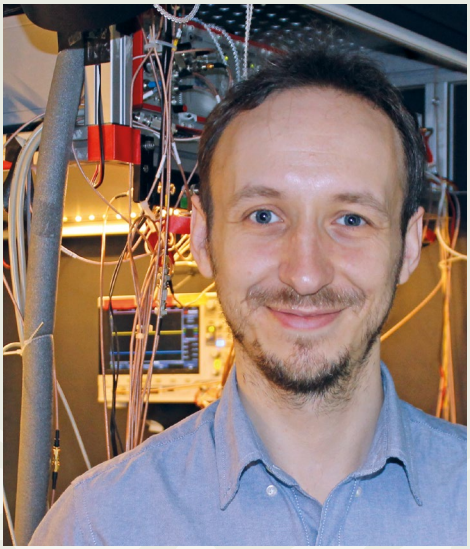


Steven King received his MSci degree from the University of Durham in 2008. After graduating, he joined the group of Prof. Patrick Gill at the National Physical Laboratory (NPL) in the UK, where he worked to develop an optical atomic clock based on trapped ytterbium ions. He received his DPhil from the University of Oxford in 2013 for this work, after which he joined the NPL group as a research scientist.
Since 2016 he has worked with Prof. Piet Schmidt at the QUEST Institute at the Physikalisch-Technische Bundesanstalt (PTB) in Braunschweig, where he led the successful development of the first optical atomic clock based on cold highly charged ions. Since the start of 2022 he holds the position of Senior Quantum Scientist at Oxford Ionics, with the aim of building a practical and scalable quantum computer based on trapped ions.

NOVEL ATOMIC CLOCKS

Steven King

Atomic Clocks using Highly Charged Ions

I. Introduction

The history of atomic clocks stretches back more than seventy years. During that time, multiple technological revolutions have occurred that allowed ever lower levels of measurement uncertainty to be reached. Many everyday applications such as satellite navigation would be impossible without the level of performance that is offered by atomic clocks.

The development and maturity of optical atomic clocks over the last three decades led to exceptionally rapid improvement in the achievable performance. State-of-the-art systems now demonstrate systematic uncertainties below the level of one part in 10^{18} [1]. If such a clock had been started at the moment of the Big Bang, it would have lost less than half a second over the intervening 14 billion years. Such extraordinary levels of accuracy and precision have opened up a wide range of technological applications such geodesy on the millimetre scale [2]. In addition, it is possible to test fundamental physical theories at unprecedented levels, including searching for potential time-variation of fundamental constants which would be a signature of new physics beyond the Standard Model [3]; or any violation of Lorentz invariance, which is a key pillar of Einstein's theory of relativity and states that the outcome of an experiment should not depend on factors such as its velocity or orientation [4].

Progress has not slowed down, and modern clocks continue to reach ever lower levels of systematic uncertainty through improved control and measurement of external electromagnetic fields, such as the blackbody radiation emitted by surfaces visible to the atom or ion used as the reference for the clock. These fields lead to so-called Stark shifts which act to perturb the frequency of the clock transition. The more accurately that these perturbations can be determined, the more accurate the clock. In addition to better characterisation of the fields themselves,

Resume:

Optical atomic clocks are the most accurate measurement devices ever constructed. Their potential applications extend beyond timekeeping to precision navigation, geodesy, and testing fundamental physics at unprecedented levels.
Highly charged ions (HCI) have long been proposed as candidates for the next generation of ultra-accurate clocks. Their atomic structure makes them significantly less sensitive to some of the main systematic perturbations that affect modern state-of-the-art systems, along with showing enhanced sensitivity to some effects from fundamental physics. In this work, we present the main technological breakthroughs that allowed the realisation of the world's first HCI-based clock. Through active cooling of the HCI and the use of quantum logic spectroscopy, we improve the spectroscopic resolution by eight orders of magnitude over the previous state of the art and unlock the use of HCIs for use in atomic clocks, quantum information processing, and tests of fundamental physics at low energies.

