted during the collision event affects the motional state distribution, which consequently has an effect on the time-dilation also known as second order Doppler shift (see section 3.3.1). The second one is due to the fact that interactions during the collision can lead to changes in the phase of the atomic superposition. For the case of trapped-ion clock experiments, collisions are a source of systematic frequency shifts and linewidth broadening. Lattice and trapped-ion clocks reaching fractional uncertainties at the low 10^{-18} level [23, 16, 18, 17] report contributions due to background collisions at the mid 10^{-19} level.

In order to properly estimate this frequency shift and uncertainty it is necessary to calculate the motional-state distribution of trapped ions that have experienced background gas collisions in an ultra-high vacuum environment as described in [148]. The paper presents a model to calculate the differential background collision rate for collisions ($\frac{d\Gamma}{dE_{\text{ion}}}(E_{\text{ion}})$) that impart E_{ion} kinetic energy onto the ion in the laboratory frame. The method in the paper is experimentally validated through the determination of

the background-gas pressure *in-situ* using measurements of the rate of collisions that causes reordering of the mixed-species ion pairs, following a similar approach than the one introduced in [149]. This experimental method is, however, limited to a range of energies that goes from 0.1 K to 10 K. Following the notation used in the paper energies throughout this chapter are given in temperature units (K).

In this chapter, in Section 7.2, I present the results obtained from the application of this method to our experimental setup and additionally I introduce two other methods that facilitate the determination of the differential background collision rate for more energy ranges: One, in Section 7.1, implementing composite pulses to detect collisions on the energy range that goes from 10^{-3} K to 10^{-1} K. And a second technique, in Section 7.3 that measures the energy of the collisions in the range from 10^1 K to 10^4 K through characterization of the re-cooling dynamics of a single calcium ion after a collision. Then in Section 7.4 the collision rates from each method are put together and compared with a numerical simulation that models classically the interaction of the trapped ion with the background gas. Probing the differential collision rate for a broad range of energies might open the door to a deeper understanding of the background gas composition and its effect on trapped ion experiments.

7.1 Composite pulse technique (10^{-3} K to 10^{-1} K)

7.1.1 Experimental pre-requisites

The goal of this technique is to detect collisions that transfer very little energy (10^{-3} – 10^{-2} K) to a trapped ion by implementing a coherent pulse sequence. According to [148], the expected differential rate of collisions between $^{27}\text{Al}^+$ at rest and 5×10^{-10} mbar of H_2 background gas at 295 K that result in a final ion kinetic energy E_{ion} of 10 mK is about $1.5 \text{ s}^{-1}\text{K}^{-1}$ and of $0.1 \text{ s}^{-1}\text{K}^{-1}$ for a final energy of 100 mK. Putting it in other terms, this translate to a collision rate of 0.015 s^{-1} at 10 mK with a range of $\Delta E = 10$ mK and 0.01 s^{-1} at 100 mK with a range of $\Delta E = 100$ mK. The challenge consists in developing a technique that allows the detection of such collision events that might occur every 5 to 10 minutes without being drowned out by a background of false positives.

A more intuitive way to understand these energy ranges is by translating them in terms of vibrational mode energies. For an ion oscillating at a frequency $\nu = 1$ MHz, an energy of 10 mK corresponds to a vibrational quantum number of about 200 and an energy of 100 mK corresponds to 2000. With these values in mind, the considered energy range of 10-100 mK is substantially higher than the mean phonon number $\bar{n}$ obtained for laser cooled ions. And, the tail of the thermal distribution for a laser-cooled ion with phonon numbers above 200 or 2000 is very small. For a Doppler-cooled ion with $\bar{n} = 15$ the probability of finding phonon numbers above 200 is $e^{-n/\bar{n}} \approx 10^{-6}$. This means, that nearly 1 million experiments could be carried out before getting a false positive due to insufficient cooling. However, it is important to consider that the assumption that the phonon number distribution after laser cooling is really thermal up to very high quantum numbers, may not be justified [150]. A nonthermal distribution can result from perturbations due to micromotion, from zero crossings in the cooling transition Rabi rate as a function of the Fock state or from cooling durations insufficient to reach equilibrium. This effect should be considered and probed by a technique that detects high phonon numbers and that is used for experiments with probe pulses that are applied directly after laser cooling or after a fairly long waiting time. The detection of such non-thermal tails after laser cooling is also relevant for

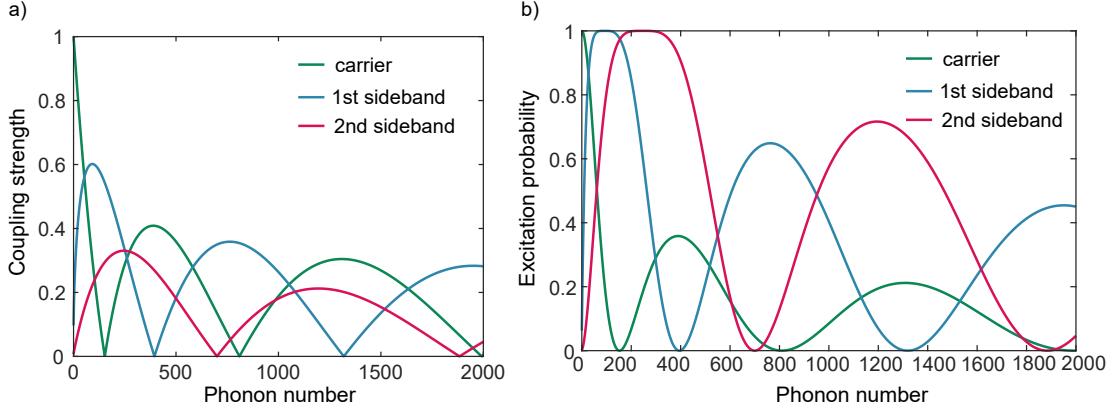


Figure 7.1: Coupling strength and excitation probability of carrier and sidebands as a function of phonon number. a) The figure shows the relative coupling strength as a function of the phonon number, using Equation 7.1 for a calcium ion oscillating at 1 MHz and a laser beam (729 nm) parallel to the motional mode. For the first sideband there are three maxima in the plotted phonon range. For the second one there are two. b) By choosing the right pulse duration a maximum excitation probability can be induced on the sidebands. The excitation probability as a function of the Fock state is plotted. However, using this technique, for both sidebands we observe two maxima in the plotted phonon range.

clock experiments since they are sensitive to relativistic frequency shifts induced by the ion motion.

7.1.2 Detecting high phonon numbers using sideband pulses

As it was described in Section 2.3, sidebands can be used as mediators between the internal and external degree of freedom of the ion. In Section 5.2.2 they are used as a way to determine the mean phonon number in the system and in Section 2.4.3 they are used to transfer information between ions. In this section, the idea is to use them as a way to detect collisions that transfer energies in the range from 10 to 500 phonon numbers. In Section 2.3, the coupling strength of the sidebands as a function of the mean phonon number was estimated in the Lamb-Dicke regime, where $\eta^2(2\bar{n} + 1) \ll 1$. To obtain the coupling strength for higher phonon numbers, we followed the development described in [50], where the coupling strength of a sideband as a function of the mean phonon number is calculated using:

$$\Omega_{n+m,n} = \Omega \langle n+m | e^{i\eta(\hat{a} + \hat{a}^\dagger)} | n \rangle = e^{-\frac{\eta^2}{2}} \eta^{|m|} L_n^{|m|}(\eta^2) \left(\frac{\eta!}{(n+m)!} \right)^{\text{sign}(m)/2}, \quad (7.1)$$

where m is the sideband number and

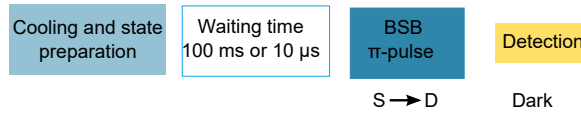
$$\mathcal{L}_n^\alpha(x) = \sum_{k=0}^n (-1)^k \binom{n+\alpha}{n-k} \frac{x^k}{k!} \quad (7.2)$$

corresponds to the associated Laguerre polynomial. Figure 7.1(a) shows the relative coupling strength as a function of the phonon number, using Equation 7.1 for a calcium ion oscillating at 1 MHz and a laser beam (729 nm) parallel to the motional mode. For the first and second sideband a maximum is observed at approximately 90 and 250

phonons, respectively. The position of the maxima can be easily changed by increasing the trap frequency, changing the direction of the beam or by working with more than a single ion. As observed in Figure 7.1 b) close to the maximum, the sideband pulse acts similar to a carrier pulse, in that, by choosing the right pulse duration, a π -pulse can be induced over a fairly wide range of phonon numbers.

As described in Figure 7.2a) a first approximation of the probing scheme consists of the following steps: The ion is first Doppler-cooled and ground-state cooled. Then the ion is prepared in the S state. The sequence is then followed by a waiting time. Next, we apply a pulse on the sideband which enacts a π -pulse if the ion is in the desired phonon range, and finally fluorescence detection is carried out. The idea is that any collision that would impart an amount of phonons in the pre-selected range would be detected through the dependence of the $S \rightarrow D$ transfer probability on the phonon number.

a) Single detection scheme with one single blue side band pulse



b) Triple detection scheme using composite pulses (narrow band)



Figure 7.2: Detection schemes to detect high phonon numbers collisions. Both sequences start by cooling and preparing the ion in the S state followed by a variable waiting time, during which collisions can occur. a) The wait time is followed by a blue sideband pulse with a transfer probability that depends on the energy transferred during the collision. b) For the triple detection, if a collision events in the selected energy range occur, the first 5 composite pulses on the blue side band transfer the population from S to D and a "dark" event is detected. The second set of 3 composite carrier pulses is applied to depump any false positive due to heating rate, a positive event would be detected as "dark" and a false one as "bright". Finally a third set of composite pulses on the blue side band would transfer the population back to the S state.

However, care needs to be taken to avoid false positives. As the probability for a collision in the right energy range is very small, and because it is challenging to achieve near-unity transfer probability on a sideband transition, it is quite easy for false positives to dominate the detected signal. The challenge consists in reducing the number of false positive events, while still maintaining a signal. To approach this problem three different approaches can be implemented:

- Events where an ion in the S-state is falsely classified as being in D are mitigated using long detection times to clearly separate the fluorescence distribution. However, this reduces the sensitivity of detecting a collision, which is not as problematic as getting false events. Great care needs to be taken also to minimize the stray light signal hitting the PMT to assure a narrow photon count distribution in the D-state.
- False positive events that occur at other phonon numbers can be reduced by implementing a double pulse probe and detection scheme: instead of pumping

out the D-state with 854 nm and starting the next experiment, another sideband π -pulse is applied to transfer the ion back followed by another detection. If the phonon number is in the right range, then the second pulse should efficiently transfer the ion back to S. An event would be classified as a collision only if we get a "dark" followed by a "bright" detection event.

- In addition both of these issues could also be mitigated by using two ions and implementing a scheme where only events where both ions are transferred to the D-state are considered as collisions.

However, one problem still remains with the proposed scheme: As shown in Figure 7.1 a), the coupling strength on the sideband has multiple maxima. For the first sideband, a first maximum is observed where the coupling strength is weaker by about 0.6 as compared to the maximum carrier strength, but a second maximum is also observed where the coupling strength is about 0.35 times weaker than the carrier strength. Therefore there is no single phonon number range where the transfer to the D-state is efficient but multiple such ranges. As can be seen in Figure 7.1 b), where the excitation probability is plotted as a function of the phonon number, even if the π -pulse was only set to detect collisions within a phonon range on the order of the first maximum, there would still be a probability of about 40% for a successful double detection event for phonon numbers around this second maximum. For this reason the scheme needs to be improved to make the π -pulse more selective to a specific phonon range. To solve this problem we integrated composite π -pulses into our scheme, which are described in the following section.

7.1.3 Composite π pulses

The paper by Torosov et al. [151] describes the implementation of a technique that consists in concatenating multiple π -pulses with different laser phases. The laser phase defines the orientation of the rotation axis within the equatorial plane of the Bloch sphere (see Section 2.2.1). Choosing a specific combination of laser phases generates either a broad or narrow-band π -pulses. As presented in the paper, this technique is commonly implemented in nuclear magnetic resonance and has recently been also applied to quantum information. The phases of the so called *composite pulses* or CP are implemented in a way that they can be used as a control parameter to correct for errors that emerge during the interaction between a single pulse and a qubit or to define the shape of the excitation profile.

The paper describes the numerical procedure to calculate the composite phases to create either a broad and a narrow excitation profile. For our purposes we are interested in the generation of a narrow excitation profile. A sequence of five π -pulses with the appropriate phases is shown to substantially narrow the range of coupling strengths over which the pulse achieves a state transfer with high probability. The idea is to swap our sideband π -pulse against such a series of π -pulses in such a way that the state transfer probability is high only in a fairly narrow window around the first maximum of the coupling strength.

Figure 7.3 shows the case of such a composite pulse on the first sideband with a pulse length set to achieve an optimum transfer at the maximum coupling strength and choosing the phases calculated in [151] (phases = $(\{0, 0.238, 1.580, 0.923, 1.161\}) \times \pi$). As can be seen from the simulation data in the Figure 7.3 a), the transfer probability for the composite narrow π -pulse is high in a phonon-number window close to the one obtained with the standard single-detection technique and drops below 0.01 everywhere else. As shown in Figure 7.3 b) if the triple-detection is also implemented

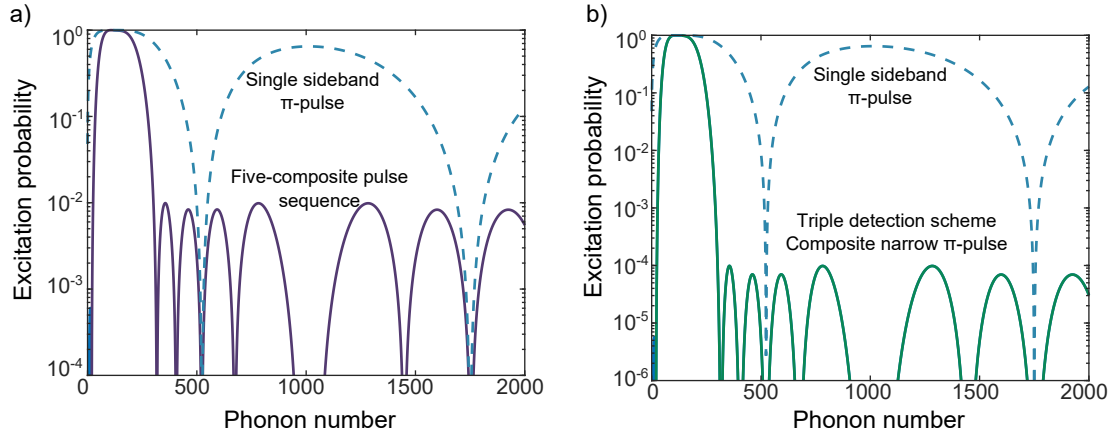


Figure 7.3: Excitation probability for composite pulse sequences on sideband transitions. a) Theoretical calculation of the excitation probability for a set of 5 pulses with the pulse length set to achieve an optimum transfer at the maximum coupling strength with the respective phases set following [151] (Purple solid line). b) Theoretical calculation of the excitation probability using the triple detection scheme illustrated in Figure 7.2 b) (green solid line). As a reference in both plots the excitation probability for a standard π -pulse is also plotted (dashed blue line).

the suppression drops to about 10^{-4} . With this technique we could achieve our goal: To detect energies only in a limited range. Collisions at higher energies that might heat the ion resulting in a reduced fluorescence level could lead to false positive detection. To deal with these collisions, another detection period after re-pumping is added, a low fluorescence count during this detection period would flag problematic collisions. To reduce any possible false positive due to the intrinsic heating rate (on the order of 20 phonons per second) a triple detection scheme is implemented: A three-component carrier pulse is added between the pair of five-component sideband pulses. The sequence is illustrated in Figure 7.2 b), the sequence starts by Doppler and ground state cooling the ion, followed by a waiting time, during which we wait for collision events. Then 3 sets of composite pulses followed by detection pulse are applied. If a collision in the selected energy range occurs, the first 5 composite pulses on the blue side band transfer the population from S to D and a "dark" event is detected. The second set of 3 composite carrier pulses is applied to depump any false positive due to heating rate, a positive event would be detected as "dark" and a false one as "bright". Finally a third set of composite pulses on the blue side band would transfer the population back to the S state. Any collision that would transfer energy in the select range has to be: "dark", "dark" and "bright". The waiting times alternate between short ($10 \mu\text{s}$) and long (100 ms) to ensure the detection of false positives due to insufficient cooling that might be explained by the non-thermal tails after laser cooling.

