Coherent laser spectroscopy of highly charged ions using quantum logic

Like a microscope aimed at the quantum world, laser spectroscopy pursues ever higher resolving power. Every increase in resolution enables deeper insights into the subtle effects that all known fundamental interactions have on the atomic wavefunction. Advances in optical-frequency metrology have improved resolution drastically in the last three decades and have made laser spectroscopy an extremely sensitive tool for studying open physics questions, such as the nature of dark matter, the strength of parity violation and a possible violation of Einstein’s theory of relativity. However, only a few atomic and ionic species are currently within the reach of cutting-edge optical-frequency metrology. Expanding this field of exploration to systems with high sensitivity to such effects is therefore crucial. Owing to the very high binding energies of their outer electrons, highly charged ions (HCIs) are promising candidates for such fundamental tests. The fractional contributions to the electronic transition energies from special relativity, quantum electrodynamics (QED) and the nucleus are several orders of magnitude larger than those in neutral atoms. This renders them ideal systems for benchmarking the most advanced theories and calculations, which has repeatedly demonstrated via optical fluorescence spectroscopy in electron-beam ion traps (EBITs), X-ray spectroscopy in storage rings and ground-state g-factor studies in Penning traps. The hyperfine splitting of the 1s state in heavy hydrogen-like ions can even shift into the optical range, providing laser-accessible transitions (see, for example, refs. with nuclear-size contributions of the order of several per cent of the total transition energy.

It was realized recently that non-gravitational coupling of dark matter to ordinary matter would affect atomic energy levels and thus become observable in optical-clock comparisons as an apparent drift or modulation of the fine-structure constant \( \alpha \). HCIs offer narrow-linewidth optical transitions that are among the most sensitive to a possible variation of \( \alpha \) (ref. 1). In addition, their inherent insensitivity to external electric fields leads to considerably smaller systematic perturbations compared to neutral and singly charged atoms. This makes them potentially superior references for high-accuracy optical atomic clocks, with many proposed species reviewed in ref. 1. However, so far no experiment has performed laser spectroscopy at the required level of precision. The major limitation was set by the high temperature of a few million kelvins at which HCIs are produced and typically stored. This induces Doppler broadenings with full-width-at-half-maximum (FWHM) linewidths of several tens of gigahertz and corresponding line-centre uncertainties of a few hundreds of \( \alpha \) or modulation of the fine-structure constant \( \alpha \). HCIs offer narrow-linewidth optical transitions that are among the most sensitive to a possible variation of \( \alpha \) (ref. 1). In addition, their inherent insensitivity to external electric fields leads to considerably smaller systematic perturbations compared to neutral and singly charged atoms. This makes them potentially superior references for high-accuracy optical atomic clocks, with many proposed species reviewed in ref. 1. However, so far no experiment has performed laser spectroscopy at the required level of precision. The major limitation was set by the high temperature of a few million kelvins at which HCIs are produced and typically stored. This induces Doppler broadenings with full-width-at-half-maximum (FWHM) linewidths of several tens of gigahertz and corresponding line-centre uncertainties of a few hundreds of gigahertz in the best cases. Because HCIs generally do not offer suitable transitions for direct laser cooling, sympathetic cooling of multiple HCIs by laser-cooled \(^{13} \text{Be} \) ions was implemented in a Penning trap at the Lawrence Livermore National Laboratory, reaching an ion temperature of around 4 K. More recently, the Cryogenic Paul Trap Experiment demonstrated reliable Coulomb crystallization of single \(^{40} \text{Ar}^{13+} \) ions in a crystal of many \(^{13} \text{Be} \) ions. Sympathetic Doppler cooling down to the 10-mK level and two-ion crystal preparation paved the way for high-accuracy spectroscopy. Even so, spectroscopy of narrow transitions in single ions requires efficient state detection on a different, fast-cycling transition, which is typically also used for laser cooling. If such a transition is not available, quantum logic spectroscopy (QLS) can be employed. In QLS, the ‘spectroscopy ion’ (in
cooled and finally co-crystallized with $^{9}\text{Be}^+$. It appears as a large dark void (see also Extended Data Figs. 1, 2). In brief, argon HCIs are produced by a single $^{40}\text{Ar}^{13+}$ ion is injected along the crystal axis, sympathetically cooled and finally co-crystallized with $^{9}\text{Be}^+$. It appears as a large dark void owing to the repulsion of the $^{9}\text{Be}^+$ by the high charge state. Excess $^{9}\text{Be}^+$ ions are removed by modulating the Paul trap radio-frequency potential in the absence of laser cooling, resulting in heating and ion losses. Finally, the $^{40}\text{Ar}^{13+}$-$^{9}\text{Be}^+$ two-ion crystal is prepared.