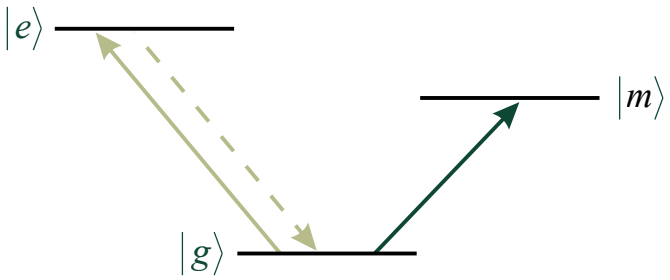


Figure 1:
Simplified level scheme for a typical atom or ion used for an optical atomic clock. The strong, dipole-allowed transition between the ground state $|g\rangle$ and excited state $|e\rangle$ can be used for laser cooling and state detection via the electron shelving technique. The transition to the metastable state $|m\rangle$ is electric-dipole forbidden and is used as the frequency reference for the clock. Solid lines indicate excitation by a laser, dashed lines are spontaneous decays.

the uncertainty on the shift is reduced through ever better theoretical calculations and measurements of the atomic response to such fields.

In parallel, researchers are investigating species that show inherently lower sensitivity to external perturbing fields. Highly charged ions (HCI) are a large group of such candidates for ultra-high-accuracy clocks [5,6]. The primary reason for their reduced sensitivity is that the remaining electrons are increasingly more tightly bound to the nucleus as the charge state of the ion is increased. For high enough charge states, the Stark shifts induced by the kinds of stray electromagnetic fields that exist in a typical optical clock apparatus are reduced by many orders of magnitude compared to singly charged or neutral atoms. Until now, however, a clock based on HCIs has remained an elusive goal.

II. Optical atomic clocks

Most atomic clocks operating today follow the same basic operating principles [7]:

1. Confine an atom (or ion) in an environment where the systematic conditions (e.g., magnetic field) can be very well controlled

For ions, their charge allows them to be confined using electric fields. As Earnshaw's theorem prohibits a static potential that confines the ion in 3 dimensions, the ion is instead confined by a combination of static and radiofrequency oscillating fields applied to electrodes in a device referred to as a Paul trap. If the frequency of oscillation is high enough, this creates a pseudopotential that can confine the ion practically indefinitely.

To isolate the ion from the environment, the ion trap is enclosed within a vacuum chamber which is evacuated to pressures in the ultra-high vacuum range or below. Careful attention is paid to the materials used for construction of the trap, as they will heat up under the application of the radiofrequency trapping field and lead to changes in the blackbody radiation that the ion experiences. All of the voltage supplies connected to the trap electrodes are specially designed and filtered in order to minimise their noise, and the electrode surfaces are cleaned to a very high standard to avoid contamination. Often, magnetic shielding is then assembled around the chamber to further isolate the ion from external noise. In this manner, the systematic conditions experienced by the ion can be controlled and characterised at a level that allows total clock uncertainties at the 10^{-18} level and below to be reached.

2. Cool the atom to as close as possible to absolute zero in order to suppress systematic shifts caused by thermal motion

Optical clocks employ laser cooling in order to reach equivalent temperatures of below a millikelvin for the atom. At such low temperatures, shifts due to thermal motion of the atom are suppressed to the 10^{-18} level and below. A simplified level structure for a typical atom used for an atomic clock is shown in *Figure 1*. The key features for laser cooling are a completely stable ground state $|g\rangle$ and a short-lived excited state $|e\rangle$, which decays naturally back to the ground state after only a few nanoseconds. These two states are typically separated by an energy that is equivalent to a photon in the visible range of the electromagnetic spectrum. If a laser of sufficient intensity is applied to the atom with its frequency carefully tuned so that its photons are close to the exact energy of this transition, the atom or ion will absorb and re-emit millions of these photons per second. The probability of absorption of a particular photon drops off as the laser frequency is detuned from the exact resonance frequency. This can be taken advantage of in order to produce the desired cooling effect. If the atom is moving towards the source of the laser beam, then it will see the laser frequency increase as a consequence of the Doppler effect. If the laser was originally tuned to have a frequency slightly below resonance, the Doppler shift causes the laser to appear to be closer to resonance in the reference frame of the atom, increasing the rate at which photons are scattered. If the atom is moving away from the source of the beam, then the Doppler shift is in the opposite direction and the probability of absorbing a photon is reduced. Since the momentum of the photon is transferred to the atom when it is absorbed and emission occurs in a random direction, this preferential absorption of photons when the atom is moving towards the laser leads to a net cooling effect over many absorption and

