The measurement of time [1] has been historically important to much of human endeavor. Over the centuries the accuracy of astronomical and mechanical time-keeping devices has improved steadily, and sometimes spectacularly when triggered by the demands of science or society. One famous example is the chronometer invented around 1750 by the clockmaker Harrison with sufficient accuracy (1 second uncertainty per day) to determine longitude over large distances. This finally solved the outstanding problem of safe navigation across the Atlantic Ocean [2], after a long period in which the standard in clocks was set by Huygens’ pendulum (with an uncertainty of 1 minute per day). With the advent of quantum mechanics it became quickly clear that transitions between energy levels in atomic systems are excellently suited for defining time intervals because of their high intrinsic accuracy. The idea of an atomic clock was first conceived by I. I. Rabi in the early 1940’s (and announced publicly in the New York Times of January 21st, 1945). The subsequent revolution in microwave electronics in the second world war moved clocks into the atomic era: the first cesium (Cs) atomic clock, which is based on the microwave (∼10^{-10} Hz) frequency of the ^{133}\text{Cs} ground-state hyperfine structure transition, became operational in 1955. In 1967 this precisely measured frequency was chosen to be the basis for the definition of the second. The 13th Conférence Générale des Poids et Mesures (1967/68, Resolution 1) defined the second as: “The second is the duration of 9,192,631,770 periods of the radiation corresponding to the transition between the two hyperfine levels of the
ground state of the caesium 133 atom.”

Now, after 50 years of improvements in precision spectroscopy, the cesium atomic clock has reached fractional uncertainties of about 1 part in $10^{15}$ (see Figs. 1.1 and 1.2), corresponding to an error of about 100 picoseconds per day. In the meantime atomic clocks have found applications in many areas of technology, from voice and data communication to the GPS system, and in science, where for instance novel tests of Einstein’s theory of relativity have become possible as well as laboratory tests of the constancy of fundamental constants.

A good clock is accurate, precise, and reliable: i.e. it is a device with a dynamical period that is well-defined, short, not easily perturbed, and ideally constant. In particular, transitions between energy levels in atoms that are to a (very) large extent immune to perturbations by external electromagnetic fields that would change the frequency of the transition are ideal candidates for a clock oscillator. The precision $\sigma$ of an atomic clock is proportional to the resonance

Figure 1.1: (left) Simplified scheme of a fountain clock based on laser-cooled cesium atoms; (right) Picture of the NIST-F1 cesium fountain clock. Figures taken from [3].
frequency $\nu$ of the transition and it is inversely proportional to its linewidth $\delta \nu$,

$$\sigma \propto \frac{\nu}{\delta \nu},$$  \hspace{1cm} (1.1)  

where $S/N$ is the signal-to-noise ratio [4]; the intrinsic accuracy (or $Q$-value) is given by $\nu/\delta \nu$. High precision is equivalent to a large value of $\sigma$. While the cesium-clock frequency operates in the microwave regime ($\nu \approx 10^{10}$ Hz), a frequency standard based on an optical transition ($\nu \approx 10^{15}$ Hz) that is sufficiently narrow (small $\delta \nu$) has the potential to be several orders of magnitude more accurate. Such a clock holds the promise to achieve fractional uncertainties approaching 1 part in $10^{18}$, which would correspond to an error of some 100 femtoseconds per day. For the operation of the clock, the atom must be excited by electromagnetic waves from a coherent external oscillator: Cesium clocks require microwave oscillators and optical clocks require optical oscillators, i.e. lasers. The potential of optical clocks had been recognized for a long time [4], but the
technology to measure optical frequencies for the clockwork mechanism was not available. Only quite recently it has become practical to consider such optical atomic frequency standards after improvements in laser stabilization and the invention of the femtosecond laser frequency comb [5]. This technology provides for a direct measurement in this high-frequency regime by converting optical frequencies to the microwave regime, where the fastest available counting electronics can operate.