7.1.4 Probing the composite pulse technique by "tickling" the ion

To probe that the technique is useful to detect only the collisions that transfer energy in the desired narrow range, we implemented the "tickling" method. This technique was also used in Chapter 6.1 as a way to confirm the composition of a two-ion crystal: A weak electric field with a tunable frequency is applied to the "tickle-electrode" (see Section 4.1) to excite one of the motional modes of the ion. By controlling the pulse duration and intensity of the "tickle-voltage" and using a frequency slightly detuned

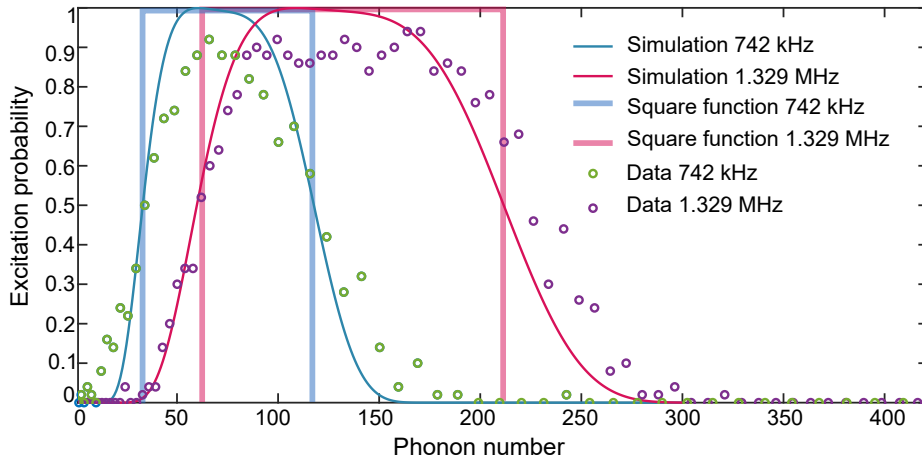


Figure 7.4: Probing the composite pulse technique by "tickling the ion. The waiting time in the sequence, illustrated in Figure 7.2, is replaced by a "tickle" pulse where the ion is coherently excited. By scanning the pulse length of the "tickle voltage" using a slightly detuned frequency (≈ 600 Hz) the mean phonon number is "scanned". The excitation probability using the triple detection scheme is measured as a function of the mean phonon number. The measured data for two different axial confinements (green circles for 742 kHz and purple for 1.329 MHz) matches closely the predicted theoretical calculations (blue and pink solid lines). The square functions illustrated by shaded blue and pink lines define the energy range such that the area below the curves matches the area below the filter function.

(≈ 600 Hz) from the resonance with the motional mode, the ion can be coherently excited. To probe the technique we replace the "waiting time" in the sequence, illustrated in Figure 7.2, by a tickling pulse that transfers a controlled phonon number to the ion. The pulse length of the tickle voltage is scanned and thus the phonon number is varied and the measured excitation probability is compared to the predicted values. As was previously mentioned, to access different energy ranges the axial confinement is modified by changing the voltage of the end-cap electrodes (see 4.1). As illustrated in Figure 7.4, the technique is successfully implemented to detect two distinct energy ranges, using an axial frequency of 742 kHz and 1.329 MHz. The measured excitation probability as a function of the mean phonon number for both energy ranges is in close agreement with the theoretical estimations. As can be seen in the figure, only energies in the defined energy ranges are detected as "positive" events by the triple detection method: between 35 and 119 phonons for the 742 kHz axial confinement and between 63 and 213 phonons for the one at 1.329 MHz. As can be seen in the figure, the excitation of the measured data points does not reach the maximum value, this effect can be explained on one side by decoherence processes (electric or magnetic field noise) during the 13 pulses, or it can also be explained by imperfections on the coherent excitation of the ion by means of the "tickle-voltage". However, these effects do not hinder the distinction between events inside and outside the energy range, confirming that the triple-composite pulse method is suitable to detect collisions that would transfer energies between 10^{-3} K to 10^{-2} K to the ion.

7.1.5 Composite pulses: Measurements

To perform the measurements we implemented the scheme illustrated in Figure 7.2 b) with a single $^{40}\text{Ca}^+$ ion using two different axial confinements (742 kHz and 1.329 MHz). The composite pulses are applied on the $S_{1/2} \leftrightarrow D_{5/2}$ transition (see Section 3.1) using a 729 nm laser beam parallel to the quantization axis (see Figure 4.2), so that the beam has only a projection onto the axial mode. A dataset for each axial confinement was taken at the typical background pressure of about 10^{-10} mbar (see Section 7.2) for a measurement time of approximately 10^4 s. A third data set was taken with a single axial confinement of 1.329 MHz at a pressure of about 10^{-9} mbar. To increase the pressure in the chamber we fired the non-evaporative getters (NEGs) while constantly monitoring the pressure gauge (see Section 4.2). The duration of the third data set is limited by the time that the chamber can be maintained at the higher pressure (approximately 1200 s). To identify false-positive events, caused not by collisions but by non-thermal effects, sequences with two different waiting times (10 μs and 100 ms) are interleaved. Given the estimated rates presented in Section 7.1, the probability of having more than 1 collision event in 100 ms is quite low. The number of false-positive events is estimated from the sequences with a 10 μs waiting time. To estimate the number of collision-events, we subtract the number of "false"-positive events from the number of detected-events during the 100 ms waiting time. We obtain a distribution of the collision rate for sets of 15 points, consisting each of 50 cycles, from which we extract the mean collision rate and the corresponding standard deviation. To estimate the energy range we determine a square function, illustrated in Figure 7.4, with an amplitude or energy range defined such that the area below the curve matches the area of the filter function. The results of the three measurement sets are plotted in Figure 7.14. The rate of low energy collisions is expected to increase linearly with the variation of the background gas pressure [148], the measurements plotted in the figure appear to be consistent with this trend.

The differential collision rate for a given energy range is obtained by dividing the collision rate by the energy range. To confirm that our measurements are consistent with theoretical predictions we compare our results with the model described by Hankin et al.[148]. In the Figure 1 of the paper the differential collision rate as a function of the energy transferred to the ion is calculated for a pressure approximately 5 times higher than ours. The calculations in the paper are done at a gas pressure of 5.47×10^{-10} mbar while in Section 7.2.2 we estimate that the gas pressure in our chamber is approximately 1×10^{-10} mba. Assuming that the pressure scales linearly, their model predicts that for our background pressure at a range of energies between 10^{-3} and 10^{-2} the differential collision rate spans between $0.2 \text{ s}^{-1}\text{K}^{-1}$ and $2 \text{ s}^{-1}\text{K}^{-1}$. Our measurements are consistent with these predictions: For a pressure of $(1.4 \pm 0.2) \times 10^{-10}$ mbar (see Section 7.5) we measured a differential collision rate of $0.740 \text{ s}^{-1}\text{K}^{-1}$ for an energy of 2.7 mK and $0.159 \text{ s}^{-1}\text{K}^{-1}$ for an energy of 8.8 mK.

If we now look at the false-positive events, linked to non-thermal effects: for an energy of 2.7 mK there is a rate of 0.0017 per second, for an energy of 8.8 mK a rate of 0.00054 per second. In both cases the percentage of false-positive events is equivalent to approximately 0.3 % of the total number of positive events. This can be explained by the fact that the filter for energies in the range of 2.7 mK is more sensitive to low energies fluctuations and consequently is more susceptible than the one set in the higher range. A possible way to fully characterize the thermal tail could be by measuring the probability to detect these "false"-positive events as a function of the energy range of the filter.

7.2 Swapping rate technique (10^{-1} K to 10^1 K)

7.2.1 Kinematics model

We have implemented the technique described in the reference [148]: Through the measurement of the rate of collisions that cause the reordering of a two-ion-mixed-species crystal we infer the pressure of the background gas at the position of the ions. This pressure can be considerably different from the one measured at the position of the pressure gauge and in most cases below the range which the pressure gauge can measure. As described in the reference [148], the reorder rate is estimated by integrating the collision rate with the reorder probability and summing over the two ions:

$$\Gamma_{\text{reorder}} = \sum_{i=1}^2 \int_0^{\infty} P_{i,\text{reorder}}(E_{\text{ion}}) \frac{d\Gamma_i}{dE_{\text{ion}}}(E_{\text{ion}}) dE_{\text{ion}}, \quad (7.3)$$

where $P_{i,\text{reorder}}(E_{\text{ion}})$ corresponds to the reorder probability and $\frac{d\Gamma_i}{dE_{\text{ion}}}(E_{\text{ion}})$ to the differential collision rate for an ion i . To estimate the reorder probability we use a simplified expression that assumes that the probability that the ions swap position is 0.5 for any collision whose final energy is bigger than a threshold corresponding to the reorder energy, or written in more mathematical terms:

$$P_{i,\text{reorder}}(E_{\text{ion}}) = 0.5 \text{ for } E_{\text{ion}} > E_{\text{reorder}}. \quad (7.4)$$

The reorder energy E_{reorder} corresponds to the the potential-energy barrier between a ground-state axial configuration and a two ion radial crystal. This energy depends on the trapping conditions and can be estimated using the following formula [148]:

$$E_{\text{reorder}} = \frac{3}{4} \left(\frac{\sqrt{m}\omega_z Q^2}{2\pi\epsilon_0} \right)^{2/3} \left[\left(\frac{2(\epsilon^2 + \alpha - 1)(\epsilon^2 + \mu(\alpha - 1))}{\epsilon^2(\mu + 1) + 2\mu(\alpha - 1)} \right)^{1/3} - 1 \right], \quad (7.5)$$

where we follow the same notation as the one used in Section 2.1.1 to describe the motion of the ion in the trap. As a reminder, $\epsilon = \omega_p/\omega_z$, $\mu = m_2/m_1$ corresponds to the ratio of the two masses and ω_z to the axial axial secular frequency of a single ion of mass m_1 . We can see that the closer the axial frequency is to the radial one the lower the energy barrier is and the easier is for the ions to swap positions. By changing the voltage applied to the endcaps (see Section 2.1.1) the axial frequency of the ion ω_z can be easily modified allowing us to control the magnitude of the energy barrier E_{reorder} . Using the simplified expression described in Equation 7.4 we can calculate the swapping rate as a function of the energy barrier using the empirical expression, found in Ref. [148]:

$$\Gamma_{\text{reorder}} \lesssim \frac{1}{2} \left(\frac{p}{902 \text{ nPa s}} \right) \left(\frac{E_{\text{reorder}}}{1 \text{ K} \times k_B} \right)^{-0.278}, \quad (7.6)$$

for $^{40}\text{Ca}^+ - ^{27}\text{Al}^+$ in 296 K H_2 background gas pressure p . In simple terms, the measurement technique consists in measuring the rate at which the calcium and aluminum ions swap position as a function of the voltage applied to the endcaps. To obtain the pressure we fit the data using Equation 7.6. This data gives also an estimate of the collision rate at the corresponding reorder energy range allowed by the experimental parameters (0.1-10) K.

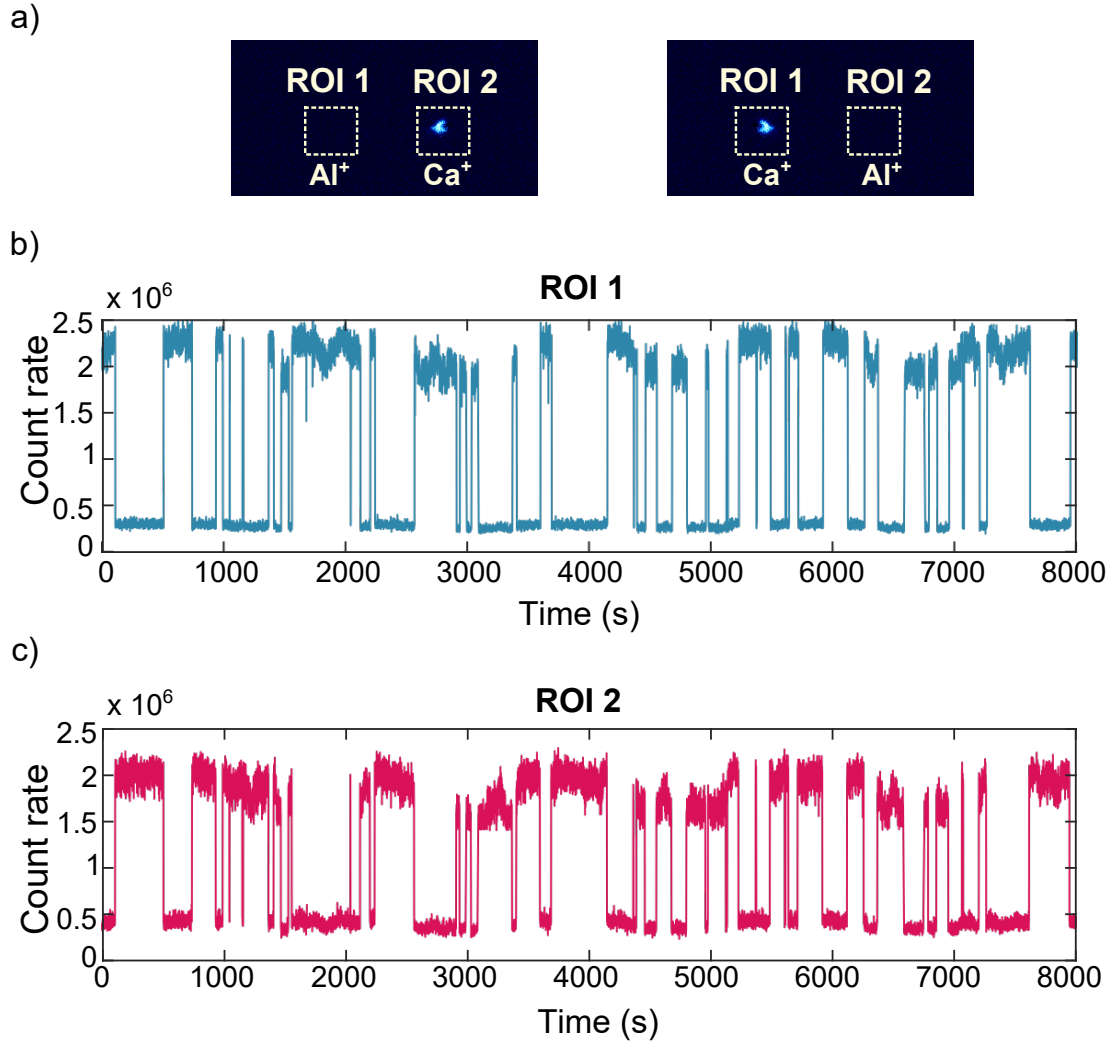


Figure 7.5: Ion reordering events detection. a) Two regions of interest (ROI 1 and ROI 2) are defined with the camera software, corresponding to the position of each ion. When the calcium ion swaps from one region to the other the number of pixels in the first region decreases, and increases in the second. b) and c) The pixel counts in each region are measured as function of time. The swapping events are clearly detected as jumps of the pixel counts.