> *” Optical clocks are the most accurate man-made devices ever built, with the best systems displaying fractional systematic uncertainties below the 10^{-18} level. “*
>
> *Steven King*

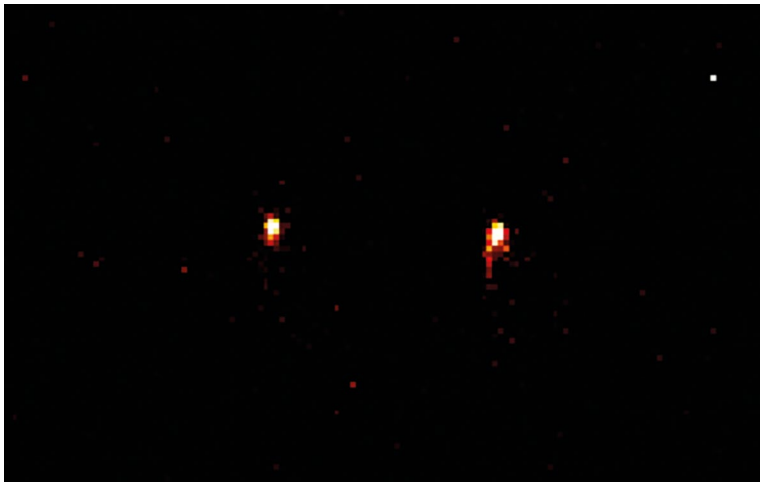


Figure 2:
False colour CCD image of a 3-ion Coulomb crystal composed of a single ion of Ar^{13+} and two Be^{+} ions, confined together in a linear Paul trap. The Be^{+} ions appear bright under illumination from the cooling laser, whereas the HCI in the middle of the image appears dark as it does not interact with this laser. The Be^{+} ions provide sympathetic cooling of the HCI, allowing it to be cooled to below 1 mK.

emission cycles. The scattered fluorescence photons can be collected by a lens with a high numerical aperture and imaged onto a photomultiplier tube (PMT) or CCD camera, allowing imaging of even a single atom, as shown in *Figure 2*.

3. Using highly spectrally pure radiation, interrogate a narrow transition in the atom which will be used as the reference for the clock

The next key feature of the level structure in *Figure 1* is a metastable excited state $|m\rangle$. These states take between milliseconds and even several years to naturally decay back to the ground state. Driving an atom from the ground state into this metastable state requires the frequency of the laser to be tuned around a million times more precisely than for the kinds of transitions used for laser cooling and hence they provide very precise frequency references. Typically, when exciting such a transition the observed width of the resonance is not determined by the natural linewidth of the resonance itself but rather by the properties of the laser used for the excitation. The achievable stability of the atomic clock based on this transition depends crucially on minimising this observed linewidth, and hence to produce the narrowest possible width for the resonance places very strong requirements on the so-called 'clock' laser that will be used to drive this transition. The laser is typically pre-stabilised to an ultra-stable, vibration-insensitive optical resonator in order to reduce its linewidth as far as possible. State-of-the-art lasers are now able to achieve linewidths in the millihertz range [8].

4. Determine the success of the interrogation, and use this signal to actively stabilise the frequency of the radiation to keep the radiation tuned to resonance

If the atom is excited by the clock laser, it remains in the metastable excited state for a relatively long period of time without decaying. During this time, the laser used to cool the ion is no longer resonant with any transitions out of this state, leading to a previously bright ion appearing dark on the PMT or camera. This is referred to as a quantum jump and can be used as a signal to determine the internal state of the atom. If the probability of excitation of the atom to the metastable state is monitored as the clock laser frequency is varied, the exact resonance frequency can be found. This signal can be used to generate an error signal that can, in conjunction with a feedback loop, keep the clock laser precisely tuned to the atomic resonance. For a clock based on a single ion, individual measurements of the locked laser frequency show relatively large statistical fluctuations caused by the intrinsically probabilistic nature of the detection process. The locked laser stability is typically in the range of 10^{-14} to 10^{-15} for typical operating parameters and a total measurement time of one second. This noise can be averaged away by making repeated measurements of the locked laser frequency over hours, days, or even weeks, allowing statistical uncertainties in the 10^{-18} range to be reached.