This technique and variations thereof have been successfully employed for optical atomic clocks based on $^{40}\text{Ar}^{13+}$, for internal state detection and spectroscopy of molecular ions$^{28,29}$ and for spectroscopy of broad transitions in atomic ions$^{30,31}$.

Here, we demonstrate QLS of an HCI—specifically, of the electric-dipole-forbidden transition between the $^2\text{P}_{1/2}$ and $^2\text{P}_{3/2}$ fine-structure levels of $^{40}\text{Ar}^{13+}$ at a wavelength of 441 nm, the most accurately known transition in any HCI$^\text{I}$. We achieve an FWHM well below 100 Hz, close to the natural linewidth of 17 Hz. Single line scans taken on a timescale of a few minutes determine the line centre with an uncertainty of less than 2 Hz. This corresponds to a fractional statistical uncertainty of $3 \times 10^{-15}$ for a transition frequency of approximately 680 THz and compares favourably to previous measurements taken over hours or even days, which achieved relative uncertainties$^8$ of $2 \times 10^{-5}$. Quantum logic-assisted state preparation of the $^{40}\text{Ar}^{13+}$ ion allows us to measure all six Zeeman components of the transition, which split up on a megahertz scale in a 160-$\mu$T magnetic quantization field. This allows us to determine the $g$-factor of the $^2\text{P}_{3/2}$ excited state with unprecedented accuracy. Furthermore, we demonstrate a quantum logic-assisted excited-state lifetime measurement.

**Preparation of a single HCI**

A detailed description of the experimental setup is given in Methods (see also Extended Data Figs. 1, 2). In brief, argon HCIs are produced by an EBIT, PTB-EBIT$^1$, and ejected from it in triggered bunches of ~200 ns duration with a mean kinetic energy of approximately 700 eV, where $q$ is the ion charge. The HCIs are guided to the spectroscopy trap through an ion optical beamline. Based on their time of flight, we select the $^{40}\text{Ar}^{13+}$ ions by rapidly switching a gate electrode. A pulsed gradient potential decelerates them electrodynamically$^3$ to about 146 V. Then, a single $^{40}\text{Ar}^{13+}$ ion stochastically enters the cryogenic linear Paul trap$^4$. The trap is globally biased to +138 V, thereby slowing the HCI down to 8 V upon entry. After passing through the trapping region, the HCI is reflected back by an electrode at the end of the Paul trap. A mirror electrode in front of the trap is switched up to prevent the ion from escaping again, thereby capturing the HCI in an oscillatory axial motion. The repeated crossing through a pre-prepared laser-cooled $^{9}\text{Be}^+$ Coulomb crystal within the trap dissipates the residual kinetic energy of the HCI. After sufficient sympathetic cooling, the $^{40}\text{Ar}^{13+}$ ion joins the Coulomb crystal. Excess $^{9}\text{Be}^+$ ions are removed until a two-ion crystal has been prepared (see Fig. 1). The entire preparation procedure of the two-ion crystal takes only a few minutes. The Paul trap is refrigerated to less than 5 K by a mechanically decoupled, closed-cycle cryostat to provide a vacuum below 10$^{-12}$ Pa (corresponding to a particle density of less than 20,000 cm$^{-3}$), thus suppressing charge-exchange collisions and achieving HCI storage times$^5$ of the order of 45 min.

**Ground-state cooling and quantum logic**

The implementation of QLS requires control and preparation of the motional and internal states of both ions using coherent laser pulses on carrier and sideband transitions. After the two-ion crystal preparation, the strong Coulomb coupling between the two ions results in joint motional modes within the trap. Sympathetic cooling, state preparation and QLS are performed by repeating the experimental sequence shown in Fig. 2. First, Doppler cooling and optical pumping on the $^{9}\text{Be}^+$ $^2\text{S}_{1/2}$ $^2\text{P}_{1/2}$ cycling transition (see Fig. 2a) are applied. The two axial normal
Coherent laser spectroscopy of 40Ar$^{13+}$

By applying this technique, we carried out the first coherent laser spectroscopy of an HCl. Figure 3a shows the excitation profile of the $m_{Jz} = -1/2$ to $m_{Jz} = -3/2$ Zeeman component of the 40Ar$^{13+}$ $P_{1/2} - P_{3/2}$ fine-structure transition. The blue curve shows a fit to the line by a Rabi line shape, as expected for the top-hat laser pulse of 12-ms duration. This pulse length results in a Fourier-limited linewidth of 65 Hz FWHM.

