Energy of the $^{229}$Th nuclear clock transition

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Owing to its low excitation energy and long radiative lifetime, the first excited isomeric state of thorium-$^{229}$, $^{229}\text{m}^{9}\text{Th}$, can be optically controlled by a laser$^{1-8}$ and is an ideal candidate for the creation of a nuclear optical clock$^{9}$, which is expected to complement and outperform current electronic-shell-based atomic clocks$^4$. A nuclear clock will have various applications—such as in relativistic geodesy$^6$, dark matter research$^9$ and the observation of potential temporal variations of fundamental constants$^{10,11}$—but its development has so far been impeded by the imprecise knowledge of the energy of $^{229}\text{m}^{9}\text{Th}$. Here we report a direct measurement of the transition energy of this isomeric state to the ground state with an uncertainty of 0.17 electronvolts (one standard deviation) using spectroscopy of the internal conversion electrons emitted in flight during the decay of neutral $^{229}\text{m}^{9}\text{Th}$ atoms. The energy of the transition between the ground state and the first excited state corresponds to a wavelength of 149.7 ± 3.1 nanometres, which is accessible by laser spectroscopy through high-harmonic generation. Our method combines nuclear and atomic physics measurements to advance precision metrology, and our findings are expected to facilitate the application of high-resolution laser spectroscopy on nuclei and to enable the development of a nuclear optical clock of unprecedented accuracy.

The first excited isomeric state of $^{229}\text{Th}$, denoted as $^{229}\text{m}^{9}\text{Th}$, has the lowest excitation energy of all known nuclear states. Whereas typical transition energies in nuclear physics range from several kiloelectronvolts to the mega-electronvolt scale, the excitation energy of $^{229}\text{m}^{9}\text{Th}$ is in the electronvolt region$^{6-11}$. $^{229}\text{m}^{9}\text{Th}$ has a long radiative lifetime, possibly as high as $10^4$ s (refs. 12,13), resulting in a narrow relative linewidth of $\Delta E/E \approx 10^{-20}$.

These properties make $^{229}\text{m}^{9}\text{Th}$ the only candidate for a new type of optical clock that uses a nuclear transition, instead of an electronic transition, for time measurement$^4$. The single-ion nuclear optical clock is considered a complementary technology to existing atomic clocks and is expected to achieve a systematic frequency uncertainty of $1.5 \times 10^{-19}$ (ref. 4), thereby reaching and even surpassing existing atomic-clock technology. Moreover, the possibility to dope $^{229}\text{Th}$ nuclei into a vacuum-ultraviolet-transparent host crystal could enable the operation of a solid-state optical clock, which would benefit from a high density of addressable nuclei$^4$.

Research on $^{229}\text{m}^{9}\text{Th}$ over the past years includes the theoretical prediction of its isomeric properties$^{12,13,15}$, as well as experimental work aiming at further characterization of the isomer$^{16-28}$. Recently, controlled population of the $^{229}\text{Th}$ isomer was achieved by exciting a higher-lying nuclear state in $^{229}\text{Th}$ with synchrotron radiation$^{27}$. To date, the energy of $^{229}\text{m}^{9}\text{Th}$ has been exclusively inferred from indirect measurements$^{1,8-11}$ probing the $\gamma$-ray emission from higher-lying excited states populating the ground and isomeric states. The latest of these measurements$^{11}$ constrained the energy to 7.8 ± 0.5 eV (all uncertainties are one standard deviation). The uncertainty of this result is due to the energy resolution of the detectors. The direct detection of the isomeric decay in the internal conversion decay channel$^9$ has been used in the determination of the isomeric half-life in neutral, surface-bound $^{229}\text{m}^{9}\text{Th}$ atoms$^{28}$. Additionally, laser spectroscopic characterization of the isomeric state has been recently achieved$^{29}$.

In this Letter we report the first energy measurement of the $^{229}\text{Th}$ nuclear isomer and the direct detection of one of the products of the isomer-to-ground-state decay. We use the internal conversion decay of the isomeric excited state in a $^{229}\text{Th}$ atom. In this decay channel, the nuclear energy is transferred to the electronic shell through ionization of the atom. The kinetic energy of the emitted electron can be measured, which allows us to deduce the energy of the isomer. This approach has the advantage that it relies on the atomic structure of the Th atom, which is known with high precision and is on the same energy scale as that of the isomer. Our results are sufficiently precise to enable the use of a laser for the direct excitation of the isomeric state of $^{229}\text{Th}$ and pave the way for the development of a nuclear clock.