III. Specific challenges of highly charged ions

For most of the last three decades, the most precise and accurate measurements of optical transitions in HCI were performed using ions trapped in electron beam ion traps (EBIT). These devices use an energetic electron beam emitted by a cathode and focused by a strong, inhomogeneous magnetic field to produce a hot plasma of HCI from a neutral gas. The trapped ions are excited by the electron beam or laser spectroscopy and emit light that can be collected and analysed using a grating spectrometer. The trapped plasma typically has a temperature on the order of one megakelvin. The high velocities of the ions at such temperatures lead to the emission lines being Doppler-broadened to the level of tens of gigahertz. This is around eleven orders of magnitude larger than that the linewidths that can be achieved by modern optical clocks and limits the achievable measurement uncertainty to the 10^{-7} level in the best cases [9]. Recently, spectroscopy with a total uncertainty below the 10^{-8} level was achieved by cooling HCIs to the kelvin level in a Penning trap [10], but this still lies ten orders of magnitude behind state-of-the-art clocks.

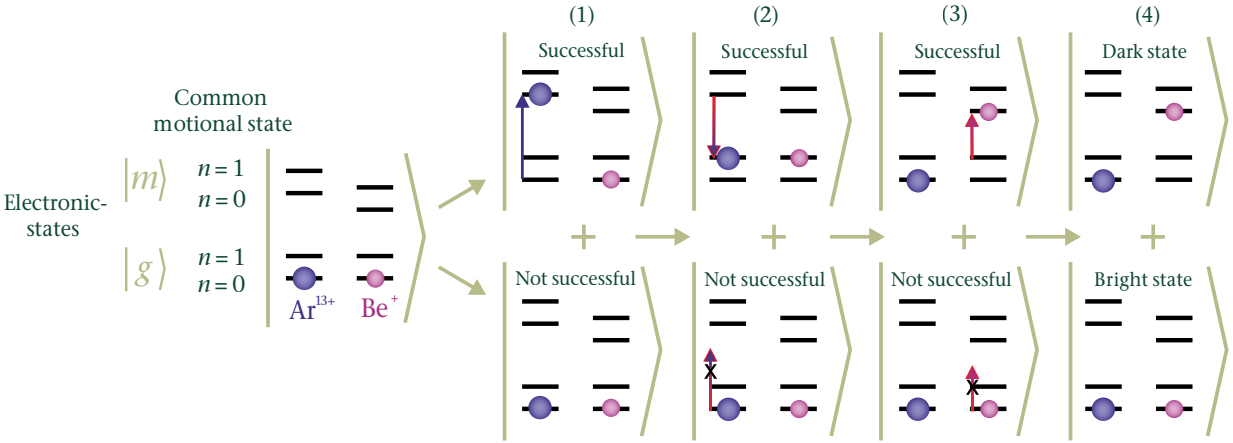
> *”Highly charged ions are exciting candidates for use in optical clocks due to their inherent insensitivity to external perturbing fields, but they are generally incompatible with traditional laser cooling and clock spectroscopy techniques.“*
>
> *Steven King*

"We have used techniques inspired by quantum information processing to cool and perform the first clock-like spectroscopy of highly charged ions. Our spectroscopic resolution is eight orders of magnitude higher than the previous state of the art."