To suppress the residual noise, the laser is then further stabilized by phase-locking it to an ultrastable laser operating at a wavelength of 1.5 μm. The latter is itself stabilized to a cryogenic cavity made from crystalline silicon (referred to as Si2) \cite{ref}. This achieves a fractional frequency instability at the thermal noise limit of the cavity of $4 \times 10^{-17}$ at averaging times of 1–50 s. Using a femtosecond optical frequency comb as a transfer oscillator, we generate a virtual beatnote between the two lasers \cite{ref}. By demodulating it, we register their relative frequency and phase fluctuations, which are dominated by the substantially higher noise level of the 882-nm prestabilization cavity. The demodulated beatnote is used to generate a feedback signal for phase-locking the two lasers, which is applied to an acousto-optic modulator between the ECDL and the prestabilization cavity. The considerably lower bandwidth of the second locking stage ensures that the two loops do not compete with one another, but drifts and noise on the prestabilization cavity of up to kilohertz level are suppressed at the ECDL output, from which the spectroscopy light is derived. This suppresses the residual noise of the 882-nm clock laser, narrows its linewidth and reduces the daily drift to a level of about 10 Hz, which is dictated by Si2. The laser is frequency-doubled to 441 nm in an external enhancement cavity containing a periodically poled potassium titanyl phosphate crystal. Active power stabilization on a pulse-by-pulse basis at the ion trap is implemented for the clock, Doppler cooling and Raman lasers to achieve stable system parameters such as Rabi frequencies and a.c. Stark shifts.

**Fig. 3** Rabi spectroscopy and excited-state lifetime measurement. a, Clock laser frequency scan across Zeeman component 1 (see Fig. 4c) of the 40Ar$^{13+}$ fine-structure transition. The fixed probe time of 12 ms is longer than the excited-state lifetime of 9.6 ms. The line is fitted by a Rabi line shape (blue curve), reaching a Fourier-limited FWHM of about 65 Hz. b, On-resonance coherent excitation of this transition. The coherent state Rabi flopping signal (fitted by the red curve, which represents a damped sine with offset) exhibits a 2.2 ms rise-time (in which the maximum transferable population is transferred to the excited state) and decays exponentially with the excited-state lifetime (red-shaded envelope). The error bars in a and b represent the quantum projection noise of 255 measurements per data point. c, Excited-state lifetime measurement. Quantum logic sequences (see text) are carried out as a function of the wait time between carrier and red-sideband clock laser pulses. During the wait time, the excited state can decay spontaneously. From a three-parameter maximum-likelihood estimation, we obtain a lifetime of 9.97(27) ms, limited by the quantum projection noise of 1,100 measurements per data point (error bars). The black curve and grey-shaded area show the estimated exponential decay with the corresponding 1σ uncertainty band.
of 30–40 dB in the frequency range 60 Hz–1 kHz (ref. 34). The maximum fringe contrast of about 0.4 at this probe duration was mostly limited by the excited-state lifetime, with contributions from the ~90% fidelity of the sideband operations on the two ions, as well as from imperfect state preparation and detection. Frequency scans with longer probe times can in principle resolve the natural linewidth, albeit at a reduced excitation probability. Figure 3b shows the on-resonance excitation probability as a function of the probe time for a higher intensity of the clock laser. Under continuous illumination, Rabi flopping between the two electronic states is observed (fitted by the red curve). The coherence decays with the known excited-state lifetime of $9.573(\pm 4)_{\text{stat}}(\pm 12)_{\text{syst}}$ ms (where the statistical and systematic standard deviations are given in parentheses), indicated by the red-shaded exponential envelope of the fit. This measurement confirms coherence beyond this timescale for both the clock laser and the magnetic field.

We also performed a direct measurement of the excited-state lifetime. For this, a carrier π-pulse (step (1) in Fig. 2) with maximum laser intensity was applied, which populated the 40Ar$^{13+}$ excited state in about 16 μs. After a variable wait time, the full transfer sequence was performed, and the remaining 40Ar$^{13+}$ excited-state fraction was mapped onto the 9Be$^+$ qubit state (see also Methods). During the wait time, a series of ground-state-cooling pulses on both axial motional modes was applied every millisecond to keep the two-ion crystal in the motional ground state in the presence of anomalous heating of 12 and 29 phonons per second for the out-of-phase and in-phase modes, respectively. By incrementing the wait time in 1-ms steps, an axial mode temperature independent of the wait time was ensured. The observed exponential spontaneous decay of the excited state is shown in Fig. 3c and results in a lifetime of 9.97(27) ms. This is about 1.5 standard deviations longer than the more accurate experimental result of
Conclusions

We have cooled HCIs to the ground state of motion in a linear Paul trap, making them the coldest HCIs prepared in a laboratory so far. This enabled us to perform coherent, optical-clock-like laser spectroscopy of an electric-dipole-forbidden optical transition in an HCI using quantum logic, at a level of precision that is eight orders of magnitude higher than the previous state of the art. This proves the feasibility of hertz-level optical spectroscopy of HCIs and opens up this large class of atomic systems to the tools of cutting-edge frequency metrology and quantum information processing.