In our experimental setup, $^{229}\text{m}^{9}\text{Th}$ was generated by a 2% decay branch in the $\alpha$ decay of $^{235}\text{U}$. The setup used to produce the thorium ion beam and for bunch formation is described in refs. 2,28 and shown in Fig. 1. Bunches containing 400 $^{229}\text{m}^{9}\text{Th}^{3+}$ ions were generated at a repetition rate of 10 Hz. As this setup did not allow us to measure the kinetic energy of internal conversion electrons, it was extended by an ion-neutralizer (inset of Fig. 1, Extended Data Fig. 1) and a magnetic-bottle-type retarding-field electron spectrometer (Fig. 1, Extended Data Fig. 2). The ions were guided by four focusing electrodes onto two layers of graphene set to $-300 \text{V}$; the graphene layers were supported by lacy carbon on a copper transmission electron microscopy grid, 300 mesh, with 50% transmission. When passing through these foils, the ions were neutralized and continued their flight as neutral atoms (Fig. 1). The extraction and neutralization of thorium ions was monitored by a multi-channel plate (MCP) detector placed on the central beam axis (MCP II in Fig. 1 and Extended Data Figs. 3, 4). In contrast to the long lifetime of the isomeric state in the $\text{Th}^{3+}$ ions, its lifetime in neutral thorium is about $10^4$ times shorter because the internal conversion channel opens up energetically owing to the availability of more loosely bound valence electrons. Therefore, the isomer decays within microseconds$^{28}$ by emitting an electron. The kinetic energy of the electron was measured without any surface influences (such as those present in refs. 2,28), using a magnetic-bottle-type retarding-field electron spectrometer$^{29}$ placed at 90° off-axis behind the graphene (Fig. 1). Secondary particles—such as electrons generated when the ions passed through the graphene or ions that were not fully neutralized—were removed by bending electrodes placed between the point of neutralization and the spectrometer (inset of Fig. 1). The detected electrons could be unambiguously attributed to the nuclear decay of $^{229}\text{m}^{9}\text{Th}$. Comparative measurements with $^{230}\text{Th}$, which has no such isomer, that were performed under identical conditions did not show a signal (Extended Data Fig. 5). Therefore, we can safely exclude $^{229}\text{Th}$ atoms in the nuclear ground state, secondary electrons, and auto-ionizing states populated in the neutralization process as the origin of the measured signal.

The spectrometer$^{29}$ consisted of a strong permanent magnet that generated an inhomogeneous magnetic field (about 200 mT in the area above the magnet) and a solenoid coil that generated a weak
homogeneous field (typically 2 mT). Electrons emitted in a spherical region with a radius of about 1 mm above the permanent magnet were collected by the magnetic field and directed towards the solenoid coil. In this way a collimated electron beam was generated. The kinetic energy of the electrons was analysed by retarding fields, which were applied to a gold grid (electroformed gold mesh, transmission 90%) that was surrounded by ring electrodes to ensure a smooth gradient and terminated by additional gold grids (Extended Data Fig. 2). Electrons with kinetic energies sufficient to overcome the applied retarding voltage were counted with an MCP detector (MCP I in Fig. 1). This resulted in an integrated spectrum that decreased monotonically with increasing retarding voltage and in which transition lines were visible as edges. The spectrometer reached a full-width-at-half-maximum resolution ($\Delta E/E$) of about 3% (Extended Data Fig. 6) and its performance and calibration were verified regularly during the measurements. The integrated spectrum of the internal conversion electrons, as measured in a graphene foil. They continue their flight as atoms towards the electron spectrometer while decaying via internal conversion. Bending electrodes (to which a d.c. field is applied) are placed between the graphene layer and the entrance of the spectrometer to prevent charged particles from entering the spectrometer. Internal conversion electrons, which are emitted above a strong permanent magnet, are collected and guided towards a retarding-field unit placed in a solenoid coil. The kinetic energy of the electrons can be analysed by applying a retarding voltage to a grid and counting the electrons that reach MCP I.