Steven King

Before HCI could be used in clocks, specific challenges for each of the points discussed in Sec. II had to be addressed. Firstly, as discussed in the previous paragraph, HCIs are typically produced at high temperatures in environments with large magnetic fields which leads to large perturbations of the frequency of the clock transition. Additionally, HCIs are highly susceptible to charge-exchange collisions with residual background gas in the vacuum chamber, which limits their storage time to a matter of seconds in a room temperature environment, requiring them to be frequently replaced. To overcome both of these problems, we extract the HCIs from the EBIT where they are produced [11] and use an electrodynamic beamline to slow and transfer them to a cryogenic linear Paul trap [12] located approximately 3 m away in a separate laboratory. The cryopumping that occurs in the cryogenic environment [13] allows us to reach vacuum levels that are at least three orders of magnitude better than what can be achieved at room temperature, resulting in a mean time of more than an hour before a catastrophic charge-exchange collision occurs and the HCI must be replaced. The cryostat is of a custom design, intended to supress the vibrations of the cryocooler by around three orders of magnitude. The use of 99.999 % pure, annealed copper for the critical parts ensures that a high level of thermal conductivity is maintained despite the vibration decoupling stages. The Paul trap is designed to have extremely low levels of electrical and magnetic noise, leading to small and easily characterised systematic shifts. In fact, the trap used in this experiment displays the lowest level of anomalous electric field noise that has ever been measured in an ion trap that uses radiofrequency trapping fields.

Secondly, in general HCI do not possess a suitable electronic structure to allow for laser cooling. As discussed in the introduction, the remaining electrons in HCI are much more tightly bound than for singly charged or neutral atoms. The kinds of transitions that would normally be used for cooling are shifted to the extreme ultraviolet or even X-ray parts of the electromagnetic spectrum, out of the reach of modern laser technology. Instead, we employ a technique referred to as sympathetic cooling. If a second ion species (referred to as the 'cooling ion') is confined simultaneously in the same trap as the HCI, the charges on the two ions mean that they will couple together via the Coulomb interaction. Energy is exchanged between them, and laser-cooling of the cooling ion then leads to energy being removed from both ions. After sufficient cooling, the ions form an ordered structure referred to as a Coulomb crystal, which possesses well-defined, quantised modes of oscillation which are shared between the two ions in the trap. Such a Coulomb crystal is shown in *Figure 2*.



Thirdly, similarly to the lack of a transition suitable for laser cooling, the typical transitions that would be used as a clock reference in singly charged or neutral atoms lie far beyond the reach of lasers. We must therefore find alternative kinds of transitions for this purpose. For this proof-of-principle clock, we use the ground state fine-structure transition in Ar^{13+} as our clock reference. This transition can be excited by a visible wavelength of 441 nm, well within the reach of modern lasers.

Finally, in order to produce a feedback signal to stabilise the frequency of the interrogation laser to the transition in the HCI, it is necessary to determine the success of the attempted excitation of the HCI. The lack of a suitable transition for laser cooling prohibits determination of the internal state of the HCI via the electron shelving technique described in Sec. II. Instead, a technique known as quantum logic spectroscopy is used [14], which bypasses the need for such a transition in the HCI. The basic scheme for the quantum logic sequence is shown in *Figure 3* and exploits the quantised nature of the motional modes of the ion crystal, along with the fact that the cooling ion (in our case singly ionised beryllium, Be^+) also possesses the kind of level structure shown in *Figure 1*.

Before the process begins, all of the remaining phonons are removed from one of the motional modes of the ion crystal using a technique referred to as ground state cooling. This works by using a laser to address the $|g\rangle \rightarrow |m\rangle$ transition in the Be^+ ion, which is sufficiently narrow that the sidebands caused by the motion of the ion in the trap are resolved from the carrier. If the frequency of the laser addressing this transition is reduced compared to the resonant frequency by the eigenfrequency of the motional mode, then the cooling ion is driven to its metastable state $|m\rangle$ and a phonon is removed from the mode. This is referred to as a red sideband pulse. The Be^+ ion is then returned to state $|g\rangle$ by a separate laser.

Figure 3:
Simplified depiction of the quantum logic sequence. In pulse (1), an attempt is made to excite the HCI out of its ground state $|g\rangle$ and into the metastable excited state $|m\rangle$. In pulse (2), the electronic state of the HCI is transferred into the motional state of the ion crystal, resulting in the presence ($n = 1$) or lack ($n = 0$) of a phonon in this mode. As the motional modes are shared between the ions, the motional state of the crystal can be transferred to the Be^+ ion in pulse (3), leaving it in either its ground or metastable state. Finally, the internal state of the Be^+ ion can be read out by the presence (bright) or absence (dark) of a fluorescence signal using the cooling laser.