7.2.2 Swapping rate measurement

We measure the reordering rate of a two-ion Ca^+/Al^+ crystal for four different energy barrier E_{reorder} values obtained by modifying the voltage applied to the end-caps (see Section 4.1). The crystal is loaded and cooled following the same procedure described in Section 6.1. As a reminder to the reader (see Section 3.4), the aluminum ion does not have an accessible detection and cooling transition, so only the Ca^+ ion can be detected by the camera (see Section 4.5.2). As it is shown in Figure 7.5, the fact that only one ion is visible facilitates the detection of reordering events: It is only necessary to track the position of the fluorescing calcium ion to detect any change of position of the two ions. Two regions of interest are defined with the camera software, using the video mode (see Section 4.5.2) the count rate is detected as a function of time. As illustrated in Figure 7.5 the swapping events can be easily detected by a clear anti-correlation between the counts in Figure 7.5(b) and (c). Keeping the ions

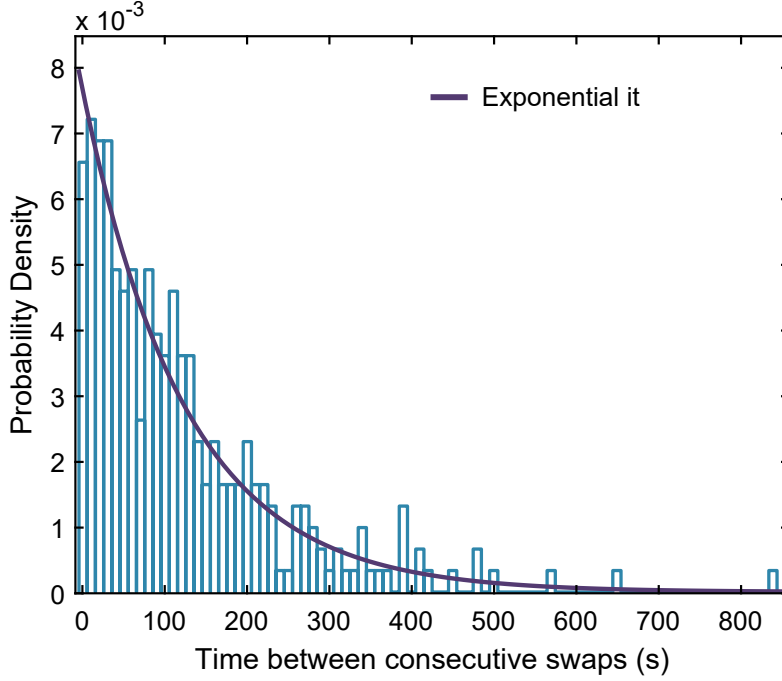


Figure 7.6: Probability distribution of time between consecutive swapping events: obtained from the analysis of the measurements described in Figure 7.5. An exponential fit is performed (purple solid line) from which the average rate is extracted.

Doppler-cooled in the trap, we continuously measure the fluorescence on both regions of interests for a time duration between 3 and 4 hours. From this measurements, we extract the time between consecutive swaps, and get the probability distribution, illustrated in Figure 7.6. From these measurements the average reorder rate is extracted as a function of the different trapping configurations. The measurements are repeated for 4 different axial trap confinements corresponding to 4 energy barriers $E_{reorder}$. The results are plotted in Figure 7.7. Considering the simplified model described in the previous Section 7.2.1, using Equation 7.6, the data follows the predicted reordering rate as a function of the energy barrier for a 295 K H_2 gas background pressure of $(1.4 \pm 0.2) \times 10^{-10}$ mbar (blue solid line and green shaded area).

7.3 Recooling time (10^1 K to 10^4 K)

The technique is based on the implementation of Doppler cooling thermometry to estimate the ion's energy through the determination of the recooling fluorescence dynamics after collisions with the background gas. As described in [152, 153], this technique takes advantage on the relation between the ion's kinetic energy and the fluorescence rate due to the Doppler effect. During Doppler cooling, a red detuned, linearly polarized laser is set to interact with the "cooling" transition of the ion (see Section 3). When the laser is red detuned by $\Gamma/2$, as the ion scatters photons its energy decreases and consequently its fluorescence rate increases. This process continues until the Doppler cooling limit ($T_D = \hbar\Gamma/2k_B$) [54] is reached. At this point the ion is cooled to an energy where Doppler shifts are too small to generate any observable variation of the

¹Here Γ is the linewidth of the cooling transition. The Doppler cooling limit is achieved when the cooling laser is red-detuned by $\Gamma/2$ from the resonance, and the laser intensity is much below the transition's saturation limit.

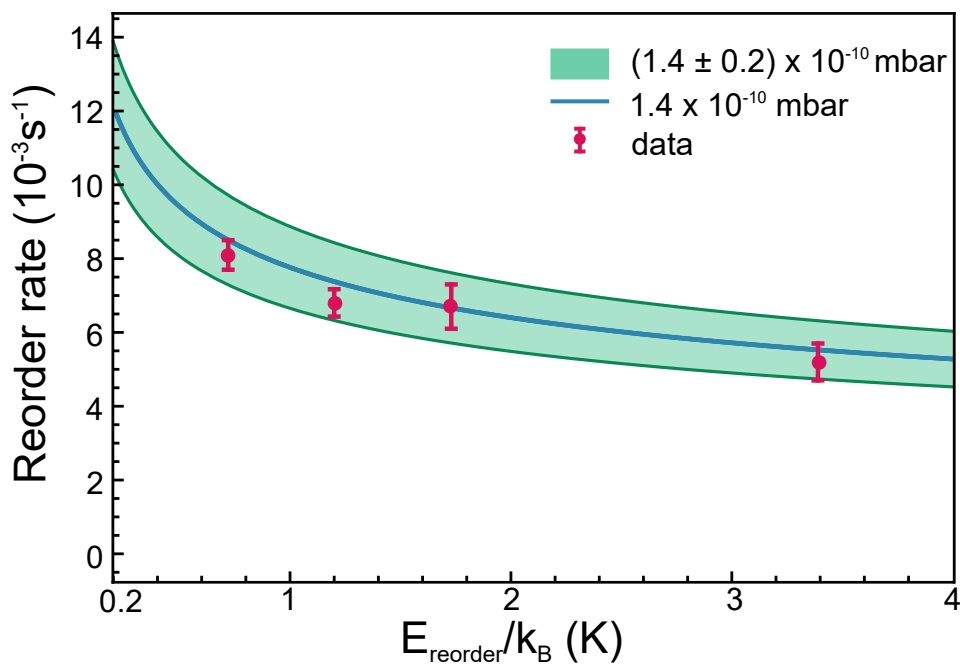


Figure 7.7: Reorder rate as function of the energy barrier. The re-ordering rate measurements are repeated for 4 different energy barriers (pink points). Equation 7.6. The data follows the predicted reordering rate as a function of the energy barrier for a 295 K H_2 gas background pressure of $(1.4 \pm 0.2) \times 10^{-10} \text{ mbar}$. The solid blue line corresponds to the theoretical model for a H_2 pressure of $1.4 \times 10^{-10} \text{ mbar}$. The green solid lines and shaded green area correspond to the model applied to pressures of $(1.4 \pm 0.2) \times 10^{-10} \text{ mbar}$

fluorescence rate. Consequently, Doppler cooling thermometry is only useful to detect energy variations above the Doppler cooling limit. When a collision event transfers an energy above the Doppler cooling limit to the ion, a decay of the fluorescence is observed, once the ion is Doppler cooled again, a recovery of the fluorescence is detected. The energy of the ion after the collision is determined by monitoring the fluorescence recovery time during Doppler cooling.

7.3.1 Doppler thermometry of a quasi-two level system

To model the fluorescence recovery dynamics of the ion after a collision that transfers an energy bigger than the Doppler cooling limit we simulate the dynamics of a laser-cooled ion in a linear RF trap. For modeling laser cooling our program combines single-ion dynamics in an RF-trap with atom light interaction of a two-level system. A quantum trajectory approach is used for simulating the coherent excitation of the ion by a laser in the presence of spontaneous decay. The velocity of the ion with respect to the laser beam's wavevector enters as a velocity-dependent detuning of the laser from the transition. The motion of the ion in the trap is calculated using a Forest-Ruth (symplectic) integrator that provides accurate trajectories when using 1 ns time steps. The technique can be implemented to detect collisions resulting in ion's final kinetic energy E_{ion} on the order between 10^1 K to 10^4 K.

Our usual Doppler cooling scheme is based on the $S_{1/2} \leftrightarrow P_{1/2}$ cooling transition at 397 nm. Since there is a 5 % probability that the ion decays from the $P_{1/2}$ to the $D_{3/2}$ level we apply an infra-red laser at 866 nm to the $D_{3/2} \leftrightarrow P_{1/2}$ transition to repump the ion. As can be seen in Figure 7.8 a), this scheme actually involves multiple levels in a Λ structure. The application of a two-level model to such a scheme neglects dark resonances which might lead to errors in the energy estimation [152]. To solve this problem we modified our Doppler cooling scheme. We implemented the scheme described in [154], where the ion is repumped via the $P_{3/2}$ level using a laser at 850 nm. This state decays quickly to the ground state by emitting a photon at 393 nm. Since there is also a 5% probability of decay into the $D_{3/2}$ level we repump back to the $P_{3/2}$ using a laser at 854 nm. The detunings and intensities of the infra-red lasers are set to maximize the fluorescence detected. The intensity of the 854 nm laser is set to be low enough with respect to the 850 nm laser intensity to avoid dark resonant population trapping in the $D_{3/2}$ and $D_{5/2}$ levels. This technique was originally developed to increase the emitted 397 nm light, by approximately 70%, without increasing the background noise. For our purposes, this repumping scheme transforms our multi-level system into a quasi-two level system, in which no coherent population trapping occurs, as illustrated in Figure 7.8 b).

7.3.2 Experimental verification of the model: "Kicking" the ion

To experimentally validate the application of our model we use the "tickling" method. As described in the previous sections of this chapter, the method consist in a weak electric field applied to excite one of the motional modes of the ion. In this case however, we follow a similar approach to the one described in [152]: A fixed "tickle-voltage" pulse that gives a controlled "kick" to the ion is applied, followed by cooling and repump laser pulses. During the cooling time, the fluorescence is detected by a CCD camera (see Figure 7.9) or by a PMT detector (see Figure 7.10) as a function of time. By looking at the camera images, see Figure 7.9, the energy transferred to the ion with

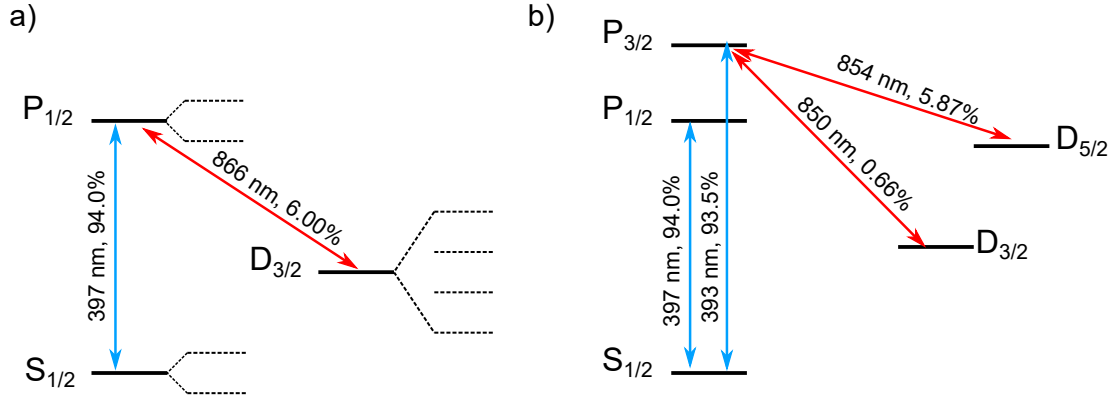


Figure 7.8: Doppler cooling schemes. A laser on the main cooling transition at 397 nm is applied in both schemes. a) Our usual Doppler cooling scheme involves multiple levels in a λ structure through the application of an 866 nm laser as repumper. b) A Doppler scheme involving a quasi 2 level system can be achieved using a laser at 850 nm as a repumper via the $P_{3/2}$ level and a laser at 854 nm to repump any decay into the $D_{3/2}$.

the tickle pulse is estimated using

$$E = \frac{1}{2} m \omega^2 A^2, \quad (7.7)$$

where ω corresponds to the frequency of the axial mode and A to the amplitude of oscillation of the ion extracted from the intensity profile.

The cooling dynamics are estimated from the fluorescence measurements. The fluorescence dynamics of the ion depend on the detuning and coupling strength of the cooling laser at 397 nm. To estimate both experimental values, we scan the 397 nm laser detuning Δ , measure the fluorescence rate $\rho(S_{1/2} \leftrightarrow P_{1/2})$ and fit the steady-state solution of the optical Bloch equation for a two level system as a function of the coupling rate Ω following

$$\rho(S_{1/2} \leftrightarrow P_{1/2}) = \left(\frac{\Omega^2}{2\Omega^2 + \Gamma^2 + 4\Delta^2} \right) \Gamma \alpha_{eff}, \quad (7.8)$$

where Γ is the spontaneous decay rate and α_{eff} the [PMT](#) detection efficiency. In [Figure 7.10](#) we can see how the experimental data follows the values predicted by the simulation. As more photons are scattered by the ion, its energy decreases approaching the Doppler cooling limit and increasing its fluorescence rate. At the point where the ion is cooled to an energy where Doppler shifts are too small to induce an appreciable change to the scattering rate, Doppler cooling thermometry loses its sensitivity. The simulation terminates when the ion is cooled below that threshold. To further corroborate our model, we repeated the experiment using a fixed energy "kick" of about 61 K, and measured the recoiling time as a function of the detuning of the 397 nm laser for three different coupling strengths of the laser. As it is shown in [Figure 7.11](#), the experimental data is in agreement with the results obtained using the model for different laser parameters. These measurements give on one hand, validation to our model and on the other hand, allow us to estimate the ideal parameters for the cooling laser to detect collisions that would transfer an energy between 10 K and 10^4 K to the ion. As it can be seen in the figure, the closer the laser is to resonance the longer is the recoiling time, hence the more sensitive the method is to low-energy collisions. However,

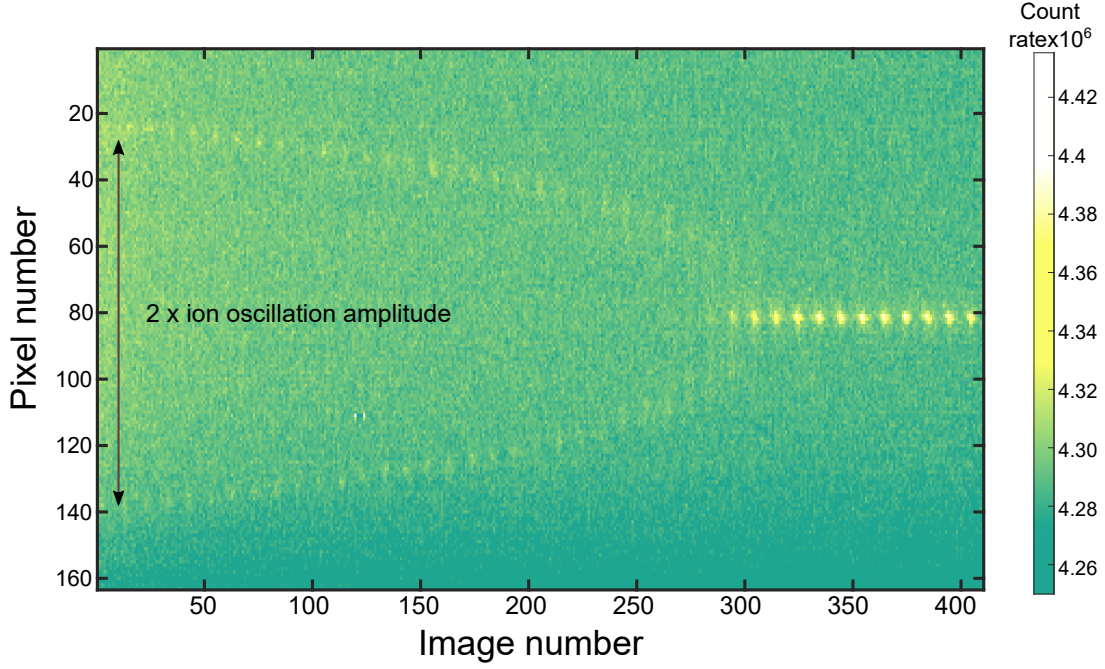


Figure 7.9: CCD camera images of the time evolution of the recooling fluorescence dynamics of an ion after a 61 K "kick" in the axial direction. The ion is prepared in a classical coherent state using the "tickle-voltage" for a fixed pulse length duration, followed by a cooling and repump laser pulses. The fluorescence is detected using the "fast-kinetics" mode of the CCD camera (see 4.5.2). The measurement is repeated 10 times and the images are overlapped. The ion oscillation amplitude is extracted from the intensity profile. Every image number corresponds to approximately 100 μ s

the closer the laser is to resonance, the more sensitive it is to frequency and intensity fluctuations. We choose a detuning and a coupling strength such that the recooling time measurements for collisions that transfer an energy in the desired range are easily detected (with recooling times longer than 2 ms) but are also less influenced by laser frequency or intensity fluctuations ($\Delta = 2\pi \times 10$ MHz and $\Omega = 2\pi \times 40$ MHz).