**Fig. 1** | Experimental setup used for the determination of the isomeric energy of $^{229}$mTh. The experimental setup comprises three parts: the ion extraction part (dashed contour), the neutralization part (inset) and the electron spectrometer setup (right). A $^{233}$U source is placed in a buffer-gas stopping cell and $^{229}$mTh recoil ions are thermalized and guided with a funnel-shaped ring electrode structure (radiofrequency and d.c. funnel) towards a de Laval exit nozzle. The ions are then injected into a segmented radiofrequency quadrupole structure that allows the formation of ion bunches. A quadrupole mass separator guides the ions to focusing electrodes that collimate the ion beam, and the ions are then neutralized with kinetic energies sufficient to overcome the applied retarding voltage were counted with an MCP detector (MCP I in Fig. 1). This resulted in an integrated spectrum that decreased monotonically with increasing retarding voltage and in which transition lines were visible as edges. The spectrometer reached a full-width-at-half-maximum resolution ($\Delta E/E$) of about 3% (Extended Data Fig. 6) and its performance and calibration were verified regularly during the measurements. The integrated spectrum of the internal conversion electrons, as measured in a graphene foil. They continue their flight as atoms towards the electron spectrometer while decaying via internal conversion. Bending electrodes (to which a d.c. field is applied) are placed between the graphene layer and the entrance of the spectrometer to prevent charged particles from entering the spectrometer. Internal conversion electrons, which are emitted above a strong permanent magnet, are collected and guided towards a retarding-field unit placed in a solenoid coil. The kinetic energy of the electrons can be analysed by applying a retarding voltage to a grid and counting the electrons that reach MCP I.

**Fig. 2** | Measured and predicted internal conversion electron spectra. a. The internal conversion electron spectrum, as measured with the magnetic bottle retarding-field analyser. Error bars indicate one standard deviation (which is given by the square root of the measured counts). b. Expected internal conversion electron energy spectrum. Thin blue lines show simulated internal conversion spectra (with a simulated isomeric energy of $E_{\text{isom}} = 8.3$ eV) from 500 different arbitrary selections of five initial excited states. The plot shows the fluctuation of internal conversion electron spectra under the influence of different excited-state distributions. Dark blue markers show an exemplary spectrum, together with the fitted equivalent complementary error function (red line). c. Scattering of the reference energy $E_0$ around a central value for different initial-state distributions. To obtain the reference energy values plotted in the histogram, 20,000 population distributions were generated from different sets of five initial excited states. The $1\sigma$ width of the distribution defines the systematic uncertainty of the analysis method.
by the electron spectrometer, is shown in Fig. 2a. Data were collected for three days continuously, and the applied voltages were monitored throughout the measurement (Extended Data Fig. 7).

The neutralization process of the original Th ion in the graphene layer and after separation from the graphene has to be considered to determine the isomeric energy. Accordingly, all electronic states of Th that have come into resonance with the graphene valence band during and after transit may be occupied details on the neutralization process are provided in Methods and Extended Data Fig. 8.) Thus, internal conversion occurs through interaction with electrons from excited electronic states (listed in Extended Data Table 1). The kinetic energy of an electron, $E_{\text{kin}}$, that is emitted during internal conversion is connected to the energy of the isomer, $E_{\text{is}}$, via $E_{\text{kin}} = E_{\text{is}} - 1 \text{P} + E_{\text{f}} - E_{\text{i}}$, where 1P is the thorium ionization potential, $E_{\text{f}}$ is the excitation energy of the Th atom undergoing internal conversion and $E_{\text{i}}$ is the final electronic state energy of the Th ion generated during the internal conversion process. The ionization potential of thorium is 6.308 ± 0.003 eV (ref. 33) and the uncertainty of this value does not increase the uncertainty of our energy measurement. The pairs of initial and final states are subject to selection rules, and each initial state generates a spectrum from the standard deviation of the normal distribution shown in Fig. 2c from 3.5 eV within one standard deviation. On the basis of our findings, we determine that the wavelength required for precision laser spectroscopy can be reached by high-harmonic generation (for example, the 7th harmonic of an Yb-doped fibre laser). Our improved precision reduces the time needed for laser-based scanning in search for the nuclear excitation, for example, to less than one day using the scheme proposed in ref. 26. This paves the way for precision nuclear spectroscopy and for the development of a nuclear optical clock, which is expected to have major implications for future frequency metrology.

Online content

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METHODS

Experimental setup. The experimental setup consists of three parts, dedicated to: the formation of a 229(m)Th ion beam from a 235U α-source, the neutralization of these ions and the measurement of the kinetic energy of the internal conversion electrons.