Repeatedly applying these two laser pulses cools the mode to the ground state, at which point the red sideband pulse becomes ineffective as there are no more phonons to be removed from the mode. This cooled mode can then be used as the bus to transfer the internal state information between the two ions.

The sequence then runs as follows: (1) An attempt is made to excite the HCI to the metastable state $|m\rangle$ using a pulse from the clock laser. (2) A second laser pulse is then applied to the HCI, but similarly to the red sideband pulses applied to the Be^+ ion during the ground state cooling, the laser frequency is detuned from resonance by the eigenfrequency of the motional mode. If the HCI is still in state $|g\rangle$, this pulse has no effect as the mode has been cooled to the ground state and no more phonons can be removed from the mode. But if the HCI was excited by the first pulse, this pulse will instead add a phonon to the mode and return the HCI to state $|g\rangle$. Hence the internal state of the HCI has been coherently transferred to the motional state of the ion crystal. (3) As the motional modes are shared between the two ions, the motional state can then be transferred to the internal state of the cooling ion using another red sideband pulse addressing the transition in the Be^+ ion that was used earlier for ground state cooling. The Be^+ ion will only be excited by this pulse if the HCI was excited in the first step. (4) The internal state of the Be^+ ion can then be read out as normal using the electron shelving technique, thereby determining the success of the initial pulse on the HCI.

"The apparatus and spectroscopy techniques we have developed are universal and can be applied to a wide variety of species."

Steven King

Using this technique, we were able to demonstrate the first optical-clock-like spectroscopy of an HCI [15]. We were able to observe transition linewidths as narrow as 65 Hz, as shown in *Figure 4*, nine orders of magnitude narrower than what is possible in EBITs. The statistical uncertainty on the fitted line centre is below 2 Hz, corresponding to a fractional uncertainty of 3×10^{-15}, eight orders of magnitude beyond the previous state of the art. Our measurements confirmed previous measurements of the natural lifetime of the $^2P_{3/2}$ state in Ar^{13+} and allowed us to make measurements of the Landé *g*-factor of this state that were more than two orders of magnitude more precise than previous measurements, settling a discrepancy between theoretical predictions.

IV. Algorithmic cooling

After the demonstration of ultra-high-resolution spectroscopy, it was then necessary to characterise the systematic shifts of the Ar^{13+} transition in order to realise an atomic clock. Particular attention must be paid to the efficiency of the sympathetic cooling process, which depends on how well the charge-to-mass ratio of the cooling ion is