The cesium clock is limited not only because of its frequency, but also by Doppler shifts and collisional effects caused by the many atoms that are measured at the same time. It is, however, also possible to capture a single ion in a trap for high-precision spectroscopy. The ion can be cooled with lasers to the zero point energy of its motion, which eliminates most (unwanted) shifts in the resonance frequency. It can be probed while trapped, which enables long interaction times needed for accurate measurements. In certain atomic spectra measurements of the weak intensities of narrow transitions ($\delta \nu \approx 1 \text{ Hz}$) in single trapped particles are possible without imposing impossibly low statistics. Atomic clocks based on such ultra-narrow optical transitions in single laser-cooled trapped ions have demonstrated a precision and accuracy which are significantly better than that of the $^{133}\text{Cs}$ atom microwave frequency standard. Transitions in various ions are presently under investigation as candidates for optical frequency standards. This includes in particular electric quadrupole transitions in $^{40}\text{Ca}^+$ [6, 7], $^{199}\text{Hg}^+$ [8–10], $^{88}\text{Sr}^+$ [11, 12], and $^{171}\text{Yb}^+$ [13, 14], hyperfine-induced electric dipole transitions in $^{27}\text{Al}^+$ [15–17], and $^{115}\text{In}^+$ [18] and an electric octupole transition in $^{171}\text{Yb}^+$ [19]; proposals exist for $^{137}\text{Ba}^+$ [20] and $^{43}\text{Ca}^+$ [21], and with the work in this thesis, $^{88}\text{Sr}^+$ [22]. Some of these ion clocks operate currently at fractional frequency uncertainties $\delta \nu / \nu$ ranging from $10^{-18}$ to below $10^{-17}$, with projected accuracies reaching the level of $10^{-18}$. It is evident that optical clocks outperform microwave clocks by one order of magnitude already, and that an optical transition in a single ion will be most likely the next frequency standard, redefining the second. The ultimate performance of each atomic clock depends on the atomic structure of the atomic system, the complexity of the experimental setup needed to operate the clock, and the sensitivity of the transition to the external environment. An illustration to this last point is an addendum to the 1967-definition of the second made in 1997: “This definition refers to a cesium atom at rest at a temperature of 0 K.” Importantly, it was realized that the temperature of the environment has a non-negligible influence on the clock oscillation frequency. This effect is known as the black-body radiation shift [23]. There are many more such shifts caused by external fields. The sensitivity of the optical oscillation frequency to variations and fluctuations in these external fields and the ability the suppress subsequent detrimental effects to the clock’s accuracy is the limiting factor in all clocks. These sensitivities depend strongly on the atomic structure. As such, the
choice of the ion itself is clearly crucial for developing an improved clock. The singly-charged radium ion Ra$^+$ is an excellently suited optical clock candidate [22]. Radium offers a wide range of short- and long-lived isotopes with even and with odd nuclear spin that could be considered for use as optical frequency standards (see Table 1.1). Only trace quantities of radium are needed to operate a single-ion Ra$^+$ clock, although demands on the half-life and the ease of production limit the options. Excellent clock candidates are readily available from low-activity sources. The lasers needed for the trapping and the frequency read-out are readily available “off the shelf” as semiconductor laser diodes, in contrast to the more awkward lasers needed for, e.g., mercury, where the clock transition is excited at 282 nm wavelength. This makes the Ra$^+$ clock setup compact, robust, and low-cost compared to clocks that operate in the ultraviolet. Moreover, a particular frequency shift from stray trap fields called the electric quadrupole shift that is an important limiting factor for several other ion clocks [27], is absent in certain Ra$^+$ isotopes. In particular, certain hyperfine transitions in odd isotopes of radium are not affected by electric-quadrupole shifts nor by linear Zeeman shifts. Ion traps are ideal because of the near-absence of line-broadening mechanisms; in particular first-order Doppler broadening of lines is absent in a strongly confining ion trap due to the Lamb-Dicke effect. Moreover, in a single-ion setup, all inter-ion broadening effects are absent. Second-order Doppler effects are negligible since the ion is prepared with very low kinetic energies. The minimization of the remaining interference with (stray) trap fields requires theoretical and experimental study.

Radium offers also very promising perspectives for a high precision measurement of the breaking of left-right, or mirror, symmetry using a single trapped ion. This breaking of mirror symmetry in an atom is known as atomic parity violation (APV). APV experiments [10, 29–37] are sensitive probes of the electroweak

<table>
<thead>
<tr>
<th>$A$</th>
<th>Half-life</th>
<th>$I$</th>
<th>$\mu_I$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>212</td>
<td>13.0 s</td>
<td>0</td>
<td>0</td>
<td>$^{206}$Pb + $^{12}$C $\rightarrow$ $^{212}$Ra + 6n</td>
</tr>
<tr>
<td>213</td>
<td>2.73 m</td>
<td>1/2</td>
<td>0.6135(18)</td>
<td>$^{206}$Pb + $^{12}$C $\rightarrow$ $^{213}$Ra + 5n</td>
</tr>
<tr>
<td>223</td>
<td>11.43 d</td>
<td>3/2</td>
<td>0.2705(19)</td>
<td>$^{227}$Ac (21.8 y)</td>
</tr>
<tr>
<td>224</td>
<td>3.66 d</td>
<td>0</td>
<td>0</td>
<td>$^{229}$Th (1.9 y)</td>
</tr>
<tr>
<td>225</td>
<td>4.9 d</td>
<td>1/2</td>
<td>-0.7338(5)</td>
<td>$^{229}$Th (7.34 ky)</td>
</tr>
<tr>
<td>226</td>
<td>1.6 ky</td>
<td>0</td>
<td>0</td>
<td>$^{226}$Ra, $^{228}$Th (75.4 ky)</td>
</tr>
<tr>
<td>228</td>
<td>5.75 y</td>
<td>0</td>
<td>0</td>
<td>$^{228}$Ra</td>
</tr>
</tbody>
</table>