229Th ion beam formation. The setup used for the generation of an isotopically pure 229Th–Th ion beam is described in detail in refs. 2,28,34,35. The experimental setup (Fig. 1) contains a 235U α-source36 (900 kg, diameter of 90 mm) placed in a buffer-gas-stopping cell filled with ultrapure helium at a pressure of 32 mbar. 229Th recoils are stopped and thermalized in the buffer gas and guided with a radiofrequency and d.c. funnel towards a de Laval nozzle that connects the buffer-gas stopping cell with the subsequent vacuum chamber (pumped differentially to 5 × 10⁻⁵ mbar). This chamber houses a segmented radiofrequency quadrupole (RFQ) that serves as an ion guide and buncher. Ion bunches are formed in the next-to-last quadrupole segment, where a trap is created to store and cool the ions at a potential of ±15 V. After cooling, the ion bunches are injected into a subsequent quadrupole mass separator (QMS)37, which is biased at −2 V. Bunches are generated at a repetition rate of 10 Hz and contain about 400 229Th ions (about 200 229Th ions) each with a kinetic energy of 51 eV (34 eV).

The QMS allows us to select ions with a specific mass-to-charge ratio. In the experiments described here, however, it is used as an ion guide, and Th ions in different charge states are separated according to their time of flight. The distance from the RFQ buncher to the detection region is about 400 mm, and the time of flight (from the release to the detection of the ion bunches) is 80 μs. A strong permanent magnet (diameter 10 mm, height 10 mm; VACODYM, Vacuumshmelze) with the subsequent vacuum chamber (pumped differentially to 5 × 10⁻⁵ mbar) is used to separate different charge states according to their time of flight. The discharge of the two RFQ-buncher electrodes (which have a potential difference of ΔU = ±15 V and a separation of 5 mm) is measured. The measured flight times are consistent with our estimates, which allows us to perform experiments with 229Th and 229Th ions in parallel. Because the experiment is optimized for 229Th ions, 229Th ions are used only to check for consistency.

Ion neutralization. The generation of a collimated atom beam is critical for achieving a high count rate of internal conversion electrons in the spectrometer. The 229Th ions are generated by sending 229mTh ions through a dual layer of graphene (EM-Tec, Micro to Nano). At the point of neutralization, the ion beam is collimated by adjusting four focusing electrodes so that the count rate of the atoms (generated from 229Th ions) measured with an MCP detector placed behind the neutralization region is maximized. The graphene layers are attached to a transmission electron microscopy (TEM) grid set to −300 V that accelerates the ions. After neutralization the atoms retain the kinetic energy that the ions had immediately before neutralization (945 eV for neutralized Th ions). The bending electrodes are set to +100 V and +1,800 V to ensure that secondary electrons generated by the ions in the graphene, as well as ions that were not neutralized, cannot enter the spectrometer region. The neutralization of 229mTh ions in our setup is discussed in detail in ref. 38.

Electron collection region. Special care was taken in the design of the electron collection region of the spectrometer. Sectional views of the setup are shown in Extended Data Fig. 1. To achieve good energy resolution, the d.c. electric fields from the deflection electrodes and the radiofrequency electric fields from the QMS need to be shielded. Therefore, a shielding grid is placed at the entrance of the spectrometer. To prevent generation of secondary electrons from atoms impinging on surfaces, material is removed from the central region above the strong permanent magnet. The distance between the magnetic coil and the retarding-field unit is shielded. Therefore, a shielding grid is placed at the entrance of the spectrometer. About 0.7% of the atoms decay within the collection region of the spectrometer after 570 ns. Transit through this region generates the required count rates for calibration. The calibrant used is argon, which emits electrons with energies of 5.28 eV (Ar 2P1/2) and 5.46 eV (Ar 2P3/2). The results of a measurement are shown in Extended Data Fig. 6a. The linearity of the spectrometer is demonstrated using photoelectrons emitted from molecular nitrogen/air. The kinetic energy of the electrons emitted from N₂ is in the range of 3 eV to 6 eV (refs. 40,41). The performance of the spectrometer in the energy region of interest for internal conversion electrons can be determined using He I radiation, which ionizes neon atoms and generates electrons with kinetic energies of 1.43 eV (Ne 2P1/2) and 1.52 eV (Ne 2P3/2). The corresponding measurement results are shown in Extended Data Fig. 6b. The spectrometer reaches a relative energy resolution of 3% full-width at half maximum.