The determination of the absolute frequency of the $^{40}\text{Ar}^{13+}$ fine-structure transition with a fractional uncertainty of $3 \times 10^{-15}$ and even higher levels of precision requires further evaluation of systematic shifts, such as the small time dilation shift from the residual motion of the ion\(^{40}\) or the electric quadrupole shift\(^{49}\), which is typically suppressed in HCIs. By restricting measurements to the points of maximum frequency sensitivity of each line, frequency information can be obtained faster than when scanning the full line profiles, as demonstrated here, further reducing the statistical uncertainty at a given averaging time\(^{40}\). At the same time, averaging over the Zeeman components on second—rather than minute—timescales will suppress systematic uncertainties arising from drifting magnetic fields\(^{40}\).

The presented techniques are not limited to our proof-of-principle HCI, $^{40}\text{Ar}^{13+}$, but can be applied more generally to forbidden transitions in other HCIs. Several of the candidate species have properties that are even better suited for optical-clock experiments, including much longer excited-state lifetimes and suppressed systematic shifts. Certain HCIs are particularly sensitive to physics beyond the standard model, such as possible variations of the fine-structure constant\(^1\), or to effects arising from fundamental interactions. Particularly, HCIs allow the systematic study of relativistic effects in bound electronic systems and of bound-state QED along isoelectronic sequences at ultrahigh precision\(^2\).

Furthermore, the techniques that we have demonstrated here are not limited to the optical domain. Our work also unlocks the new frontiers of the vacuum ultraviolet and X-ray regimes for ultrahigh precision spectroscopy—regions of the electromagnetic spectrum that are incompatible with neutral and singly charged atoms owing to unavoidable photoionization. This will enable novel high-accuracy atomic clocks based on HCIs and unrivalled tests of fundamental physics.

We note that during the revision of the manuscript, a complementary work demonstrating incoherent laser spectroscopy of $^{40}\text{Ar}^{13+}$ in a Penning trap was published\(^{41}\).

Online content

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of authors contributing and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41586-020-1959-8.

1. Ludlow, A. D., Boyd, M. M., Ye, J., Peik, E. & Schmidt, P. O. Optical atomic clocks. Rev. Mod. Phys. 87, 637–701 (2015).
2. Safronova, M. S. et al. Search for new physics with atoms and molecules. Rev. Mod. Phys. 90, 025008 (2018).
3. Schiller, S. Hydrogen-like highly charged ions for tests of the fine structure independence of fundamental constants. Phys. Rev. Lett. 98, 180801 (2007).
4. Berengut, J., Dzuba, V. & Flambaum, V. Enhanced laboratory sensitivity to variation of the fine-structure constant using highly charged ions. Phys. Rev. Lett. 105, 120801 (2010).
5. Karlow, M. G., Safronova, M. S., Crespo López-Urrutia, J. R. & Schmidt, P. O. Highly charged ions: optical clocks and applications in fundamental physics. Rev. Mod. Phys. 90, 045005 (2018).
6. Draganić, I. et al. High precision wavelength measurements of QED-sensitive forbidden transitions in highly charged argon ions. Phys. Rev. Lett. 91, 183001 (2003).
7. Soria Orts, R. et al. Zeeman splitting and g factor of the $^{1}S_{2}+^{2}S_{2}^{p}$ $^{3}P_{3/2}$ and $^{3}P_{1/2}$ levels in Ar$^{13+}$. Phys. Rev. A 76, 052501 (2007)
**Methods**

**HCl production, transfer and recapture**

We show a top view of the laboratory setup in Extended Data Fig. 1 and a simplified schematic of the potential landscape in Extended Data Fig. 2a. HClIs are produced by electron impact ionization and stored by PTB-EBIT, a Heidelberg-type compact EBIT32. After extraction of ions in bunches, a beamline with multiple electrostatic elements is used to guide the ions towards the Paul trap and to manipulate their kinetic-energy distribution. Five segmented einzel lenses33 and an electrostatic double-focusing 90° deflector4 are employed for focusing and steering. A pair of pulsed drift tubes (following the approach described in ref. 33) is used for deceleration and pre-cooling, reducing the phase-space volume of the bunches. Downstream, two microchannel plate (MCP) detectors can be moved into the ion beam in front of and behind the Paul trap to optimize ion yield and beam transmission. The first MCP detector also features a retarding field analyser that is used to determine the mean kinetic energy and the energy spread of the ion bunches. Although this method of HCl production, transfer and recapture combining the EBIT, beamline and Paul trap can handle a large variety of elements and charge states, the following section refers specifically to the present case of optimized 40Ar13+ capture.