7.3.3 Recooling measurements

We implement the quasi-two level Doppler cooling scheme illustrated in Figure 7.8 using the three lasers at 397 nm, 850 nm and 854 nm. The 397 nm laser is set to have a coupling strength of $\Omega = 2\pi \times 40$ MHz and a detuning of $2\pi \times 10$ MHz with respect to the cooling transition. The frequencies of the three lasers are stabilized to a WLM (see Section 4.5). We use a trap drive frequency of $2\pi \times 32.351$ MHz and set the trapping confinement such that the axial secular mode has a frequency of 823 kHz, and the radials of 1.365 MHz and 1.167 MHz. We continuously measured the fluorescence for long periods of time (up to 27 hours), using a time tagger that records and assigns a time stamp to every PMT pulse detected (see Section 4.5.1) limiting our measurements only by the photon collection efficiency.

To do the analysis, the data is binned in 1 ms time intervals. The binned-data is processed in two steps: First collision events are detected. Using Poissonian statistics, any two consecutive measurement points with a count rate below a threshold, defined as five standard deviations below the average count rate, is considered a collision-event.

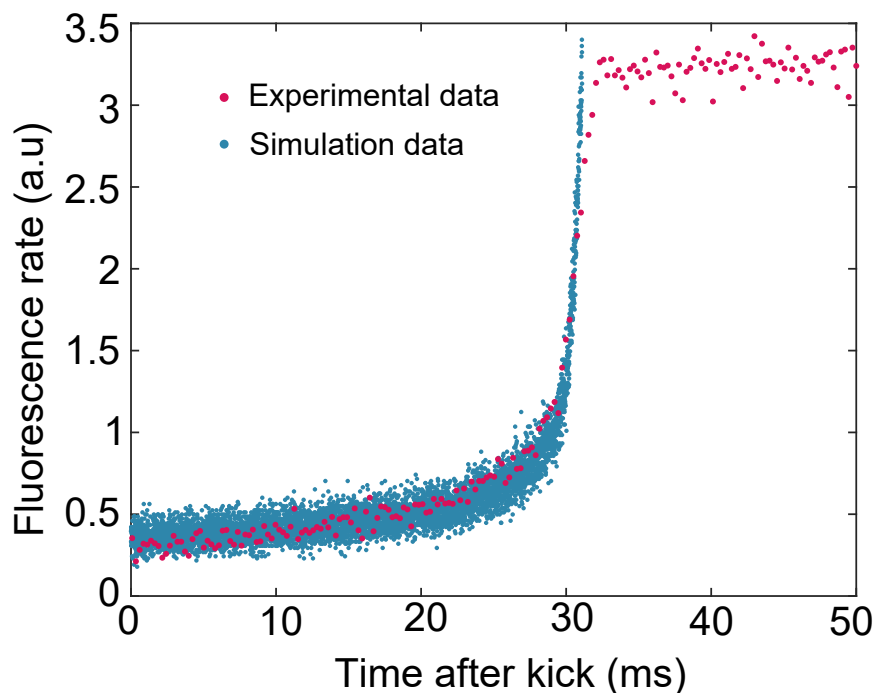


Figure 7.10: Time evolution of the fluorescence dynamics after 61 K "kick" in the axial direction. Using the same conditions as in Figure 7.9 the fluorescence is detected using a PMT detector (pink dots). All the parameter necessary for the simulation were independently determined. The time evolution of the fluorescence dynamics predicted by the simulation (blue dots) is consistent with the experimental data.

Once, the events are identified, a second step consists in identifying the starting and ending point of the collision. For this, we observe the measurement points before and after the collision event, and identify the points where the count rate is recovered and has a value within one standard deviation of the normal count rate. Once these points are identified, the time duration of each collision is determined. The energy of the ion after each event is calculated from the estimated time duration of the events using our model. From these measurement, we can extract the collision rate resulting in a final ion kinetic energy E_{ion} . A conservative uncertainty of ± 3 ms is given to the estimation of the time duration, taking into consideration errors during the analysis or the model. A first data set was taken at the typical background pressure of about 10^{-10} mbar followed by a second set taken at a background pressure of about 10^{-9} mbar. To increase the pressure we implemented the same technique described in Section 7.1.5, that consists in firing the NEG's while constantly monitoring the pressure indicated by the ion getter. The results are presented in Figure 7.12. Given the temperature of the background gas (300 K), collisions that transfer an energy to the ion between 10 K and 10^4 K are rare, the differential collision rate estimated by Hankin et al. in that energy range is between $10^{-7} \text{ s}^{-1} \text{ K}^{-1}$ and $10^{-3} \text{ s}^{-1} \text{ K}^{-1}$. As illustrated in the figure our results agree with this tendency. With the variation of the background pressure, the measurements follow a similar trend as the ones described in Section 7.1: we observe a rate of events that seems to increase proportionally with a rise in the pressure. This trend follows the theoretical expectation that the collision rate increases linearly with the variation of the background gas pressure. The differential collision rate is estimated and plotted in Figure 7.14. As can be seen, the measurements follow the tendency predicted by the theoretical simulation.

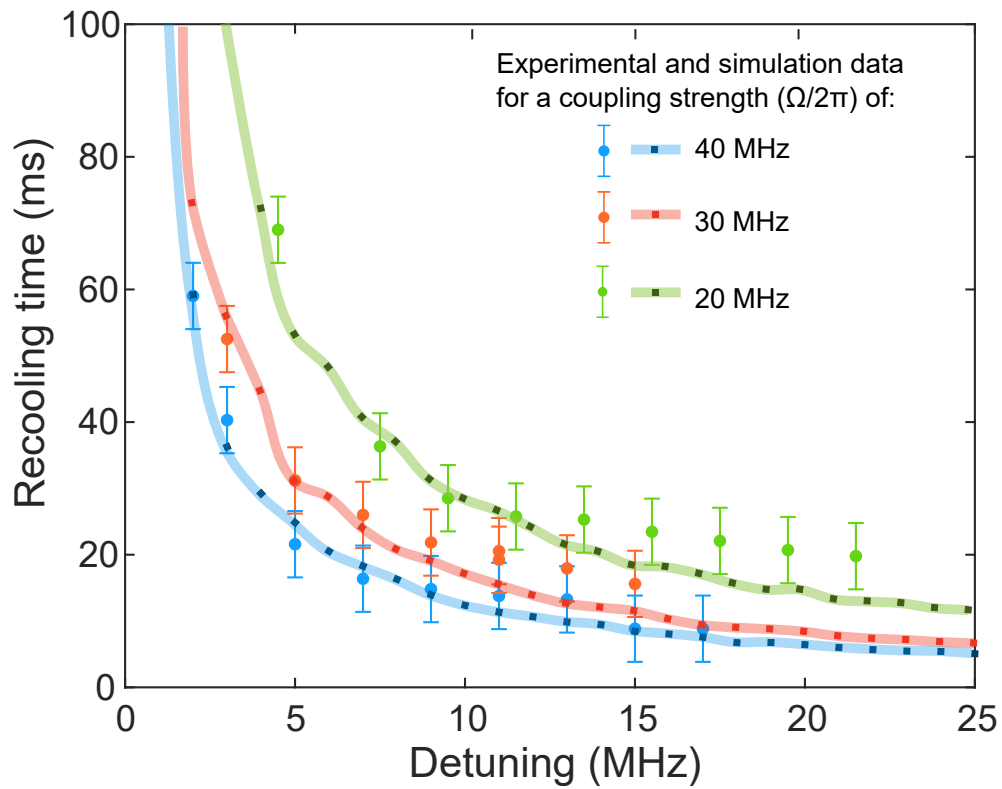


Figure 7.11: Re-cooling time after a 61 K kick as function of the 397 nm detuning for different couplings. The measurements are repeated using the same axial "kick" previously calibrated with the CCD camera images. The data measurements (blue dots for a coupling of 40 MHz, orange for 30 MHz and green for 20 MHz) agree with the the cooling times estimated using the numerical simulation (dotted points with shaded lines as a help for the eye).

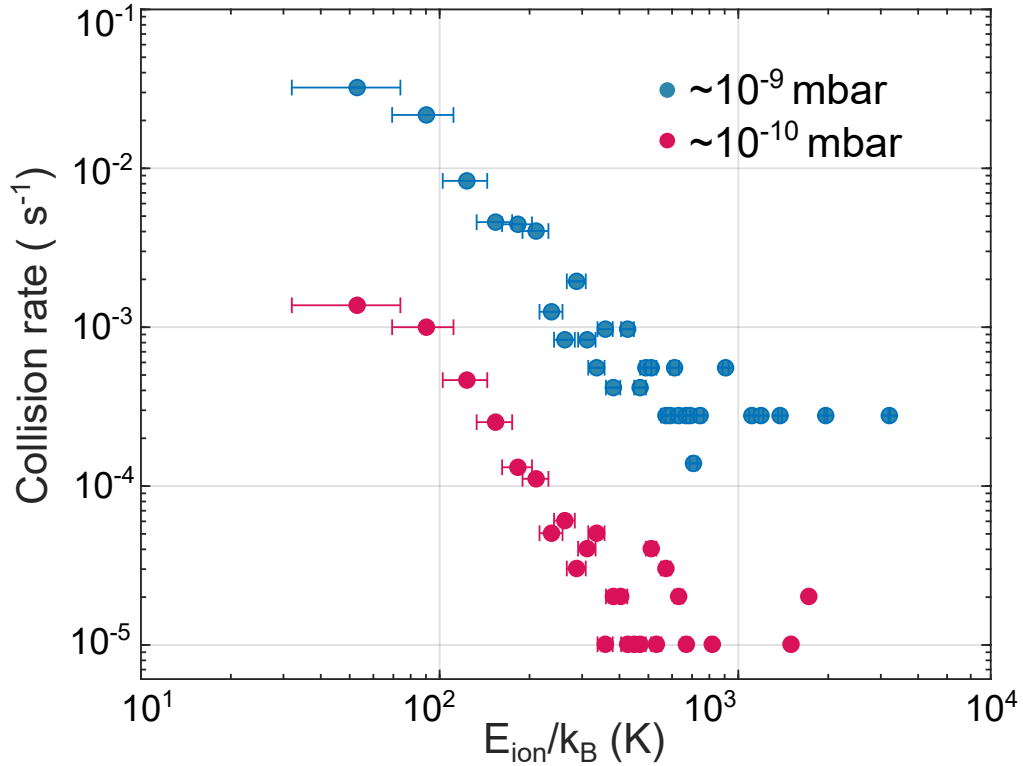


Figure 7.12: Collision rate measured using Doppler cooling thermometry. Results of two different campaigns, one taken during 27.5 hours at the standard pressure of 10^{-10} mbar (pink dots) and the second one taken during 2 hours at 10^{-9} mbar (blue dots). A time tagger is used to continuously measure the fluorescence, collisions are identified when the fluorescence level decays at a level below a defined threshold (see text), and the energy transferred to the ion is obtained as a function of the time that it takes for the ion to recover its original level. As expected, from the Boltzmann distribution, the rate of collisions decreases considerably fast as function the transferred energy, and scales with the vacuum pressure.

7.4 Differential rate of collisions

Figure 7.14 presents a summary of the results: The differential rate of collisions between a $^{40}\text{Ca}^+$ ion at rest and the background gas at 300 K for two different pressures resulting in a final ion kinetic energy E_{ion} . Experimental measurements are taken in three different energy ranges, for the two background pressures (pink dots for 10^{-10} mbar and blue dots for 10^{-9} mbar), using the techniques previously described:

- The composite pulses technique is used for a range from 10^{-3} K to 10^{-2} K.
- The swapping rate technique is used for a range from 10^0 K to 10^1 K.
- The recoiling time technique is used for a range from 10^1 K to 10^4 K.

The lines (pink for a pressure of 10^{-10} mbar and blue for 10^{-9} mbar) correspond to results from a numerical simulation that models the interaction of the trapped ion with the background gas classically. The ion is considered a particle at rest and the background particle is given a physical accurate set of initial conditions defining its trajectory (velocity and impact parameter). Following the same approach as the one described in [155], the interaction between the ion and the background neutral particle is assumed to be a long-range charge-induced-dipole interaction, in which the charge of the ion polarizes the atom, giving rise to an attraction between them, as well as short-range repulsion:

$$V(r) = -\frac{C_4}{r^4} + \frac{C_6}{2r^6}, \quad (7.9)$$

where C_4 and C_6 are the long-range attraction and short-range repulsion interaction coefficients, respectively. $C_4 = \alpha_{bg}Q^2/(8\pi\epsilon_0)$, α_{bg} is the polarizability of the background molecule, Q is the charge of the ion, ϵ_0 the vacuum permittivity and r , the internuclear separation. As described in [155, 156], C_6 indicates the point at which the interaction becomes repulsive and its value is given as fraction of C_4 , leading to a zero-crossing of the potential at a distance of $r = \sqrt{2C_6}$. As described in the references the exact value of C_6 is unimportant as long the r^{-6} starts to dominate at a short enough length scale of approximately 1 nm, for our simulations we used the value prescribed in [156]. After a collision event, given the initial conditions of the background particle, the trajectories of both particles are calculated. The simulation is repeated multiple times selecting randomly initial conditions from a Boltzmann distribution at a given temperature (300 K). After each simulated collision two parameters are recorded: the initial velocity of the background particle and the energy of the trapped ion E_i . From these two parameters the differential rate of collisions between the trapped ion at rest and a background gas at a given pressure and temperature is estimated. As illustrated in Figure 7.13, collisions are categorized in two types depending on how their trajectories are modified after the collision. Theoretically, "Langevin collisions" are defined as collisions for which the impact parameter smaller than the critical value b_{crit} estimated using [42]

$$b_{crit} = (\alpha_{bg}q^2/\pi\epsilon_0\mu v^2)^{1/4}, \quad (7.10)$$

where v is the mean velocity of the gas particles at a fixed temperature. The attraction between the background-particle and the ion is so strong that it is predicted to result into an inward-spiraling trajectory. The so-called "Glancing collisions" are defined as collisions for which the impact parameter is bigger than the critical value b_{crit} , defined in Equation 7.10, and is predicted to lead to a weak deflection or deviation of the particles trajectory.

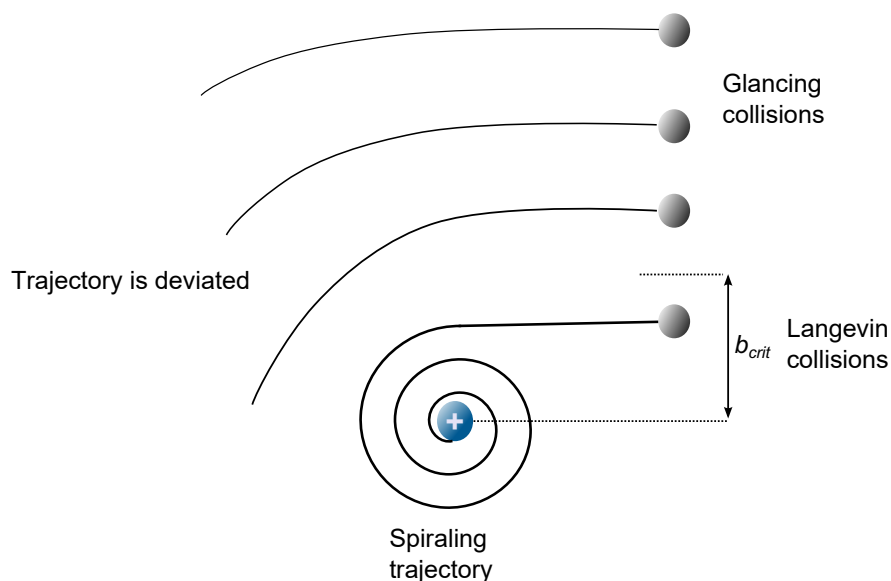


Figure 7.13: Illustration of collisions types. Collisions are categorized in two types depending on the value of the impact parameter: The so-called "glancing collisions" have an impact parameter bigger than the critical value b_{crit} , defined in Equation. 7.10 leading to a weak deflection or deviation of the particle trajectory. The so-called "Langevin collisions" have an impact parameter smaller than the critical value. The attraction between the background particle and the ion is so strong that it results into an inward-spiraling trajectory.