Measurement procedure. In the measurements, Th ion bunches are sent through graphene, where they neutralize. The experimental scheme is depicted in Extended Data Fig. 3. Data are taken with two detectors in parallel: MCP I counts the internal conversion electrons that are emitted from 229Th as the isomer decays inside the collection region of the spectrometer. The count rate of internal conversion electrons expressed as a function of the applied retarding voltage gives the electron spectrum that is used for the energy determination. MCP II measures the number of extracted 229mTh atoms.

Internal conversion electron spectra are typically recorded for several days. The applied retarding voltages are logged throughout the measurement and the temporal behaviour of the retarding voltages is shown in Extended Data Fig. 7. To ensure that the measurements are insensitive to possible instabilities in the ion extraction, they consist of several cycles. One cycle consists of a predefined number of retarding voltages that are held until 1,000 bunches have been released. Internal conversion electrons that surpass the applied retarding potential are counted with MCP I and are registered in a 6-μs-wide region of interest, as shown in Extended Data Fig. 3. The centre of the region of interest coincides with the peaks measured in the extraction measurements (performed with MCP II shown in Fig. 1, Extended Data Fig. 3). The time of flight from the ion bunch release to the spectrometer/MCP II is measured at 80 μs. Detector noise from MCP I is subtracted from the internal conversion electron counts.

Count rate. The count rate at a retarding voltage of 0 V ranges between 5 and 10 electrons in 1,000 ion bunches, which leads to an absolute count rate of (5–10) × 10⁻⁷ electrons per second. Assuming 400 ions per bunch, this number can be explained as follows: 2% of the ions are in the isomeric state (8 ions in the isomeric state per bunch). We assume that 50% of the ions that pass the TEM grid (50% transmission) are neutralized and reach the collection region of the spectrometer. About 0.7% of the atoms decay within the that region (see Extended Data Fig. 3); the ions pass through the graphene foil at a velocity of 2.8 × 10⁶ m s⁻¹ and reach the collection region of the spectrometer after 570 ns. Transit through this 2-mm-wide region takes 71 ns. This means that internal conversion electrons can only be counted in a time window from ~570 ns to ~640 ns after neutralization. Assuming an isomeric lifetime of 10 ps, 0.7% of the nuclei decay within the collection region. The transmission efficiency of the retarding field analyser (three gold grids with the subsequent vacuum chamber (pumped differentially to 5 × 10⁻⁵ mbar) is 50%. This leads to a combined collection, transmission and detection efficiency of 7.5 × 10⁻⁴ and yields an expected number of 6 electrons per 1,000 ion bunches, which is comparable to the detected number of internal conversion electrons.
We expect a purely Poissonian background of 3 dark counts per second. As the time window in which the counts are expected is 6 µs per bunch, we obtain a signal-to-background ratio of about 300. We observed that the count rate slowly decreases over several weeks, which is attributed to a degradation of the graphite layers due to the ion bombardment.

**Signal origin.** Comparative measurements were performed with $^{230}$Th ions under conditions identical to those of the measurements with $^{232}$Th ions, and no comparable signal was observed. Extended Data Fig. 5 shows the time-of-flight spectra of $^{228}$mTh and $^{230}$Th ions, measured at a retarding voltage of 0 V. The $^{230}$Th ions generate a signal at the detector about 80 µs after the bunches have been released. The signal at $\sim$97 µs is attributed to Th$^{3+}$. The background (mean number of counts between 250 µs and 500 µs) was subtracted, and the number of counts was normalized to the number of extracted atoms measured with MCP II (see Extended Data Fig. 3). In the measurements performed with $^{230}$Th, no signal was detected. This confirms that secondary electrons generated in the graphene foil or originating from ionic impact can be fully suppressed and that the detected signal does not correspond to any shell-related effects (for example, auto-ionizing states). The kinetic energies involved are large compared with typical molecular binding energies. Therefore, the formation of molecules (such as ThO or ThC) is expected to occur very rarely, and it is not anticipated to affect the internal conversion electron spectra.