Highly charged argon ions are produced in a distribution of charge states using a 13-μA, 1-kV electron beam in the approximately 50-V-deep axial trapping potential of the EBIT. In each cycle, the central trap electrode is rapidly switched from about 450 V (for the aforementioned 50-V-deep trap) to a repulsive extraction potential of 700 V (200 V higher than the outer trap electrode potential) for a period of 200 ns at a rate of 4 Hz to eject the ions. The kinetic energy relative to the ground potential of the beamline (0 V), and thus the velocity of the extracted ions, depend on the total extraction potential of 700 V and on the ionic charge q, allowing separation of the different charge states by their different times of flight (Extended Data Fig. 2a, b). 40Ar13+ is selected with the help of an electrode of the third segmented einzel lens immediately behind the 90° deflector. This electrode acts as a gate by rapidly switching to a passing voltage at the 40Ar13+ arrival time, and back to a deflecting voltage after the ion passage. Thus, the trajectories of all other charge states are deflected away from the Paul trap. We measure a mean kinetic energy of 694 ± 7 V with respect to ground for the fast 40Ar13+ bunches using the retarding field analyser (Extended Data Fig. 2e). An associated axial energy spread of 32 μg/V was also determined. To decrease the mean kinetic energy and its spread to values more amenable for trapping and efficient cooling in the cryogenic Paul trap, we perform an electrodynamic deceleration step with the pair of pulsed drift tubes. By biasing them to approximately 510 V and 590 V before the extraction, a linear axial potential gradient is generated on the beamline axis between the two electrodes. Thus, when the ion bunch arrives at that position, about 9.7 μs after ion ejection, it is exposed to a mean potential of 550 V. Then, both drift tube potentials are rapidly grounded using a fast high-voltage switch. This slows down the ion bunch to a kinetic energy of 146 μg/V and reduces the axial energy spread to 13 μg/V (Extended Data Fig. 2f). The deceleration step also shortens the length of the ion bunches considerably, from about 5.2 cm to about 1.7 cm FWHM, while their temporal width is only slightly reduced. After passing through a final einzel lens and an unbiased mirror tube, the 40Ar13+ ions enter the Paul trap. The trap voltages are commonly biased to 138 V to accomplish the axial electrostatic deceleration potential of about 12 V (above the biased ground of 138 V). In the meantime (17.1 μs after initial ion extraction from the EBIT), the mirror tube at the entrance of the Paul trap is rapidly switched up to a confining axial electrostatic potential to complete the capture of 40Ar13+. Then the trap remains closed for 1.9 s, during which the HClIs can dissipate their residual kinetic energy by repeated interactions with the laser-cooled “Be ions. If these steps are successful for an 40Ar13+ ion, it joins the “Be Coulomb crystal (Fig. 1). Otherwise, the mirror tube potential is lowered again to let the next HCl bunch enter the Paul trap. This whole recapture process is rather efficient and succeeds in less than 30 s on average.

**Excited-state lifetime measurement**

The data for the lifetime measurement were acquired from 440 measurements, each of which includes 100 experimental realizations, adding up to a total measurement time of about two hours. Eleven measurements were averaged for every single wait time, with the error bars in Fig. 3c indicating the quantum projection noise of 1,100 experimental implementations. To cancel the effects of parameter drifts on the observed signal, the wait time was scanned in a pseudo-random sequence.

Drifts of the atomic resonance frequencies could lead to systematic variations in the detected excitation probabilities. The shortest achievable π-times, 16 μs for the initial HCl excitation and 225 μs for the HCl sideband transition, lead to an interaction broadening of the respective lines of 62 kHz and 4.4 kHz, respectively. Our typical short-term magnetic-field fluctuations lead to line shifts of <10 Hz level, and thus affect the measured excited-state population of the order of 10−4. The axial trap frequency has fluctuations below 100 Hz over the course of a day. The distribution of data points for a given wait time is consistent with the expected quantum projection noise, thereby ruling out systematic drifts at the level of the statistical uncertainty.