By simply observing the particle trajectories, collisions exhibiting a spiraling trajectory can be distinguished from the glancing collisions. In our simulation model, spiraling collisions are identified as particles whose trajectory change direction radically after the collision. The solid lines (orange for a pressure of 10^{-10} mbar and green for 10^{-9} mbar) correspond to the differential rate of collisions extracted from our model that exhibit a spiraling trajectory. For low energies (between 10^{-3} K and 10 K) our estimation of the so-called spiraling-trajectory collision differential rate deviates by a factor of approximately five from the predicted values by the Langevin cross section [42]. The way that our simulation model distinguish between spiraling-trajectory collisions and glancing collisions might underestimate the number of collisions that are considered to result in a spiraling-trajectory based on the theoretical definition following Equation. 7.10.

The estimation of the number of glancing collisions is nonetheless in agreement with the values predicted by the model used by Hankin et al. [148] for energies higher than 10^{-2} K. Our model follows a classical approach that fails to account for quantum effects that occur at low energies (between 10^{-3} K to 10^{-2} K). These effects are accounted in the model used in [148], where the differential cross section is calculated semiclassically following the approach of Zipkes et al. [157]. The measured data for this range of energies, using the composite pulse technique, appears to be in agreement with the values predicted following the semiclassical approximation. For a range of energies from 10 K to 10^4 K both models coincide with each other and with the measured data confirming the validity of the three measurement techniques presented.

The results of the simulation in Figure 7.14 assume that the background gas is mainly composed by H_2 , Figure 7.15 shows the result of the simulation when applied to a background mainly composed by O_2 (dotted orange line), N_2 (green), He (purple) and CH_4 (blue). To do the simulation we used the parameters listed in table 7.1. To

have a better understanding of the underlying dynamics it is easier to split the analysis in three energy ranges: a first one from 10^{-3} K and 10^{-1} K, a second one from 10^{-1} K and 10^2 K and, a third one from 10^2 K to 10^4 K.

Most of the collisions transferring low energies to the ion, between 10^{-3} K and 10^{-1} K, are glancing collisions. For these type of collisions, using our classical approximation, the critical range at which particles transfer energy to the ion is dominated by the polarizability of the background gas particle. In Figure 7.15, we can see that species with higher polarizability, such as CH_4 or N_2 have a higher differential rate of collisions that transfer an energy to the ion between 10^{-3} K and 10^{-1} K.

The rate of collisions transferring an energy between 10^{-1} K and 10^2 K is still dominated by glancing collisions. However, in this case the dominant parameter is the mean velocity of the background gas particles. In this case the collision rate is proportional to the mean velocity of the particles. From the Maxwell-Boltzmann distribution the mean velocity of background gas particles at a fixed temperature is inversely proportional to the square root of the mass ($\propto \frac{1}{\sqrt{m}}$). As we can see, in Figure 7.15, particles with lower mass, such as hydrogen or helium, have a higher differential rate of collisions transferring an energy between 10^{-1} K and 10^2 K.

Collisions that transfer high energies, between 10^2 K to 10^4 K, are mostly composed by spiraling or Langevin collisions. Before comparing the differential collision rate due to different species it is important to understand why the differential collision rate seems to decrease faster in this energy range compared to the previous ones. At this energy range, the collision rate is closely linked to the velocity distribution of the particles. To transfer an energy on this range, particles need to have a high enough velocity. Following the Maxwell-Boltzmann distribution at a given temperature, particles with velocities much higher than the mean velocity are at the tail of the distribution function. This means that the probability to find particles with a velocity high enough to transfer an energy on the range between 10^2 K to 10^4 K diminishes for the higher energies. This explains why the differential collision rate for particles transferring an energy between 10^2 K to 10^4 K decreases for higher energies. Focusing now on a comparison between the different atomic species. The rate at which these collisions occur is determined by the square of the critical parameter b_{crit} . As seen in Equation 7.10, the critical parameter, depends of the polarizability following $\propto \alpha_{bg}^{1/4}$ and of the mean square velocity following $\propto v^{1/2}$. As previously mentioned the mean square velocity depends on the mass following $\propto \frac{1}{\sqrt{m}}$. The critical parameter is then, dependent of both the mass and the polarizability of the background gas particles following $\propto \alpha_{bg}^{1/4} m^{1/4}$ which means that the collision rate follows $\propto \alpha_{bg}^{1/2} m^{1/2}$. This tendency is illustrated in Figure 7.15, for the case of N_2 , O_2 and CH_4 the coefficient $\alpha_{bg}^{1/2} m^{1/2}$ is equal to 6.9, 7.0 and 6.2 respectively. We can see that for these three species the differential rate of collisions transferring an energy between 10^2 and 10^3 follows an almost identical trend. For the case of He and H_2 the coefficient is also quite close, equal to 1.2 for H_2 and 0.9 for He. However, in Figure 7.15 it appears that the differential rate of collisions that transfer high energy to the ion is slightly smaller for H_2 than for He this could be explained by the fact that a higher mass leads to a more efficient energy transfer during the collision.

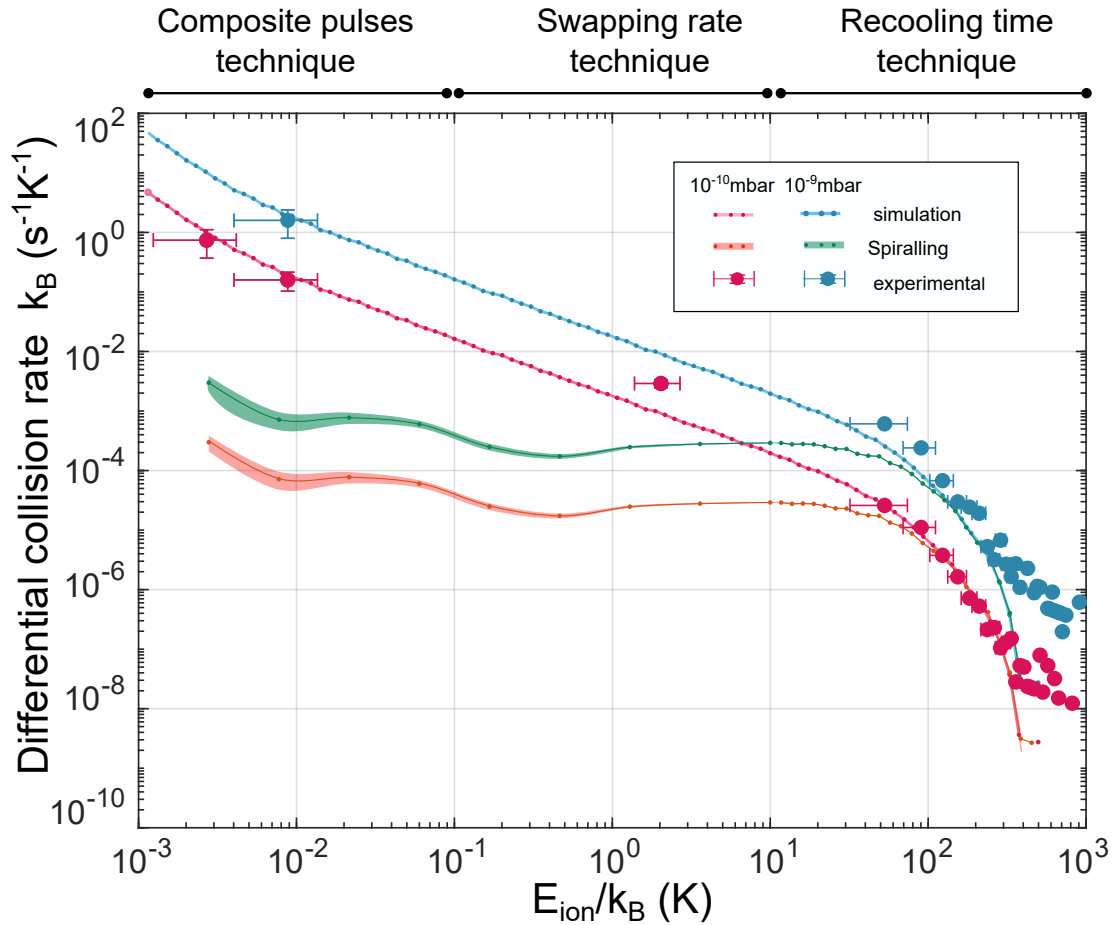


Figure 7.14: Differential collision rate. A summary of the results obtained with the three methods is presented. A numerical simulation that models classically the interaction of the trapped ion with the background particle is used to estimate the differential rate of collisions between a $^{40}\text{Ca}^+$ at rest and H_2 at 300 K at 1.4×10^{-10} mbar (pink dotted line) and at 1.4×10^{-9} mbar (blue dotted line). Spiralling collisions are identified as particles whose trajectory change direction radically. The rate of spiralling collisions is estimated for both pressures respectively in orange and green. The width of the lines corresponds to the statistical error obtained during the simulation.

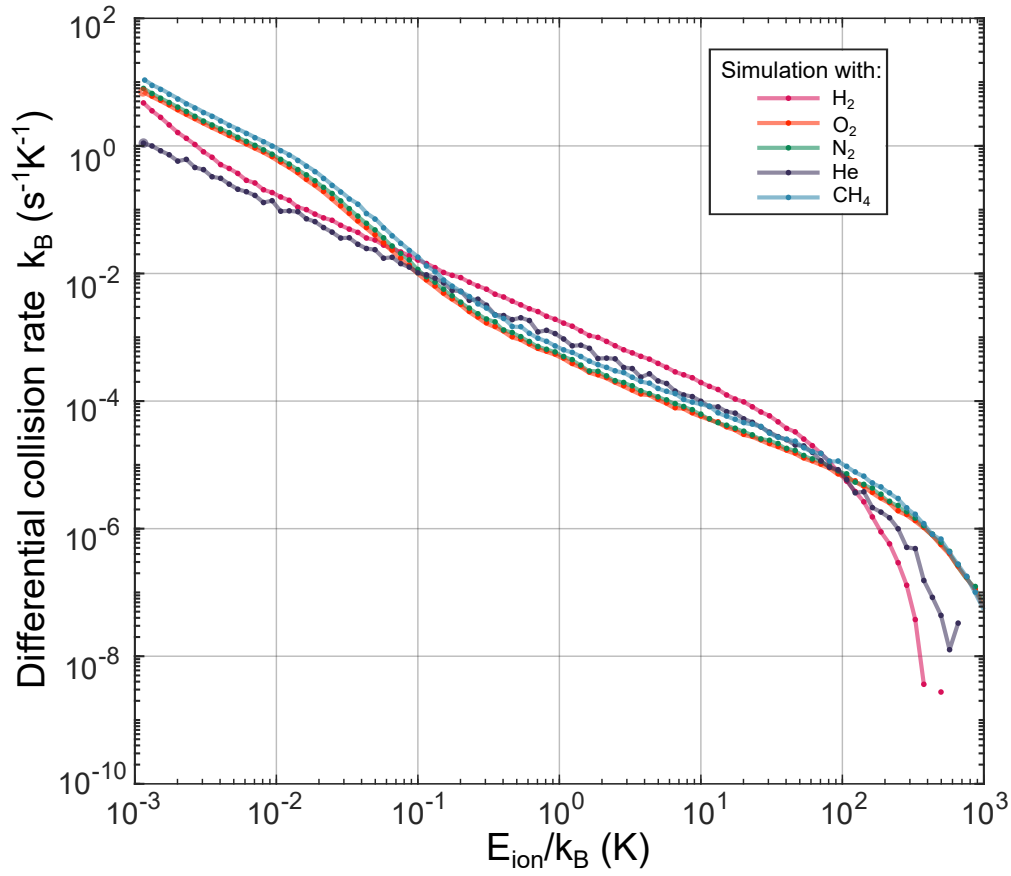


Figure 7.15: Differential Collision rate simulations between a $^{40}\text{Ca}^+$ ion at rest and a background gas composed by different types of molecules at 300 K at a pressure of about 10^{-10} mbar. The same numerical simulation implemented in Figure 7.14 is repeated assuming each time that the gas is entirely composed by one of the species listed on the top right corner. The dotted pink line correspond to H_2 , the orange one to O_2 , the green one to N_2 , the purple one to He and the blue one to CH_4 .

BG species	Polarizability (10^{-30} m^3)	mass (amu)
H_2	0.787[158]	2
He	0.209[158]	4
CH_4	2.448 [158]	16
O_2	1.562 [158]	32
N_2	1.710 [158]	28

Table 7.1: Polarizability and mass of the background gas species used in Figure 7.14

7.5 Conclusion

In this chapter I presented three different methods to estimate the differential collision rate between a trapped ion at rest and the background gas surrounding it at a given temperature and pressure resulting in a final ion kinetic energy E_{ion} . Each method is suited for a specific range of collision energies. The first one, is based on composite pulses applied to a single $^{40}\text{Ca}^+$ on the sidebands as a way to detect only collisions that transfer little energy to the ion. The second one detects the rate of collisions that transfer enough energy to cause the reordering of a mixed species ion pair. And the third one implements Doppler cooling thermometry to measure the energy transferred to the ion after a collision. The results obtained with each method are illustrated in Figure 7.14. The three methods together cover an extensive energy range from 10^{-3} K to 10^4 K.

The original goal that motivated us to study the background gas in the chamber came from the observation of the molecular ion creation by reaction of Al^+ with H_2 while probing the $^1\text{S}_0 \leftrightarrow ^3\text{P}_0$. As described in Chapter 6 the formation of these molecules occurs approximately every 15 minutes while probing the clock transition. The idea was to search for different methods to infer the background gas composition in the immediate surrounding environment of the ion and as was discussed in Section 7.4 a wide range of energies is necessary to be able to extract the partial pressure contributions of different gases to the differential collision rate observed by the ion. With the incorporation of these three methods a precise estimation of the composition of the background gas in the immediate surrounding of the ion might become more accessible. As described by Hankin et al. [148] a full characterization of the background gas collision heating is necessary to properly estimate the time-dilation and phase shift in trapped-ion clocks. In the paper the shift for a $^{25}\text{Mg}^+ - ^{27}\text{Al}^+$ is estimated to have a contribution to the uncertainty below 10^{-18} . For the case of the $^{40}\text{Ca}^+$, $^{88}\text{Sr}^+$ and $^{171}\text{Yb}^+$ the background gas collision uncertainty is estimated to be near 10^{-18} . Thus the proper and careful estimation of the distribution of the differential rate of collisions with the background gas plays an important role for trapped-ion clocks. As stated by Wineland et al. [42] background gas collisions heating has an impact on the coherence times, making this study relevant not only for clock experiments but also for quantum information, precision [149, 147, 159, 160], ultracold atom-ion [161, 155] or even for trapped nano-sphere experiments [162]. Extending the range of energies at which we can study the heating processes that affect trapped ions represents a key element to have a better understanding of the environment that surrounds it.

Chapter 8

Summary and Outlook

Using trapped ions as a platform, the work in this thesis is centered on the development of optical clocks as a tool to measure frequency. As introduced in the first chapter, we closely followed Arthur Schawlow's advice [2]: "Never measure anything but frequency!"

The first part of the thesis focuses on the theoretical background necessary to operate an ion trap setup for precision experiments. Chapter 2 presents a summary of the elements necessary to understand and operate an ion trap. It is followed, in Chapter 3, by a compendium of the theoretical tools used to calculate and measure the most relevant systematic frequency shifts that affect optical clocks with trapped ions.

The second part of the work is centered on the experimental implementation of precision experiments using $^{40}\text{Ca}^+$ and $^{27}\text{Al}^+$ trapped ions. Chapter 4 gives a description of the experimental setup used to perform the measurements described in this work. The remaining chapters focus on the three main projects carried out during my PhD.