**Prediction of internal conversion electron spectra.** The internal conversion rates for the ground state of neutral Th have been estimated, for instance, in refs. [5, 8]. For the present purpose, however, we need to take into account all possible excited initial and corresponding final electronic states. We therefore consider the internal conversion process for the case of a magnetic transition, which is described by the Hamiltonian

$$
\hat{H}_{\text{mag}} = \frac{1}{c} \nu \int \, \text{d}^3r \, \sum_{\mathbf{r}} \frac{\mathbf{J}_\mathbf{r}}{r^2(r^2 - \mathbf{r}_\mathbf{r}^2)}
$$

(2)

representing the interaction of the electronic and nuclear electromagnetic currents. Here $\nu(r)$ is the nuclear current at point $\nu$, $\nu$ is the electronic coordinate, $c$ is the speed of light in vacuum, $\nu$ is the vector of the Dirac matrices $\gamma_i$ for $i = 1, 2, 3$ and the integration is carried out over the entire nuclear volume. The internal conversion rate is then obtained using Fermi’s golden rule for $\hat{H}_{\text{mag}}$, averaging over initial nuclear and electronic bound states with different magnetic quantum numbers, summation over the final bound states, and integration over the momentum directions of the converted electron. We consider the Russell–Saunders (spin–orbit) coupling scheme for the angular momenta of the four outer electrons, taking into account the relative contributions of the spin–orbit components given in ref. 41. (The first and the second components for the final states and initial even states and the first component for the initial odd states). We make sure that inclusion of further spin–orbit components does not affect the result by evaluating their contribution using the package GRASP2K35.

We consider the magnetic dipole (M1) channel of internal conversion for the 7s electron and neglect the contribution of the other orbitals and the electric quadrupole (E2) channel on the basis of the analysis presented in ref. [5]. After application of the Wigner–Eckart theorem and using the no-penetration model, which is suitable for the considered outer Th orbitals, the expression for the internal conversion rate $I_{\text{IC}}$ takes the form

$$
I_{\text{IC}} = \frac{8\pi}{9} \frac{\mu_B}{9} \sum_{\text{even}} \frac{(2j + 1)(\gamma - 1)^2}{1} \left[ \frac{1}{2} \frac{1}{2} 1 1 \right] [R_{\gamma}]^2
$$

(3)

where $j$ is the total angular momentum, $\mu_B$ is the reduced magnetic quantum number of the continuum electron, and the summation is carried out over $\gamma$ values corresponding to even, even, quatorial angular momentum number $\gamma$. The electronic radial integral $R_{\gamma}$ is given by

$$
R_{\gamma} = \int_0^\infty r \, \text{d}r \left[ \frac{P_{\gamma \rho}(\rho)}{\rho} \right] \left( Q_{\gamma \eta}(\rho) + P_{\gamma \rho}(\rho) Q_{\gamma \eta}(\rho) \right)
$$

(4)

where $P_{\gamma \rho}$ and $Q_{\gamma \eta}$ are the relativistic Dirac radial wavefunctions; $\gamma$ is the principal quantum number $\gamma$ for bound electron orbitals and the energy $\epsilon$ of free-electron wavefunctions. The total wavefunction for the electron is expressed via $P_{\gamma \rho}$ and $Q_{\gamma \eta}$ as

$$
\gamma_{\gamma \eta}(\rho) = \frac{1}{\sqrt{2} \rho} \left[ P_{\gamma \rho}(\rho) \Omega_{\gamma \eta}(\rho) + P_{\gamma \rho}(\rho) Q_{\gamma \eta}(\rho) \right]
$$

(5)

and $A = 1$ otherwise. Here $S$, $I$, and $L$ are the spin, total angular momentum and orbital angular momentum quantum numbers for the initial ($I$) and the final ($I$) electronic configurations, respectively. For the calculation of the internal conversion rate, we consider the theoretical prediction of the reduced nuclear transition probability, $A^\gamma_\mathrm{H}^{(0.0076 \ \text{Weisskopf units})}$. The required relativistic wavefunctions for the bound electron are evaluated with the GRASP2K package42, which uses the multi-configurational Dirac–Hartree–Fock method. The continuum electron wavefunctions are obtained using the program xphoto from the RATIP package47 for calculations of photoionization cross-sections.