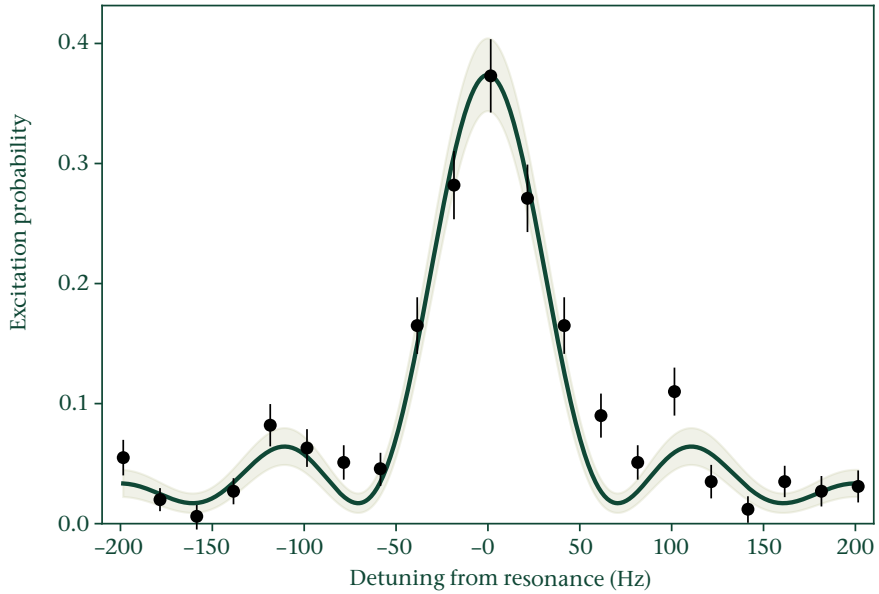


Figure 4:
Lineshape of the clock transition in Ar^{13+}, determined by scanning the clock laser frequency around the atomic resonance. The full width at half maximum of the line is around 65 Hz, nine orders of magnitude narrower than what is possible in EBITs. This is only four times broader than the natural linewidth of 17 Hz and is interaction time limited by the 12 ms-long pulse from the ultrastable laser used to excite the ion. The solid line is a fit to the lineshape, with the shaded region around the fit and the error bars on the data points indicating the expected standard deviations of the measurements.

matched to that of the HCI. If the mismatch between the two ions is too great, the coupling between the two ions is weakened. The key result of this is that the ions will have very different amplitudes of oscillation in the various motional modes, which degrades the cooling rate in modes where the cooling ion has a small amplitude and leads to higher equilibrium temperatures when any heating mechanisms are present, thereby increasing the systematic shifts associated with ion motion. For the most efficient cooling of Ar^{13+} we use Be^+ as it has the highest charge-to-mass ratio of any ion which has a suitable structure for laser cooling. Nevertheless, the mismatch to Ar^{13+} leads to a reduction in the cooling rate by around four orders of magnitude for two of the six motional modes of the ion crystal, essentially prohibiting efficient cooling of these modes using the Be^+ ion and potentially leading to a large second-order Doppler shift for the clock unless an alternative cooling technique could be found.

As the amplitude of motion for the Be^+ ion in the two modes is so low, it is not possible to cool the two problematic modes to their ground states using the standard techniques described in Sec. III as the sidebands are too

weak to be observed using the Be^+ ion. These sidebands are however clearly visible using the HCI, which has a much greater amplitude of oscillation in these modes. This allows us to apply a process referred to as algorithmic cooling. This is a quantum protocol that coherently transfers energy out of the poorly cooled modes into the mode used for the quantum logic operations, which can then easily be cooled using the Be^+ ion. This procedure was inspired by quantum logic spectroscopy and bears many similarities.

To perform the algorithmic cooling, we modify the first pulse of the quantum logic sequence to address the red sideband of one of the poorly cooled modes, transferring the motional excitation to an electronic excitation of the HCI. The rest of the quantum logic sequence is then followed as normal, which transfers the electronic excitation of the HCI into a shared motional excitation of the ion crystal, with the final step removing this phonon from the ion crystal. The result is that both ions are once again in their electronic ground states, the motional mode used for quantum logic is returned to its ground state, and a phonon has been removed from one of the poorly-cooled modes.

In this manner, we are able to prepare and maintain the two problematic modes close to their ground states, the fundamental limit to how cold a trapped ion can become, and equivalent to a temperature below 200 μK. Combined with using standard methods to cool the other modes of the ion crystal to their ground states, this makes this the coldest HCI ever produced on Earth and suppresses the systematic uncertainty of the clock caused by the ion temperature to below the 10^{-18} level [16]. This was the final breakthrough that allowed optical-clock-like levels of systematic uncertainty to be reached with HCIs for the first time.

V. Conclusions

Highly charged ions are exciting candidates for references for next-generation atomic clocks owing to their reduced sensitivities to some common perturbing electric fields, along with having numerous applications for tests of fundamental physics. We have built and demonstrated the first optical atomic clock based using these species. A combination of sympathetic and algorithmic cooling allowed us to suppress the systematic uncertainty of the clock caused by the ion temperature to below the 10^{-18} level. We employed quantum logic spectroscopy to overcome the lack of a standard readout transition in the HCI and made improved measurements of the Landé g-factor and natural lifetime of the $^2P_{3/2}$ state of Ar^{13+}. Upcoming improvements to the experimental apparatus will allow a total fractional systematic uncertainty at the 10^{-18} level to be reached and demonstrate that HCI-based clocks can be competitive with or even surpass those based on singly charged and neutral atoms.

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