Chapter 5 presents a project centered on the absolute frequency measurement of the $4s\ ^2S_{1/2} \leftrightarrow 3d\ ^2D_{5/2}$ $^{40}\text{Ca}^+$ clock transition. A GNSS link is established between PTB and Innsbruck. Using the PPP technique the absolute frequency of the $^{40}\text{Ca}^+$ clock transition is measured with respect to the coordinated universal time UTC at PTB during a ten-day campaign. After the evaluation of the systematic shifts, the measured transition frequency is $(411\,042\,129\,776\,401.2 \pm 0.6)$ Hz. The fractional uncertainty of 1.4×10^{-15} is mainly limited by the instability of the passive hydrogen maser used to establish the GNSS link. An in situ frequency comparison between our $^{40}\text{Ca}^+$ clock and one in a neighboring laboratory revealed that the stability of our spectroscopy measurements is of $8.7 \times 10^{-14} \tau^{1/2}$, limited mainly by quantum projection noise. The results of the campaign are in agreement with the latest measurements of the $^{40}\text{Ca}^+$ clock transition by the K. Gao group but disagree with the first measurements performed by our group in 2009. The frequency difference between both historical measurements remains open for further analysis. However these results represent a step forward towards the implementation of the $4s\ ^2S_{1/2} \leftrightarrow 3d\ ^2D_{5/2}$ $^{40}\text{Ca}^+$ clock transition as a secondary frequency standard.

Chapter 6, presents the implementation of quantum logic spectroscopy experiments with a $^{40}\text{Ca}^+ / ^{27}\text{Al}^+$ mixed-ion crystal. The $^1S_0 \leftrightarrow ^3P_0$ transition in Al^+ has an extremely narrow linewidth of about 8 mHz at 267.4 nm and has an intrinsically high immunity to perturbation by external fields, making it one of the most promising trapped-ion candidates for optical clocks. In this chapter, I present the implementation of sympathetic cooling and quantum logic spectroscopy to measure the absolute frequency of $^1S_0 \leftrightarrow ^3P_1$ intercombination line in Al^+ . The $S_{1/2} \leftrightarrow D_{5/2}$ quadrupole transition in $^{40}\text{Ca}^+$ is used as frequency reference by implementing a scheme that interleaves the probing of both transitions. The intercombination line frequency is determined to be $(1\,122\,842\,857\,334\,736 \pm 93)$ Hz. We also measured the Landé g-factor

of the excited state to be $g_{^3P_1, F'=7/2} = 0.428132(2)$. We have also probed the $^1S_0 \leftrightarrow ^3P_0$ clock transition in Al^+ and present a spectrum of the $(m = -5/2) \leftrightarrow (m = -3/2)$ Zeeman transition with a probe-time limited width of 1 kHz. Our measurements of the $^{27}\text{Al}^+$ clock transition are, however, hampered by the formation of molecular ions by reactions of Al^+ with H_2 molecules in the background gas. The creation of these molecules limits the probing time to about 15 minutes, which in combination with long Al^+ reloading times, prevents us from investigating the clock transition more thoroughly. The creation of these molecules inspired us to further investigate the composition of the background gas in the chamber.

Chapter 7 is dedicated to the development of methods to study the trapped-ion kinetics due to background gas collisions. The chapter presents three different methods to estimate the differential collision rate between a trapped ion at rest and the background gas surrounding it at a given temperature and pressure, resulting in a final ion kinetic energy. Each method covers a specific range of energies. The first one is based on composite pulses applied to a single $^{40}\text{Ca}^+$ on its motional sidebands as a way to detect only collisions that transfer low energy to the ion in a range between 10^{-3} K to 10^{-2} K. The second one detects the rate of collisions that transfer enough energy to cause the reordering of a mixed-species ion pair, in a range between 10^0 K to 10^1 K. This method is implemented to measure the H_2 gas background pressure in the vicinity of the ion. We determine that the H_2 gas background pressure at 300 K in our setup is $(1.4 \pm 0.2) \times 10^{-10}$ mbar. The third method implements Doppler cooling thermometry to measure the energy transferred to the ion after collisions in a range between 10^1 K to 10^4 K. The three methods together cover an extensive range that goes from 10^{-3} K to 10^4 K. The first and third method are applied to measure the differential collision rate at two different background gas pressures of $(1.4 \pm 0.2) \times 10^{-10}$ mbar and $(1.4 \pm 0.2) \times 10^{-9}$ mbar. To corroborate our measurements we used a numerical simulation that classically models the interaction of the trapped ion with the background particles. Our model follows a classical approach that does not account for quantum effects that occur at low energies (between 10^{-3} and 10^{-2} K), corrections at this range should be considered. These effects are accounted for in the model used in [148]. Our measurements are also in agreement with the values predicted by their model, for the measured vacuum pressure in our setup. We used our model to simulate the kinetics due to background gasses entirely composed of other species. The results from our simulations emphasize the importance of probing the differential collision rate for a broad range of energies. With these methods a more precise understanding of the motional heating of the ion generated by the background gas in the chamber can be experimentally accessed. These measurements are not only important for clock experiments but also for quantum information, precision, ultracold atom-ion and even for trapped nano-sphere experiments.

At the time of writing, a new version of the experimental setup presented in this work is currently being designed by Lorenz Panzl. The corresponding setup will be described in his PhD thesis. This new setup is originally intended to be implemented for quantum computation and information projects. The next steps for our group in the field of metrology, are oriented towards the integration of the knowledge acquired in the field of quantum computation and information processing to the developments of new techniques to probe and operate trapped ion clocks. Several projects have been already carried out in this direction [79, 33, 32], where entanglement is implemented to improve the signal-to-noise ratio, the tailored design of decoherence-free subspaces or as a way to enhance sensing. Our group is particularly interested in a proposal by Schulte et al. [163]: A quantum algorithmic readout is implemented to a mixed-species ion string, where quantum logic spectroscopy is required for the detection of the clock

ions. The proposed readout scheme promises an overhead that scales logarithmically with the number of clock ions using a single multispecies gate operation. Through the enhancement of the signal-to-noise ratio, clocks based on ion strings would allow one to overcome the limitation of single-ion systems where many weeks of measurements are necessary to reach low fractional uncertainties. Implementing this scheme using ion species with a negligible electric quadrupole moment such as the $^{27}\text{Al}^+$ ion or highly charged ions, which usually requires schemes such as quantum logic spectroscopy to perform the readout, would permit to avoid systematic frequency shifts generated by the interaction with electric field gradients.

Parallel to these ideas, the implementation of the established GNSS link allows us not only to have easy access to frequency standards around the world but also opens the door to frequency comparisons with other experimental groups. A frequency comparison via GNSS link between our $^{40}\text{Ca}^+$ clocks and the ones in the group of K. Gao could potentially offer an even stronger final argument to the debate surrounding the measurement of the $^{40}\text{Ca}^+$ clock transition. The capabilities of the link could be further improved with the implementation of an active hydrogen maser. The GNSS link could eventually be applied to perform frequency comparisons involving other trapped ion species experiments developed in our group such as Barium or Strontium. With the improvement of our trapped-ion references and the capabilities to perform long distance frequency comparison, our group could potentially join the growing network of clocks around the world.

Acknowledgements

About 6 years ago, a bit more maybe, I decided to cross the Atlantic and move to Innsbruck to do a PhD in quantum optics. I had a lot of expectation and ideas of what my PhD was going to be, some were a bit naive, like the idea that it was going to be finished in 3 to 4 years and some were a bit more realistic like the idea that it was going to be a lot of work. However, I don't think I could have ever imagined what ended up really happening. As it is with important things in life, there were good times and hard times. However, I can say that the good times definitely outweighed the difficult ones and for that I am extremely thankful.

I want to give special thanks to Rainer for the opportunity to do my PhD in his group. I believe that one of the most important things that I have learned from him, applicable not only in the lab but also in life is to just: "Go for it!". I was also lucky to get a silver lining out of the terrible experience of the pandemic: since Rainer could not travel as often as he usually does, I got the chance to have weekly meetings with him to discuss the measurement of the absolute frequency of calcium. This was a truly valuable and unique experience for which I am very grateful.

I am also very thankful for the opportunity to have worked with Christian Roos. I admire his passion for physics. I think in many ways Lab 2 was a sort of playground for him, to test new ideas and projects. One of the best feelings during my PhD time was to try some new measurements until very late at night, send the data to Christian and get an amazing analysis with Matlab simulations from him the next day. Following his ideas I think we literally "tickled" the ions in all possible ways.

I am very grateful for the help of the administrative staff and technicians at IQOQI and at the University, Elizabeth, Patricia, Klauss, David, Valentin, Gerhard, Andreas, Stephan and Bernhard without their help and patience our work is simply not possible.

I was in a single person experiment for most of my PhD, which, by the way I don't recommend to anybody, however I was never really alone: I had the chance to share the lab with Daniel and Irtiza for a big part of my PhD, even if we did not work always together we had a lot of fun keeping the experiment running. I briefly had a lab partner, Michi, from whom I am very thankful for the nice work he did in building the excellent setup that I got to use during my PhD time. I had also the chance to be in a big group, so anytime I had doubts or problems I could ask help to someone in the group. I could ask questions about programming, electronics, lasers, physics or anything regarding life in Innsbruck and there was always someone happy to help me.

Of course work is not everything, I am very lucky that I had the chance to also make a lot of nice friends during my PhD. The experiences that I had in Innsbruck outside work contributed the most to my happiness and helped me maintain my sanity. We went hiking, biking, climbing, for nice dinner evenings, boardgames, drinking or just for lunch and coffee at work. Christine, Christian, Leni, Josef, Pavel, Manoj, Lata, Dominik, Petar, Elisa, Lorenzo, John, Mary, Fi, Matthias, Gabriel, Gerard, Cristine, I am forever grateful for your friendship and kindness. I am especially grateful for my best friend and partner Martin, who not only helped me a lot during the PhD with

discussions and simulations but also hugged me when I was sad and laughed after at my weird jokes and strange sense of humor. The end of our PhDs is just the beginning of new adventures for us.

Estoy muy agradecida a mis amigos de Costa Rica. Isa que vino a visitarme al principio de mi doctorado cuando todo era un poco demasiado, acompañándome siempre con su inmensa sabiduría y cariño. Gracias a los físiquillos: Kim, Rafa, Santi, Mela, Jeannette, Cris y Fabián que estuvieron conmigo cuando empezó toda esta locura, estudiando métodos matemáticos y termodinámica. Gracias a Marco por su apoyo y cariño. Y por supuesto gracias a la Trama por sus buenos consejos y su sabiduría para la vida.

Gracias también a mi familia. A mi mamá y mi papá que me inculcaron una curiosidad infinita mezclada con la extraña necesidad de querer poner a prueba todos mis límites: ingredientes fundamentales para poder terminar un doctorado. Los extraño todos los días y espero que podamos vernos pronto y dar un paseo por la playa o la montaña, hablar de plantas, animales, música y de cómo funciona el mundo. Le agradezco a Bonpapa que se fue este año, por enseñarme que siempre se puede encontrar un ángulo para ver el lado bueno de la vida. Mi hermana quien dejó Costa Rica muchos años antes que yo. Llevamos más de 20 años viviendo en países diferentes y sin embargo es una de las personas más cercanas en mi vida con la que hablo casi todos los días. Le agradezco mucho su apoyo, las largas conversaciones tratando de entender cómo diablos funcionan nuestra cabezas, la buena música y los memes de llamas y perros psicóticos.

I am very and grateful for the time during my PhD and very happy that is over now.

See you space cowboy... someday, somewhere.

Appendix A

List of publications

This thesis is based on the work realized in the Precision and Ultrafast laboratory of the Quantum Optics and Spectroscopy group, between 2016 and 2022. Original results presented in this thesis have been published in the following article:

- "Frequency measurement of the $^1S_0, F = 5/2 \leftrightarrow ^3P_1, F = 7/2$ transition of $^{27}\text{Al}^+$ via quantum logic spectroscopy with $^{40}\text{Ca}^+$, M. Guggemos, M. Guevara-Bertsch, D. Heinrich, O.A Herrera-Sancho, Y. Colombe, R. Blatt, and C.F. Roos, *New Journal of Physics*, **21.10**, 103003 (2019).

During my PhD, I have also contributed to projects that led to the following publications:

- "Ultraviolet Laser Pulses with Multigigahertz Repetition Rate and Multiwatt Average Power for Fast Trapped-Ion Entanglement Operations" M.I Hussain, D. Heinrich, M. Guevara-Bertsch, E. Torrontegui, J.J García-Ripoll, C.F. Roos and R. Blatt, *Phys. Rev. Applied*, **15**, 024054 (2021).
- "Ultrafast coherent excitation of a $^{40}\text{Ca}^+$ ion", D. Heinrich, M. Guggemos, M. Guevara-Bertsch, M.I. Hussain, C. F. Roos and R. Blatt, *New Journal of Physics* **21**, 073017 (2019).

Appendix B

Combined standard uncertainty

Following the recommendations stated in the section 5.1.2 of the Guide to the expression of uncertainty in measurement (GUM) [164] to calculate the combined standard uncertainty of a measurand Y that is not measured directly, but is determined from N other quantities $(X_1, X_2, \dots, X_N)$ through a functional relationship f :

$$Y = f(X_1, X_1, \dots, X_N). \quad (\text{B.1})$$

For the case where all input quantities are independent, the combined standard uncertainty $u_c(y)$ is the positive square root of the combined variance $u_c^2(y)$, which is given by

$$u_c^2(y) = \sum_{i=1}^N \left(\frac{\partial f}{\partial x_i} \right)^2 u^2(x_i). \quad (\text{B.2})$$

Each $u(x_i)$ is a standard uncertainty. The combined standard uncertainty $u_c(y)$ is an estimated standard deviation and characterizes the dispersion of the values that could reasonably be attributed to the measurand Y .

Appendix C

Stability analysis

To do the analysis of the stability we used the Handbook of Frequency Stability Analysis by W.J.Riley [165] and the free software from the same author: stable32, available in [166]. In this section I give a short summary of the key elements described in [165] used to do the stability analysis of frequency references.

C.1 Allan variance

The Allan variance is a measure of frequency stability. It is a measure of the fractional frequency fluctuations with the advantage of being convergent for most types of clock noise. It is usually denoted by AVAR and defined as:

$$\sigma_y^2(\tau) = \frac{1}{2(M-1)} \sum_{i=1}^{M-1} [y_{i+1} - y_i]^2, \quad (\text{C.1})$$

where y_i is the i th of M fractional frequency values averaged over the measurement (sampling) interval τ .

It is more common to express the result as the square root σ_y denominated as Allan deviation ADEV. Allan deviation plots are commonly used to characterize noise sources.

C.2 Overlapping Allan variance

The overlapping Allan variance is a form of the normal Allan variance that is, nowadays, more commonly used. It makes maximum use of a data set by forming all possible overlapping samples at each averaging time τ . It can be estimated from a set of M frequency measurements for averaging time $\tau = m\tau_0$ where m is the averaging factor and τ_0 is the interval, using the expression:

$$\sigma_y^2(\tau) = \frac{1}{2m^2(M-2m+1)} \sum_{j=1}^{M-2m+1} \left\{ \sum_{i=j}^{j+m-1} [y_{i+m} - y_i] \right\}^2. \quad (\text{C.2})$$

When a text refers to the Allan variance or Allan deviation they usually refer to the overlapping Allan variation or overlapping Allan deviance.

C.3 Modified Allan variance

The modified Allan variance, $\text{Mod}\sigma_y^2(\tau)$ denoted by MVAR is a another common time domain measure of frequency stability. It can be estimated from a set of M frequency

measurements for averaging time $\tau = m\tau_0$ where m is the averaging factor and τ_0 is the interval, using the expression:

$$\text{Mod } \sigma_y^2(\tau) = \frac{1}{2m^4(M-3m+2)} \sum_{j=1}^{M-3m+2} \left\{ \sum_{i=j}^{j+m-1} \left(\sum_{k=1}^{i+m-1} [y+k+m-y_k] \right) \right\}^2. \quad (\text{C.3})$$

The result is usually expressed as the square root, $\text{Mod } \sigma_y$ and denoted as the modified Allan deviation. The main advantage of the modified Allan deviation is that it allows one to distinguish between white and flicker phase modulated noises. The instability of frequency sources can be modeled by power-law noises. By measuring the instability over time the noise type can be identified as a function of the power law associated with the averaging time τ .