**Resonant neutralization.** When multiply charged ions approach a surface, energy levels are shifted due to the interaction with the image charge of the ion and the additional shielding of the ionic core by the target electrons. During the approach, the dominant neutralization process is resonant transfer of electrons from the valence band to (excited) resonant states of the projectile48. Upon impact on the surface, loosely bound electrons are stripped from the projectile and quasi-molecular states form in the target system49. In the case of very thin target layers, enough electrons will remain with the projectile after separation to form a neutral, yet moderately excited, atom. Graphene is known to be an efficient electron donor for multiply charged ions passing through it50. We therefore expect (and also observe) that most of our Th$^{3+}$ ions leave the bilayer graphene sheet as neutral atoms. To understand which orbitals become resonant with the valence band of graphene we performed density-functional theory (DFT) calculations of the combined thorium–graphene system for different distances of the atom from the topmost layer (Extended Data Fig. 8). We use the VASP (Vienna ab initio simulation package) software with the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional51,52. For C and Th we use the 5.1.4 PBE projector-augmented wave (PAW) potentials provided with VASP, a convergence threshold of $\Delta E < 10^{-6}$ eV and a cut-off energy of 400 eV. We consider a supercell containing 5 × 5 carbon hexagons in the $x$–$y$ plane with an additional 22 Å of vacuum in the $z$ direction to electric fields from neighbouring cells. A single Th atom is positioned on a line perpendicular to the graphene sheet and through the centre of a graphene hexagon. We include spin polarization and $k$-point sampling up to $5 \times 5 \times 1$ for the supercell. Given the short timescale of the Th transit, we do not consider atomic relaxation. The PAW potentials for carbon include four active electrons and a frozen 1s$^2$ core, and for thorium they include 12 active electrons and a frozen Xe 4f$^3$5d$^0$ core, resulting in 412 active electrons in the calculation. For each value of the $z$ coordinate of Th, we extract the Kohn–Sham eigenergies and calculate the projection of all Kohn–Sham orbitals on spherical harmonics with $l = \{s, p, d, f\}$ centred around the Th atom and a radius of 2 Å. These calculations indicate that 6s and 6p electrons in Th remain atomic in the graphene target (orange and light-blue symbols in Extended Data Fig. 8 at asymptotic energies of $-40$ eV and $-20$ eV, respectively), whereas the outermost electrons of thorium have a strong $f$ characteristic while in the target (purple symbols crossing the valence band of graphene). Orbitals with 7s (orange) and 6d (green) characteristics come into resonance at larger distances from the surface ($z \approx 2$ Å). It is therefore probable that upon separation an electron will remain in an $f$ state, thereby favouring odd excited states for the outgoing Th atom.

**Energy determination.** As shown above, $^{228}$mTh atoms are in excited states after neutralization. Thus, the exact population of these initial states cannot be measured, we consider all possible initial states that are consistent with the result of our DFT calculation. Comparing the energies of different single-electron orbitals suggests an upper bound of about 20,000 cm$^{-1}$ for the excitation energies. Extended Data Table 1 presents the even and odd excited electronic states with energies of up to 20,000 cm$^{-1}$. Because the atoms pass the electron collection region only in a time window from $\approx 570$ ns to $\approx 640$ ns after neutralization, we investigate the decay channels of these states. For the corresponding excitation energies, Auger decay of the excited electronic states is ruled out. To the best of our knowledge, there is no reliable experimental information on the radiative lifetimes of excited electronic states of the neutral Th atom. To estimate the depletion of the excited states due to radiative decay, we rely on the experimental relative intensities of Th spectral lines given in ref. 53 and on theoretical calculations reported in ref. 54 for some radiative transitions. We rescale the theoretical rates using the relative intensities. The result shows that the lifetimes of all excited electronic states involved are equal to or in excess of 1 µs. From this estimate we conclude that for detection occurring in the time window 570–640 ns for Th$^{3+}$ ions, radiative decay does not lead to strong depletion of excited electronic states. Thus, all excited states generated in the neutralization process are likely to contribute to the conversion spectrum. The kinetic energy of the internal conversion electron is evaluated from the energies of the initial (E)
and final ($E_f$) electronic configurations taken from the experimental database\textsuperscript{44}, $E_\text{defl} = E_n - (IP - E_i + E_h)$.

For each possible initial excited state, we calculate the theoretical internal conversion electronic spectrum using state-of-the-art internal conversion rates obtained as detailed above. The theoretical internal conversion rates take into account specific initial states and all possible final states. The calculated internal conversion rates are shown in Extended Data Fig. 9, where larger rates are indicated by larger symbols. On average, the energy difference IP $- E_i + E_h$ is larger than the ionization potential IP (dashed vertical line). Furthermore, the energy difference is larger for even initial states than for odd states (blue and red lines in Extended Data Fig. 9, respectively).