Table 1.1: Selection of long-lived isotopes of radium with their lifetimes and nuclear spins $I$ [24], magnetic moments $\mu_I$ in units of $\mu_N$ [25], and quadrupole moments $Q$ in barns [26]. Hyperfine structure constants and isotope shifts of relevant levels and transitions have been obtained over the course of this thesis (see e.g., Tables 4.1, 4.2, and 5.2). For a more complete list of isotopes, see Table 10.1.
interaction at low energy. Whereas in electromagnetic interactions parity is a conserved symmetry, in weak interactions parity is not conserved. Parity violation in atoms is due to the exchange of a neutral (weak) gauge boson $Z^0$ between the orbiting electrons and the quarks in the atomic nucleus. This interaction is not unlike the Coulomb interaction in the sense that the nucleus possesses not only an electric charge $Q_e$, but also an effective weak charge $Q_{\text{weak}}$. Its size depends on the mixing (or “Weinberg”) angle of the photon and the $Z^0$ boson, which is a fundamental parameter in the electroweak theory. This parameter describes the relative strengths of the electromagnetic and weak interaction. The Standard Model of particle physics (SM) makes a detailed but poorly tested prediction of the variation of the Weinberg angle with the momentum scale, or energy, at which it is probed. Experiments that test this prediction have been performed at high energy (near the $Z^0$-pole), medium, and low energy (see Fig. 1.4). The excellent agreement with the SM at low energy was reached only after a decade of theoretical efforts to interpret the original experiment carried out with Cs atoms, for which the most accurate measurement has been performed [34, 35, 38]. Therefore, it is highly desirable to perform an independent competitive experiment at low energy.

APV experiments have been of key importance for the acceptance of the electroweak theory, confirming together with neutrino scattering experiments [39] the
existence of neutral currents over many orders of magnitude in momentum scale. APV experiments are competitive to experiments at high energy due to their high sensitivity to additional heavy $Z'$-bosons. In fact, the most stringent lower limit on the mass of an additional $Z'$-boson at 1.3 TeV/$c^2$ comes from the Cs APV experiment [38]. APV is furthermore sensitive to additional light neutral gauge bosons, which can decay into light dark matter candidates [33] which might help explain the nature of dark matter. Next to being competitive, APV experiments are also complementary to experiments probing the weak charge at high-energies: together they can pinpoint the microscopic origins of possible deviations if a fingerprint of new physics is found.
The APV signal is strongly enhanced in heavy atoms. This can readily be observed from the so-called faster-than-$Z^3$ law [40] for the scaling of the APV signal with atomic number $Z$. However, the atomic theory needs to be calculable to high accuracy to be able to extract the weak charge and Weinberg angle from experiment. In this light the radium ion is a promising candidate for an atomic parity violation (APV) experiment because the predicted enhancement in Ra$^+$ is about 50 times larger than in Cs atoms [32, 41, 42]. At the same time, the Ra$^+$ ion with its single-valence electron is (still) a calculable system. However, laser spectroscopy on trapped Ra$^+$ ions had not been performed up to now and certain spectroscopic information, needed to test the required atomic many-body theory calculations, was lacking [32].

**Thesis Outline**

In this work experimental and theoretical progress towards the understanding and the construction of precision experiments based on single trapped Ra$^+$ ions is presented. Experimental setups for ion trapping were designed and constructed. Experiments were performed using stable Ba$^+$ isotopes as well as short-lived Ra isotopes which were produced at the TRI$\mu$P facility of KVI. Excited-state laser spectroscopy of trapped Ra$^+$ ions was performed. The data obtained in these measurements provide crucial information needed to constrain atomic theory in turn needed for atomic clocks and APV experiments.

There are several indispensable steps to construct an atomic clock based on a single trapped and laser-cooled Ra$^+$ ion. Firstly, the concept of ion trapping for such precision laser spectroscopy is discussed in Chapter 2. Secondly, the radioactive short-lived Ra isotopes need to be produced using the AGOR cyclotron and the TRI$\mu$P facilities, as described in Chapter 3. These radium isotopes are slowed down, ionized to singly charged Ra$^+$ ions, and captured subsequently using Paul traps. Chapter 3 describes the experimental set-ups that were constructed: the dedicated Ba$^+$ laboratory, where a collector and a precision Paul trap were commissioned along with the laser systems needed for Ba$^+$ spectroscopy; the radio-frequency cooler and buncher (RFQ) in which laser spectroscopy of trapped short-lived Ra$^+$ ions was performed using laser light for Ba$^+$ and Ra$^+$ spectroscopy from the laser systems set up in the experimental hall; and the extension of the TRI$\mu$P low-energy beamline with an additional collector Paul trap installed at the end of this new beamline. Thirdly, spectroscopic information of the Ra$^+$ atomic and nuclear system needs to be extracted: The experimental results of laser spectroscopy of Ra$^+$ ions trapped in the RFQ are presented in Chapters 4 and 5. Fourthly, it is crucial to minimize the influence of (stray) trap fields and other external fields on the clock oscillation frequency in order to limit detrimental effects to the clock’s accuracy. This requires theoretical and experimental studies:
A detailed theoretical analysis of promising clock transitions in several candidate Ra\(^+\) isotopes is presented in Chapter 6.

Future steps towards an optical frequency standard based on the Ra\(^+\) system are described in the Conclusions (Chapter 7). The Chapters 8 and 9, respectively, present the Acknowledgments and the summary in Dutch; the Appendix is presented in Chapter 10.