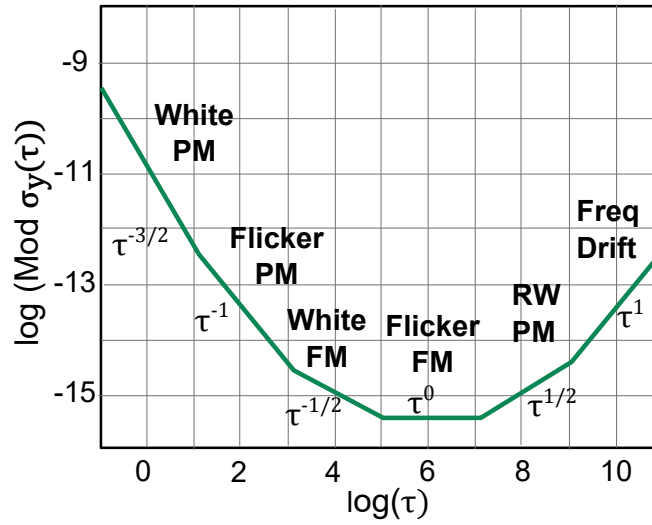


Figure C.1: Identification of noise types using a logarithmic plot of the modified Allan deviation

Each different type of noise can be identified to common noise sources. The following list is not exhaustive but gives an example of different noise sources associated to types of noise that can be identified using the modified Allan deviation.

- **White phase modulated noise (White PM):** corresponds to a broadband phase noise introduced usually in amplification stages.
- **Flicker phase modulated noise (Flicker PM):** usually introduced by noisy electronics or frequency multipliers.
- **White frequency noise (White FM):** associated to passive resonators or quantum systems. Quantum projection noise is a white frequency noise.
- **Flicker frequency noise (Flicker FM):** usually related to physical resonance mechanisms of an active oscillator. It can be associated to variations in the temperature or humidity in the environment.
- **Random walk frequency noise (RW PM):** it is usually linked to abrupt variations of the environment such as shocks, sudden temperature variations or vibrations.

Bibliography

- [1] Chad Orzel. *Brief History of Timekeeping: The Science of Marking Time, from Stonehenge to Atomic Clocks*. Oneworld, 2022.
- [2] Theodor W Hänsch. “Einstein lecture—passion for precision”. In: *Annalen der Physik* 15.9 (2006), pp. 627–652.
- [3] Fouad G Major. *The quantum beat: principles and applications of atomic clocks*. Springer Science & Business Media, 2007.
- [4] Andrew D Ludlow et al. “Optical atomic clocks”. In: *Reviews of Modern Physics* 87.2 (2015), p. 637.
- [5] Roger E Beehler. “A historical review of atomic frequency standards”. In: *Proceedings of the IEEE* 55.6 (1967), pp. 792–805.
- [6] Isidor Isaac Rabi et al. “A new method of measuring nuclear magnetic moment”. In: *Physical review* 53.4 (1938), p. 318.
- [7] Isidor Isaac Rabi et al. “The molecular beam resonance method for measuring nuclear magnetic moments of ${}^6_3\text{Li}$, ${}^7_3\text{Li}$ and ${}^{19}_9\text{F}$ ”. In: *Physical Review* 55.6 (1939), p. 526.
- [8] Norman F Ramsey. “Experiments with separated oscillatory fields and hydrogen masers”. In: *Reviews of Modern Physics* 62.3 (1990), p. 541.
- [9] Scott A Diddams et al. “Standards of time and frequency at the outset of the 21st century”. In: *Science* 306.5700 (2004), pp. 1318–1324.
- [10] Claude Audoin and Bernard Guinot. *The measurement of time: time, frequency and the atomic clock*. Cambridge University Press, 2001.
- [11] Franziska Riedel et al. “Direct comparisons of European primary and secondary frequency standards via satellite techniques”. In: *Metrologia* 57.4 (2020), p. 045005.
- [12] Harold J Metcalf and Peter Van der Straten. “Laser cooling and trapping of neutral atoms”. In: *The Optics Encyclopedia: Basic Foundations and Practical Applications* (2007).
- [13] John L Hall, Matthew S Taubman, and Jun Ye. *HANDBOOK OF OPTICS volume 14, Chapter 27: Laser stabilization*. McGraw-Hill, 1999.
- [14] Th Udem et al. “Absolute optical frequency measurement of the cesium D_1 line with a mode-locked laser”. In: *Physical Review Letters* 82.18 (1999), p. 3568.
- [15] William D Phillips. “Nobel Lecture: Laser cooling and trapping of neutral atoms”. In: *Reviews of Modern Physics* 70.3 (1998), p. 721.
- [16] Tobias Bothwell et al. “JILA SrI optical lattice clock with uncertainty of 2.0×10^{-18} ”. In: *Metrologia* 56.6 (2019), p. 065004.
- [17] S M Brewer et al. “ ${}^{27}\text{Al}^+$ quantum-logic clock with a systematic uncertainty below 10^{-18} ”. In: *Physical Review Letters* 123.3 (2019), p. 033201.
- [18] N Huntemann et al. “Single-ion atomic clock with 3×10^{-18} systematic uncertainty”. In: *Physical Review Letters* 116.6 (2016), p. 063001.

- [19] Holly Leopardi et al. "Measurement of the $^{27}\text{Al}^+$ and ^{87}Sr absolute optical frequencies". In: *Metrologia* 58.1 (2021), p. 015017.
- [20] Richard Lange et al. "Improved limits for violations of local position invariance from atomic clock comparisons". In: *Physical Review Letters* 126.1 (2021), p. 011102.
- [21] Christian Sanner et al. "Optical clock comparison for Lorentz symmetry testing". In: *Nature* 567.7747 (2019), pp. 204–208.
- [22] William F McGrew et al. "Towards the optical second: verifying optical clocks at the SI limit". In: *Optica* 6.4 (2019), pp. 448–454.
- [23] WF McGrew et al. "Atomic clock performance enabling geodesy below the centimetre level". In: *Nature* 564.7734 (2018), pp. 87–90.
- [24] Pierre Dubé et al. "Evaluation of systematic shifts of the $^{88}\text{Sr}^+$ single-ion optical frequency standard at the 10^{-17} level". In: *Physical Review A* 87.2 (2013), p. 023806.
- [25] Pierre Dubé, John E Bernard, and Marina Gertszvolf. "Absolute frequency measurement of the $^{88}\text{Sr}^+$ clock transition using a GPS link to the SI second". In: *Metrologia* 54.3 (2017), p. 290.
- [26] Y Huang et al. "A comparison of two $^{40}\text{Ca}^+$ single-ion optical frequency standards at the 5×10^{-17} level and an evaluation of systematic shifts". In: *Applied Physics B* 123.5 (2017), p. 166.
- [27] Y Huang et al. " $^{40}\text{Ca}^+$ ion optical clock with micromotion-induced shifts below 1×10^{-18} ". In: *Physical Review A* 99.1 (2019), p. 011401.
- [28] Yao Huang et al. "Liquid-Nitrogen-Cooled Ca^+ Optical Clock with Systematic Uncertainty of 3×10^{-18} ". In: *Physical Review Applied* 17.3 (2022), p. 034041.
- [29] Kyle J Arnold et al. "Precision measurements of the $^{138}\text{Ba}^+ 6s^2\text{S}_{1/2}$ - $5d^2\text{D}_{5/2}$ Clock Transition". In: *Physical Review Letters* 124.19 (2020), p. 193001.
- [30] R Kaewuam et al. "Spectroscopy of the $^1\text{S}_0$ - $^1\text{D}_2$ clock transition in $^{176}\text{Lu}^+$ ". In: *Physical Review A* 99.2 (2019), p. 022514.
- [31] R Kaewuam et al. "Hyperfine averaging by dynamic decoupling in a multi-ion lutetium clock". In: *Physical Review Letters* 124.8 (2020), p. 083202.
- [32] Christian D Marciniak et al. "Optimal metrology with programmable quantum sensors". In: *Nature* 603.7902 (2022), pp. 604–609.
- [33] Christian F Roos et al. "'Designer atoms' for quantum metrology". In: *Nature* 443.7109 (2006), pp. 316–319.
- [34] Jérôme Lodewyck. "On a definition of the SI second with a set of optical clock transitions". In: *Metrologia* 56.5 (2019), p. 055009.
- [35] Fritz Riehle et al. "The CIPM list of recommended frequency standard values: guidelines and procedures". In: *Metrologia* 55.2 (2018), p. 188.
- [36] J Leute et al. "Frequency Comparison of $^{171}\text{Yb}^+$ Ion Optical Clocks at PTB and NPL via GPS PPP". In: *IEEE transactions on ultrasonics, ferroelectrics, and frequency control* 63.7 (2016), pp. 981–985.
- [37] Boulder Atomic Clock Optical Network BACON Collaboration. "Frequency ratio measurements at 18-digit accuracy using an optical clock network". In: *Nature* 591.7851 (2021), pp. 564–569.

- [38] Katharina Predehl et al. "A 920-kilometer optical fiber link for frequency metrology at the 19th decimal place". In: *Science* 336.6080 (2012), pp. 441–444.
- [39] P Delva et al. "Test of special relativity using a fiber network of optical clocks". In: *Physical Review Letters* 118.22 (2017), p. 221102.
- [40] G Barontini et al. "Measuring the stability of fundamental constants with a network of clocks". In: *EPJ Quantum Technology* 9.12 (2022).
- [41] Norman Ramsey, Hans Dehmelt, and Wolfgang Paul. *The Nobel Prize in Physics 1989*. <https://www.nobelprize.org/prizes/physics/1989/press-release/>. Accessed: 2022-05-19.
- [42] Daniel J Wineland et al. "Experimental primer on the trapped ion quantum computer". In: *Fortschritte der Physik: Progress of Physics* 46.4-5 (1998), pp. 363–390.
- [43] Dietrich Leibfried et al. "Quantum dynamics of single trapped ions". In: *Reviews of Modern Physics* 75.1 (2003), p. 281.
- [44] Jannes B Wübbena et al. "Sympathetic cooling of mixed-species two-ion crystals for precision spectroscopy". In: *Physical Review A* 85.4 (2012), p. 043412.
- [45] Wayne M Itano et al. "Quantum projection noise: Population fluctuations in two-level systems". In: *Physical Review A* 47.5 (1993), p. 3554.
- [46] Claude Cohen-Tannoudji, Bernard Diu, and Frank Laloe. "Quantum Mechanics, Volume 2". In: *Quantum Mechanics 2* (1986), p. 626.
- [47] Christopher J Foot. *Atomic Physics*. Vol. 7. OUP Oxford, 2004.
- [48] Rodney Loudon. *The quantum theory of light*. OUP Oxford, 2000.
- [49] Rudolf Grimm, Matthias Weidemüller, and Yurii B Ovchinnikov. "Optical dipole traps for neutral atoms". In: *Advances in Atomic, Molecular, and Optical Physics* 42 (2000), pp. 95–170.
- [50] Christian Roos. "Controlling the quantum state of trapped ions". PhD thesis. *Universität Innsbruck*, 2000.
- [51] D James. "Quantum dynamics of cold trapped ions with application to quantum computation". In: *Applied Physics B* 2.66 (1998), pp. 181–190.
- [52] Cornelius Hempel. "Digital quantum simulation, Schrödinger cat state spectroscopy and setting up a linear ion trap". PhD thesis. *University of Innsbruck*, 2014.
- [53] Gerhard Kirchmair. "Frequency stabilization of a Titanium-Sapphire laser for precision spectroscopy on Calcium ions". MA thesis. *University of Innsbruck*, 2006.
- [54] David J Wineland and Wayne M Itano. "Laser cooling of atoms". In: *Physical Review A* 20.4 (1979), p. 1521.
- [55] M Guggemos et al. "Sympathetic cooling and detection of a hot trapped ion by a cold one". In: *New Journal of Physics* 17.10 (2015), p. 103001.
- [56] F Diedrich et al. "Laser cooling to the zero-point energy of motion". In: *Physical Review Letters* 62.4 (1989), p. 403.
- [57] Ch Roos et al. "Quantum state engineering on an optical transition and decoherence in a Paul trap". In: *Physical Review Letters* 83.23 (1999), p. 4713.
- [58] Piet O Schmidt et al. "Spectroscopy using quantum logic". In: *Science* 309.5735 (2005), pp. 749–752.

- [59] Mag Michael Chwalla. "Precision spectroscopy with $^{40}\text{Ca}^+$ ions in a Paul trap". PhD thesis. *University of Innsbruck*, 2009.
- [60] P Micke et al. "Coherent laser spectroscopy of highly charged ions using quantum logic". In: *Nature* 578.7793 (2020), pp. 60–65.
- [61] PO Schmidt et al. "Spectroscopy of atomic and molecular ions using quantum logic". In: *AIP Conference Proceedings*. Vol. 862. 1. American Institute of Physics. 2006, pp. 305–312.
- [62] Yong Wan. "Quantum logic spectroscopy of atomic and molecular ions". PhD thesis. *Gottfried Wilhelm Leibniz Universität Hannover*, 2014.
- [63] Walraven Jook. *Atomic Physics Lectures*. 2021.
- [64] Martin M Boyd et al. "Optical atomic coherence at the 1-second time scale". In: *Science* 314.5804 (2006), pp. 1430–1433.
- [65] Tingxian Zhang et al. "Theoretical study of the hyperfine-interaction constants and the isotope-shift factors for the $3s^{21}\text{S}_0$ – $3s3p^{3,1}\text{P}_1^0$ o transitions in Al^+ ". In: *Physical Review A* 96.1 (2017), p. 012514.
- [66] Xiao-Kang Tang et al. "Theoretical calculations of hyperfine splitting, Zeeman shifts, and isotope shifts of $^{27}\text{Al}^+$ and logical ions in Al^+ clocks". In: *Chinese Physics B* (2021).
- [67] S M Brewer et al. "Measurements of $^{27}\text{Al}^+$ and $^{25}\text{Mg}^+$ magnetic constants for improved ion-clock accuracy". In: *Phys. Rev. A* 100 (1 2019), p. 013409.
- [68] T Rosenband et al. "Observation of the $^1\text{S}_0 \leftrightarrow ^3\text{P}_0$ clock transition in $^{27}\text{Al}^+$ ". In: *Phys. Rev. Lett.* 98 (2007), p. 220801.
- [69] Michael Guggemos. "Precision spectroscopy with trapped $^{40}\text{Ca}^+$ and $^{27}\text{Al}^+$ ions". PhD thesis. *University of Innsbruck*, 2017.
- [70] M Guggemos et al. "Frequency measurement of the $^1\text{S}_0, F = 5/2 \leftrightarrow ^3\text{P}_1, F = 7/2$ transition of $^{27}\text{Al}^+$ via quantum logic spectroscopy with $^{40}\text{Ca}^+$ ". In: *New Journal of Physics* 21.10 (2019), p. 103003.
- [71] Wayne M Itano. "External-field shifts of the $^{199}\text{Hg}^+$ optical frequency standard". In: 105.6 (2000), p. 829.
- [72] K Beloy, D R Leibbrandt, and W M Itano. "Hyperfine-mediated electric quadrupole shifts in Al^+ and In^+ ion clocks". In: *Phys. Rev. A* 95 (4 2017), p. 043405.
- [73] HS Margolis et al. "Hertz-level measurement of the optical clock frequency in a single $^{88}\text{Sr}^+$ ion". In: *Science* 306.5700 (2004), pp. 1355–1358.
- [74] WH Oskay, Wayne M Itano, and James C Bergquist. "Measurement of the $^{199}\text{Hg}^+$ $5d^9 6s^2 \ ^2\text{D}_{5/2}$ electric quadrupole moment and a constraint on the quadrupole shift". In: *Physical Review Letters* 94.16 (2005), p. 163001.
- [75] T Schneider, E Peik, and Chr Tamm. "Sub-Hertz optical frequency comparisons between two trapped $^{171}\text{Yb}^+$ ions". In: *Physical Review Letters* 94.23 (2005), p. 230801.
- [76] M Chwalla et al. "Absolute Frequency Measurement of the $^{40}\text{Ca}^+$ $4s^2\text{S}_{1/2}$ – $3d^2\text{D}_{5/2}$ Clock Transition". In: *Physical Review Letters* 102.2 (2009), p. 023002.
- [77] Wayne M Itano. "Quadrupole moments and hyperfine constants of metastable states of Ca^+ , Sr^+ , Ba^+ , Yb^+ , Hg^+ , and Au ". In: *Physical Review A* 73.2 (2006), p. 022510.