The clock laser pulses are generated by the first diffraction order of an acousto-optic modulator (AOM). Despite the typical 100-dB level of extinction of the radio-frequency drive power provided by an active radio-frequency switch, the optical extinction ratio does not reach this level owing to scattered light within the AOM crystal. However, this leaked light is unshifted by the AOM and therefore detuned from the ion resonance by the radio-frequency drive frequency of about 200 MHz, or 107 natural linewidths. This alone reduces the de-excitation probability by approximately 14 orders of magnitude.

Spontaneous decay of the HCl on the red sideband is suppressed as the square of the Lamb–Dicke parameter, η2 = 0.01. However, residual decay on this sideband leads to heating of the motional mode and may thus appear as spurious excitation in the quantum logic detection. A few sideband cooling pulses applied immediately before the quantum logic transfer pulse suppress this effect by returning the crystal to its ground state. Off-resonant depumping of the excited state of 40Ar13+ by the “Be lasers is negligible because of the narrow natural linewidth and the large detuning. Collisional dehshelving, as discussed in refs. 35,36, is absent in this experiment owing to the extremely high vacuum. Furthermore, collisions of an HCl with a neutral particle probably lead to charge exchange and total, but inconsequential, ion loss.

**g-factor evaluation**

The 40Ar13+- “Be excited-state g-factor, denoted as g^Be2, is determined by a linear fit of the Zeeman substate energy shifts. We use the well-known ground-state g-factor of the clock transition from a recent high-accuracy measurement15 to operate a co-magnetometer and measure the magnetic field by an appropriate combination of the Zeeman components.
The energy shifts $\Delta E_{3/2, m_{3/2}} = m_{3/2} \mu_B B / h$ of the Zeeman substates of the excited $^2P_{3/2}$ state that are due to an external magnetic field $B$ are obtained from the measured Zeeman shifts $f_i$ (in units of frequency) of the six Zeeman components (ranging from 1 to 6, according to Fig. 4c) and analogously the shifts $\Delta E_{1/2, m_{1/2}}$ of the $^2P_{1/2}$ Zeeman substates. $h$ and $\mu_B$ are the Planck constant and the Bohr magneton, respectively. The shifts are referenced with respect to the degenerate line/level centres. One then obtains

$$\frac{\Delta E_{3/2, m_{3/2}}}{h} = f_i + \frac{\Delta E_{1/2, m_{1/2}}}{h}$$

$$m_{3/2} \mu_B B / h = f_i + m_{1/2} \mu_B B / h$$

$B$ is eliminated from the above equation by using the four inner Zeeman components 2–5, which are less sensitive to magnetic-field fluctuations than the two outer ones. Components $f_1$ and $f_2$ share the common excited state $m_{3/2} = -1/2$ (see Fig. 4c), and therefore their difference yields the ground-state Zeeman splitting directly, without relying on the excited-state $g$-factor. Using the known ground-state $g$-factor $g_{1/2}$ from the work of Arapoglou et al.\textsuperscript{17}, we obtain the magnetic field

$$B_i = h (f_i - f_2) / g_{1/2} \mu_B$$

Similarly, components $f_3$ and $f_4$ share the excited state with $m_{3/2} = +1/2$, and we acquire a second measurement of

$$B_2 = h (f_4 - f_3) / g_{1/2} \mu_B$$

Introducing $U = f_3 - f_4 + f_1 - f_2$ for simplicity, we average the magnetic field $B$ from these two relations to reduce the uncertainty

$$B = \frac{B_1 + B_2}{2} = \frac{h U}{2 g_{1/2} \mu_B}$$

This expression is inserted into equation (2) to obtain

$$y_i(m_{3/2}) = \frac{g_{3/2}}{2 g_{1/2}} \frac{U}{m_{3/2}} = f_i + m_{3/2} \frac{U}{2}$$

On the right-hand side of the equation, the measured shifts of the excited Zeeman substates are given, which fulfil a linear relation in $m_{3/2}$ (left-hand side of the equation). A linear fit (see black line in Fig. 4b) of the form

$$y_i(m_{3/2}) = a m_{3/2} + b$$

with offset $b$ to account for the global frequency offset in the measured $f_i$ allows us to determine the excited-state $g$-factor $g_{3/2}$ from the slope $a$

$$g_{3/2} = \frac{2 g_{1/2} a}{U}$$

The uncertainties $\sigma_y$ of the excited Zeeman substates are obtained from the right-hand side of equation (6) by expressing $U$ again as $U = f_3 - f_4 + f_1 - f_2$, followed by standard uncertainty propagation with the independently measured $f_i$

$$\sigma_y = \sum_j \left( \frac{\partial y}{\partial f_j} \sigma_{f_j} \right)^2$$

The uncertainties $\sigma_y$ of the Zeeman components depend on the statistical uncertainty of the line centre from the fit $f_{\text{fit}}$, (fitting the lines by Rabi line shapes) and the relative systematic magnetic-field uncertainty $\sigma_B / B$. The latter is time-dependent and is estimated from the observed magnetic-field stability measured previously by using the $^9$Be qubit transition frequency (see ref. 34 for details) to be $4.1 \times 10^{-4}$ (measurement 1) and $3.2 \times 10^{-4}$ (measurements 2 and 3) on relevant timescales. Accordingly, one has

$$\sigma_{f_i} = \sqrt{\sigma_{f_{\text{fit}}}^2 + \sigma_B^2 / B^2}$$

The linear fit shown in Fig. 4b is weighted with the $\sigma_y$ uncertainties, which are displayed in the lower panel. For completeness, we state the fit offsets for the three sets of measurements: $B = -17(3)$ Hz, $-45(2)$ Hz and $-30(2)$ Hz. The reduced $\chi^2$ of the linear fits are 1.45, 0.57 and 0.21.

To estimate the uncertainty of $g_{3/2}$, we replace $a$ and $U$ in equation (8) by their analytical expressions, $a = \langle (m_{3/2}, y_i) \rangle / \sigma_{y_{3/2}}^2$ is obtained from the closed-form solution of a linear fit. The $y_i$ values are given by the right-hand side of equation (6), and $U = f_3 - f_4 + f_1 - f_2$. We can neglect the parts-per-billion uncertainty of the experimental result $g_{1/2} = 0.6636485432(93)$ from the very recent Penning trap measurement\textsuperscript{17} because it is more than three orders of magnitude smaller than our experimental uncertainties in the 25,000-times-weaker magnetic field. Finally, the only uncertainties are introduced by the independently measured $f_i$. Thus, the uncertainty $\sigma_{g_{3/2}}$ is obtained from the typical formula of uncertainty propagation

$$\sigma_{g_{3/2}} = \sqrt{\sum_i \left( \frac{\partial g_{3/2}}{\partial f_i} \sigma_{f_i} \right)^2}$$

The calculated $g_{3/2}$ values are $1.3322989(19)_{\text{stat}}(56)_{\text{syst}}$, $1.3322897(23)_{\text{stat}}(43)_{\text{syst}}$ and $1.3322828(24)_{\text{stat}}(43)_{\text{syst}}$ for the three measurement sets obtained on two different days, where we have stated the statistical and systematic uncertainties separately. The results are shown in Fig. 5 together with recent calculations. The uncertainties of the individual measurements are the root of the sum of the squared statistical and systematic uncertainties. The measurements agree within their uncertainties, and the largest deviation between measurement 1 and the weighted average is 1.6 standard deviations. We obtain the weighted average $g_{3/2} = 1.3322895(13)_{\text{stat}}(56)_{\text{syst}}$, where we have combined the statistical uncertainties and stated the largest systematic uncertainty of the individual measurements as a conservative estimate for the systematic uncertainty of the average.

**Data availability**

The datasets generated and analysed during this study are available from the corresponding author upon reasonable request.

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53. Mandal, P., Sikler, G. & Mukherjee, M. Simulation study and analysis of a compact einzel lens-deflector for low energy ion beam. J. Instrum. 6, P02004 (2011).
54. Kreckel, H. et al. A simple double-focusing electrostatic ion beam deflector. Rev. Sci. Instrum. 81, 063304 (2010).
55. Barton, P. A. et al. Measurement of the lifetime of the metastable $^5$D$_{5/2}$ state in $^{40}$Ca. Phys. Rev. A 62, 012509 (2000).
56. Letchumanan, V., Wilson, M., Gall, P. & Sinclair, A. Lifetime measurement of the metastable $4d^4D_{5/2}$ state in $^{40}$Ca using a single trapped ion. Phys. Rev. A 72, 012509 (2005).