- [78] G.P Barwood et al. "Measurement of the Electric Quadrupole Moment of the $4d^2D_{5/2}$ Level in $^{88}\text{Sr}^+$ ". In: *Physical Review Letters* 93.13 (2004), p. 133001.
- [79] M Chwalla et al. "Precision spectroscopy with two correlated atoms". In: *Applied Physics B* 89.4 (2007), pp. 483–488.
- [80] D J Berkeland et al. "Minimization of ion micromotion in a Paul trap". In: *Journal of Applied Physics* 83.10 (1998), pp. 5025–5033.
- [81] Wayne M Itano, L.L Lewis, and D.J Wineland. "Shift of $^2S_{1/2}$ hyperfine splittings due to blackbody radiation". In: *Physical Review A* 25.2 (1982), p. 1233.
- [82] Dansha Jiang et al. "Blackbody-radiation shift in a $^{88}\text{Sr}^+$ ion optical frequency standard". In: *Journal of Physics B: Atomic, Molecular and Optical Physics* 42.15 (2009), p. 154020.
- [83] Tanja E Mehlstäubler et al. "Atomic clocks for geodesy". In: *Reports on Progress in Physics* 81.6 (2018), p. 064401.
- [84] BIPM, Circular T June 2020. <https://webtai.bipm.org/ftp/pub/tai/Circular-T/cirt/cirt.402>. Accessed: 2021-07-02.
- [85] G Tommaseo et al. "The g_j -factor in the ground state of the Ca^+ ". In: *The European Physical Journal D-Atomic, Molecular, Optical and Plasma Physics* 25.2 (2003), pp. 113–121.
- [86] Daniel Heinrich. "Ultrafast coherent excitation of $^{40}\text{Ca}^+$ ". PhD thesis. *University of Innsbruck*, 2020.
- [87] Mark Riebe. "Preparation of entangled states and quantum teleportation with atomic qubits". PhD thesis. *University of Innsbruck*, 2005.
- [88] Thomas Monz. "Quantum information processing beyond ten ion-qubits". PhD thesis. *University of Innsbruck*, 2011.
- [89] Martin Meraner. "A photonic quantum interface between trapped ions and the telecom C-Band". PhD thesis. *University of Innsbruck*, 2022.
- [90] Johannes Franke. "Magnetic field noise cancellation for quantum simulation experiment with trapped ions". MA thesis. *University of Innsbruck*, 2022.
- [91] Jwo-Sy Chen. "Ticking near the zero-point energy: Towards 1×10^{-18} accuracy in Al^+ optical clocks". PhD thesis. *University of Colorado, Boulder*, 2017.
- [92] Kevin Sheridan, Wolfgang Lange, and Matthias Keller. "All-optical ion generation for ion trap loading". In: *Applied Physics B* 104.4 (2011), p. 755.
- [93] Carsten Schuck et al. "Two-color photoionization of calcium using SHG and LED light". In: *Applied Physics B* 100.4 (2010), pp. 765–771.
- [94] Elizabeth A Donley et al. "Double-pass acousto-optic modulator system". In: *Review of Scientific Instruments* 76.6 (2005), p. 063112.
- [95] BP Lanyon et al. "Efficient tomography of a quantum many-body system". In: *Nature Physics* 13.12 (2017), pp. 1158–1162.
- [96] Petar Jurcevic et al. "Quasiparticle engineering and entanglement propagation in a quantum many-body system". In: *Nature* 511.7508 (2014), pp. 202–205.
- [97] Christian Kokail et al. "Self-verifying variational quantum simulation of lattice models". In: *Nature* 569.7756 (2019), pp. 355–360.
- [98] Roman Stricker. "Gatteroperationen hoher güte in einem optischen quanten-bit". MA thesis. *University of Innsbruck*, 2017.

- [99] Yves Colombe et al. "Single-mode optical fiber for -power, low-loss UV transmission". In: *Optics express* 22.16 (2014), pp. 19783–19793.
- [100] Hans G Dehmelt. "Mono-ion oscillator as potential ultimate laser frequency standard". In: *IEEE Transactions on Instrumentation and Measurement* 2 (1982), pp. 83–87.
- [101] Rainer Blatt et al. "Ion trap quantum computing with Ca^+ ions". In: *Quantum Information Processing* 3.1-5 (2004), pp. 61–73.
- [102] Ziv Meir et al. "Single-shot energy measurement of a single atom and the direct reconstruction of its energy distribution". In: *Physical Review A* 96.2 (2017), p. 020701.
- [103] Judah Levine. "A review of time and frequency transfer methods". In: *Metrologia* 45.6 (2008), S162.
- [104] Thorsten Feldmann. "Advances in GPS based time and frequency comparisons for metrological use". PhD thesis. *Gottfried Wilhelm Leibniz Universität Hannover*, 2011.
- [105] P Defraigne et al. "Requirements on GNSS receivers from the perspective of timing applications". In: *EFTF-2010 24th European Frequency and Time Forum*. IEEE. 2010, pp. 1–6.
- [106] Waldemar Kunysz. "A three dimensional choke ring ground plane antenna". In: *Proceedings of the 16th international technical meeting of the satellite division of the institute of navigation (ION GPS/GNSS 2003)*. 2003, pp. 1883–1888.
- [107] J R Ray and K Senior. "Temperature sensitivity of timing measurements using Dorne Margolin antennas". In: *GPS Solutions* 5.1 (2001), pp. 24–30.
- [108] Jim Ray and Ken Senior. "Geodetic techniques for time and frequency comparisons using GPS phase and code measurements". In: *Metrologia* 42.4 (2005), p. 215.
- [109] Kensuke Matsubara et al. "Direct comparison of a Ca^+ single-ion clock against a Sr lattice clock to verify the absolute frequency measurement". In: *Optics express* 20.20 (2012), pp. 22034–22041.
- [110] Y Huang et al. "Hertz-level measurement of the $^{40}\text{Ca}^+ 4s^2S_{1/2}$ – $3d^2D_{5/2}$ clock transition frequency with respect to the SI second through the Global Positioning System". In: *Physical Review A* 85.3 (2012), p. 030503.
- [111] Y Huang et al. "Frequency Comparison of Two $^{40}\text{Ca}^+$ Optical Clocks with an Uncertainty at the 10^{-17} Level". In: *Physical Review Letters* 116.1 (2016), p. 013001.
- [112] Donald B Sullivan et al. *Characterization of clocks and oscillators*. National Institute of Standards and Technology Technical Note, 1990.
- [113] Stefan Droste et al. "Characterization of a 450 km baseline GPS carrier-phase link using an optical fiber link". In: *New Journal of Physics* 17.8 (2015), p. 083044.
- [114] Diego Orgiazzi, Patrizia Tavella, and François Lahaye. "Experimental assessment of the time transfer capability of precise point positioning (PPP)". In: *Proceedings of the 2005 IEEE International Frequency Control Symposium and Exposition, 2005*. IEEE. 2005, pp. 337–345.
- [115] Jan Kouba and Pierre Héroux. "Precise point positioning using IGS orbit and clock products". In: *GPS Solutions* 5.2 (2001), pp. 12–28.

- [116] Elliott D Kaplan, Joseph L Leva, and MS Pavloff. "Fundamentals of satellite navigation". In: *Understanding GPS- Principles and applications*(A 96-41027 11-17), Norwood, MA, Artech House, 1996, (1996), pp. 15–57.
- [117] Jan Kouba. *A guide to using International GNSS Service (IGS) products*. 2009.
- [118] Julia Leute. "Characterization and evaluation of GPS PPP techniques for optical clock comparisons". PhD thesis. *Institutionelles Repositorium der Leibniz Universität Hannover*, 2018.
- [119] Heiner Denker et al. "Geodetic methods to determine the relativistic redshift at the level of 10^{-18} in the context of international timescales: a review and practical results". In: *Journal of Geodesy* 92.5 (2018), pp. 487–516.
- [120] *International Service for the Geoid*. https://www.isgeoid.polimi.it/Geoid/height_conversion.html. Accessed: 2021-07-02.
- [121] BIPM, *Mean fractional deviation of the TAI scale from that of TT 2020*. <https://webtai.bipm.org/ftp/pub/tai/other-products/sitai/sitai2020.pdf>. Accessed: 2021-07-02.
- [122] Ekkehard Peik, Tobias Schneider, and Christian Tamm. "Laser frequency stabilization to a single ion". In: *Journal of Physics B: Atomic, Molecular and Optical Physics* 39.1 (2005), p. 145.
- [123] *International Real-Time Magnetic observatory Network*. <http://www.intermagnet.org>. Accessed: 2021-11-02.
- [124] HCJ Gan et al. "Oscillating-magnetic-field effects in high-precision metrology". In: *Physical Review A* 98.3 (2018), p. 032514.
- [125] AA Madej et al. "Absolute frequency of the $^{88}\text{Sr}^+ 5s^2S_{1/2}$ - $4d^2D_{5/2}$ reference transition at 445 THz and evaluation of systematic shifts". In: *Physical Review A* 70.1 (2004), p. 012507.
- [126] Yao Huang et al. "Geopotential measurement with a robust, transportable Ca+ optical clock". In: *Physical Review A* 102.5 (2020), p. 050802.
- [127] Ichiro Ushijima et al. "Cryogenic optical lattice clocks". In: *Nature Photonics* 9.3 (2015), pp. 185–189.
- [128] Thomas Middelmann et al. "High accuracy correction of blackbody radiation shift in an optical lattice clock". In: *Physical Review Letters* 109.26 (2012), p. 263004.
- [129] Stefan Droste et al. "Optical-frequency transfer over a single-span 1840 km fiber link". In: *Physical Review Letters* 111.11 (2013), p. 110801.
- [130] Anthony Bercy et al. "In-line extraction of an ultrastable frequency signal over an optical fiber link". In: *JOSA B* 31.4 (2014), pp. 678–685.
- [131] Abdel-Hafiz Moustafa et al. "Guidelines for developing optical clocks with 10^{-18} fractional frequency uncertainty". In: *arXiv:Atomic Physics year=2019* ().
- [132] WH Oskay et al. "Single-atom optical clock with high accuracy". In: *Physical Review Letters* 97.2 (2006), p. 020801.
- [133] ZT Xu et al. "Recent progress on the $^{27}\text{Al}^+$ ion optical clock". In: *Journal of Physics: Conference Series*. Vol. 723. 1. IOP Publishing. 2016, p. 012026.
- [134] Jannes Bernhard Wübbena. "Controlling motion in quantum logic clocks". PhD thesis. *Gottfried Wilhelm Leibniz Universität Hannover*, 2014.
- [135] S Hannig et al. "Towards a transportable aluminium ion quantum logic optical clock". In: *Review of Scientific Instruments* 90.5 (2019), p. 053204.

- [136] A Kramida et al. *NIST Atomic Spectra Database (version 5.6.1)*. **National Institute of Standards and Technology**. 2018.
- [137] D J Wineland et al. “Quantum computers and atomic clocks”. In: *Proc. 6th Symposium on Frequency Standards and Metrology, St. Andrews, Scotland, Sept. 9 - 14, 2001*. Ed. by P. Gill. Singapore: World Scientific, 2002, pp. 361–368.
- [138] Till Rosenband et al. “Frequency ratio of Al^+ and Hg^+ single-ion optical clocks; metrology at the 17th decimal place”. In: *Science* 319.5871 (2008), pp. 1808–1812.
- [139] C Hempel et al. “Entanglement-enhanced detection of single-photon scattering events”. In: *Nature Photonics* 7.8 (2013), pp. 630–633.
- [140] Yong Wan et al. “Precision spectroscopy by photon-recoil signal amplification”. In: *Nature Communications* 5.1 (2014), pp. 1–6.
- [141] Fabian Wolf et al. “Non-destructive state detection for quantum logic spectroscopy of molecular ions”. In: *Nature* 530.7591 (2016), pp. 457–460.
- [142] Chin-wen Chou et al. “Preparation and coherent manipulation of pure quantum states of a single molecular ion”. In: *Nature* 545.7653 (2017), pp. 203–207.
- [143] E Träbert et al. “Measurement of the B^+ and Al^+ intercombination and Sc^{12+} forbidden transition rates at a heavy-ion storage ring”. In: *Journal of Physics B: Atomic, Molecular and Optical Physics* 32.2 (1999), p. 537.
- [144] D B Hume, T Rosenband, and D J Wineland. “High-fidelity adaptive qubit detection through repetitive quantum nondemolition measurements”. In: *Physical Review Letters*, Year = 2007, Pages = 120502, Volume = 99 ().
- [145] D J Wineland et al. “Quantum control, quantum information processing, and quantum-limited metrology with trapped ions”. In: *Proceedings of the XVII International Conference on Laser*.
- [146] Igor I Sobelman. *Atomic spectra and radiative transitions*. Vol. 12. Springer Science & Business Media, 2012.
- [147] Florian Kranzl et al. “Experimental observation of thermalisation with non-commuting charges”. In: *arXiv preprint arXiv:2202.04652* (2022).
- [148] AM Hankin et al. “Systematic uncertainty due to background-gas collisions in trapped-ion optical clocks”. In: *Physical Review A* 100.3 (2019), p. 033419.
- [149] Guido Pagano et al. “Cryogenic trapped-ion system for large scale quantum simulation”. In: *Quantum Science and Technology* 4.1 (2018), p. 014004.
- [150] J-S Chen et al. “Sympathetic ground state cooling and time-dilation shifts in an Al^{27+} optical clock”. In: *Physical Review Letters* 118.5 (2017), p. 053002.
- [151] BT Torosov, ES Kyoseva, and NV Vitanov. “Composite pulses for ultrabroadband and ultranarrow-band excitation”. In: *Physical Review A* 92.3 (2015), p. 033406.
- [152] Tomas Sikorsky et al. “Doppler cooling thermometry of a multilevel ion in the presence of micromotion”. In: *Physical Review A* 96.1 (2017), p. 012519.
- [153] JH Wesenberg et al. “Fluorescence during Doppler cooling of a single trapped atom”. In: *Physical Review A* 76.5 (2007), p. 053416.
- [154] NM Linke et al. “Background-free detection of trapped ions”. In: *Applied Physics B* 107.4 (2012), pp. 1175–1180.
- [155] Eleanor Trimby et al. “Buffer gas cooling of ions in radio frequency traps using ultracold atoms”. In: *New Journal of Physics* (2022).

- [156] HA Fürst et al. “Prospects of reaching the quantum regime in Li–Yb⁺ mixtures”. In: *Journal of Physics B: Atomic, Molecular and Optical Physics* 51.19 (2018), p. 195001.
- [157] Christoph Zipkes et al. “Kinetics of a single trapped ion in an ultracold buffer gas”. In: *New Journal of Physics* 13.5 (2011), p. 053020.
- [158] Terry N Olney et al. “Absolute scale determination for photoabsorption spectra and the calculation of molecular properties using dipole sum-rules”. In: *Chemical Physics* 223.1 (1997), pp. 59–98.
- [159] J Chiaverini and JM Sage. “Insensitivity of the rate of ion motional heating to trap-electrode material over a large temperature range”. In: *Physical Review A* 89.1 (2014), p. 012318.
- [160] Martin W van Mourik et al. “rf-induced heating dynamics of noncrystallized trapped ions”. In: *Physical Review A* 105.3 (2022), p. 033101.
- [161] L Ratschbacher et al. “Decoherence of a single-ion qubit immersed in a spin-polarized atomic bath”. In: *Physical Review Letters* 110.16 (2013), p. 160402.
- [162] Uroš Delić et al. “Levitated cavity optomechanics in high vacuum”. In: *Quantum Science and Technology* 5.2 (2020), p. 025006.
- [163] Marius Schulte et al. “Quantum algorithmic readout in multi-ion clocks”. In: *Physical Review Letters* 116.1 (2016), p. 013002.
- [164] JCGM Jcgm et al. “Evaluation of measurement data—Guide to the expression of uncertainty in measurement”. In: *International Standards Organization, Geneva* 50 (2008), p. 134.
- [165] William J Riley. *Handbook of frequency stability analysis*. US Department of Commerce, National Institute of Standards and Technology . . . , 2008.
- [166] *stable32*, software by W.J Riley. <http://www.stable32.com/>. Accessed: 2022-05-12.