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Extended Data Fig. 1 | Experimental setup. a, Top view of the setup. The apparatus extends over two rooms separated by an acoustically insulating wall. Inside the 'machine room' on the right-hand side, HCIs are produced in an EBIT\textsuperscript{22} and extracted as ion bunches along the ion beam trajectory (blue line) through a deceleration beamline. At the laser laboratory (left side), they are axially injected into a cryogenic linear Paul trap\textsuperscript{34}, which is mounted on a pneumatically floating optical table (grey-shaded). The Paul trap is refrigerated by a vibrationally decoupled pulse tube cryocooler\textsuperscript{35} located in the machine room. The beamline is composed of several ion optical elements: five segmented einzel lenses and an electrostatic 90° deflector for guiding and focusing the ions, a pair of pulsed drift tubes for deceleration, and six cylindrical electrodes arranged in line in front of and behind the Paul trap. Charge-state separation is accomplished by the different times of flight through the beamline. One electrode of the third segmented einzel lens is used as a gate to select the desired charge state. An MCP detector in front of the Paul trap includes two fine stainless-steel meshes that apply a well defined retarding field, and allows the measurement of the kinetic-energy distribution of the ion bunches (see also Extended Data Fig. 2e, f). A second MCP detector behind the Paul trap is used to optimize the ion beam transmission through the Paul trap.

b, Magnified side view of the cryogenic Paul trap region. The trap (photograph) is shown with the two adjacent electrostatic tubes. The left one (mirror tube) at the entrance of the Paul trap is used to capture the HCIs by rapidly switching to a confining potential once the HCIs have passed it. Photograph: Physikalisch-Technische Bundesanstalt.
Extended Data Fig. 2 | HCI extraction and transfer. a, Simplified illustration of the electrostatic potential used for the ⁴⁰Ar⁺⁺⁺⁺ transfer from the EBIT to the Paul trap. The entire ion inventory stored in the EBIT, with its charge-state distribution displayed as grey-shaded, is ejected by switching the axial trap to a repulsive potential. The charge states separate owing to their distinct initial kinetic energies. ⁴⁰Ar⁺⁺⁺⁺ ions (red) are selected by an electrode used as a gate (not shown). The fast ⁴⁰Ar⁺⁺⁺⁺ bunch is then slowed down upon entering the pulsed drift tubes. Having arrived there at the centre of a linear potential gradient, the electrode potentials are rapidly switched to ground, and a slower ⁴⁰Ar⁺⁺⁺⁺ bunch leaves the pulsed drift tubes. At the Paul trap, the ions are further decelerated by an electrostatic potential and enter the trapping region with a reduced residual kinetic energy of 5qV to 10qV. They then pass a Coulomb crystal of Be⁺ ions and are reflected by an electrostatic endcap electrode biased to a potential of about 12V above the biased common ground. Meanwhile, an electrostatic mirror tube in front of the Paul trap has been switched up to a confining potential at which ⁴⁰Ar⁺⁺⁺⁺ is unable to escape the Paul trap. This causes an oscillatory motion along the trap axis. Through repeated interactions with the laser-cooled Be⁺ ions, ⁴⁰Ar⁺⁺⁺⁺ dissipates its residual kinetic energy and joins the Coulomb crystal. b, Normalized ion yield as a function of the time of flight after ion ejection from the EBIT, measured by the first MCP detector in front of the Paul trap. The black curve shows the entire charge-state distribution, with Ar charge states from +7 through +15. Using the gate electrode, ⁴⁰Ar⁺⁺⁺⁺ is chosen for passage, as shown by the red curve. a.u., arbitrary units. c, d, Normalized ⁴⁰Ar⁺⁺⁺⁺ bunches as a function of time and position along the beamline axis (averaged over 16 shots). The FWHM of the fast bunch is about 250 ns (c) and that of the slow bunch is about 185 ns (d).  

e, f, Normalized kinetic-energy distributions of the ⁴⁰Ar⁺⁺⁺⁺ bunches along the beamline axis: fast bunch (e) and slow bunch after deceleration and phase-space cooling using the pulsed drift tubes (f). The red circles show the integrated ion yield of an averaged ⁴⁰Ar⁺⁺⁺⁺ bunch (16 shots) for a given retardation potential, measured by the retarding-field analyser. A Gaussian error function (red line) was fitted to the data and differentiated to obtain the Gaussian energy distribution (blue line) to show the mean kinetic energy and longitudinal energy spread.
Extended Data Fig. 3 | Quantum logic-assisted internal state preparation of Ar$^{+}$. The $m_{l_{z}} = -1/2$ state of the $^3P_{3/2}$ level is deterministically populated by a series of five clock laser sideband π-pulses (1–5), which excite the two-ion crystal from the motional ground state $|0\rangle_{m}$ (solid lines) into the excited state $|1\rangle_{m}$ (dashed lines). By means of Raman sideband cooling pulses acting on the $^9$Be ion, the crystal is returned to the motional ground state after each transfer pulse. This ensures unidirectional optical pumping. To increase the state-preparation efficiency, this sequence is repeated four times. The other Zeeman ground state ($^3P_{1/2}, m_{l_{z}} = +1/2$) is prepared in an analogous manner.