The integrated internal conversion electron spectrum generated from one initial atomic excited state $i$ can be represented as a function of the isomeric energy $E_i$ and the applied blocking voltage $U, S_i(E_i, U)$. The spectrum $S_{tot}$ is a linear combination of the spectra

$$S_{tot}(E_i, U) = \sum w_i S_i(E_i, U)$$

where $w_i$ are weighting factors that correspond to the population of the initial excited states. Although the exact population of the initial states is unknown, the isomeric energy can be determined by fitting a function of the form $f(U) = a(1 - \text{erf}(U - E_i))$ to the data, which results in $E_i = 1.77 \pm 0.03$ eV and $b = 0.63 \pm 0.1$ eV. This function does not necessarily give the best fit, but it produces a measure that can be used for energy determination. The energy of the isomer depends on the deflection point as

$$E_i = E_\text{defl} + E_0$$

where $E_0$ represents a reference energy that is determined by the simulations. The analysis procedure is examined with simulated data that sample a random distribution of initial excited states. For a fixed isomeric energy, each weighting factor $w_i$ is randomized and the linear combination $S_{tot}$ is calculated. The assumed relative energy resolution of the spectrometer is 3%. In the next step, the complementary error function is fitted to the simulated data ($f(U) = a(1 - \text{erf}(U - E_i))$).

The above steps are repeated several thousand times at a fixed isomeric energy. For each set of $w_i$, the offset parameter $E_i = E_\text{defl} + E_0$ is calculated and fitted in a histogram if the width of the $b$ function is within the interval $0.60 \pm 0.15$ eV, and thus the shape of the curve is comparable to that obtained from the measurement. A Gaussian function can be fitted to the offset parameter histogram data (Fig. 2c).

The centroid of the generated Gaussian shifts with the isomeric energy and allows us to calculate the reference energy $E_i$. The reference energy is found to be $E_i = 6.506 \pm 0.001$ eV by determining the centroid of the $E_i$ histogram (see Extended Data Table 2; five states populated, marked with an asterisk) from the simulated energy. The width of this Gaussian determines the uncertainty that is introduced by the analysis, which is quantified in the following section.

Quantitative uncertainty analysis. Because there are no distinct lines visible in the measured spectrum, we can exclude the presence of only one initial atomic excited state contributing to the measured spectrum. In addition, because there are no selection rules involved in the resonant neutralization process, we can exclude an excited state from contributing to the resulting spectrum; instead, we expect that every excited state (see Extended Data Table 1) makes a contribution to the internal conversion electron spectrum.

To quantify the influence of specific initial state configurations, the above analysis is applied to a sample of 5,000 arbitrary configurations of initial excited states. It is found that the number of samples used does not have a large influence on the results. In addition, the standard deviation of the generated histogram (Fig. 2c) is mostly influenced by the number of initial excited states that make a large contribution to the spectrum. We sample different numbers of initial excited states. For each calculation a random configuration of $n$ states out of all possible initial states (see Extended Data Table 1) is populated. The results for an assumed energy of 8.3 eV are listed in Extended Data Table 2. It can be clearly seen that the distribution narrows when more initial excited states are taken into account.

Between 1 eV and 2 eV, the energy resolution of the spectrometer is in the range 0.03–0.06 eV (full-width at half-maximum). Each initial state in the spectrum shown in Extended Data Fig. 9 contributes with 3–4 lines to this kinetic energy region. Assuming that four initial states are populated, there should be up to 16 lines present in this energy region. These lines should be separated by 0.06 eV. As it is not possible to resolve any structure in this energy region (also in measurements with a much narrower step size of 0.04 eV) we conclude that at least five initial excited states contribute to the measured spectrum. This case is taken as a conservative scenario, which is expected to cover realistic cases within its uncertainty of 0.16 eV. The resulting reference energy is $E_i = 6.51 \pm 0.16$ eV.

Energy determination. The energy of the isomeric state is determined by fitting the same error function as above to the measured data. The deflection point is finally found to lie at $E_\text{defl} = 1.77 \pm 0.03$ eV for internal conversion electron spectra. Consistency measurements with $^{223}\text{Th}^{+}$ ions (ten times fewer internal conversion electrons detected) agree with the $^{229}\text{Th}^{+}$ results within the statistical uncertainty of 1.73 ± 0.05 eV. For the energy determination, the value obtained with the $^{229}\text{Th}^{+}$ ions is used. In order to relate the position of the deflection point to an isomeric energy, the reference energy needs to be added to the deflection point.

$$E = 8.28 \pm 0.03 (\text{statistical}) \pm 0.16 (\text{systematic}) \text{ eV}$$

DFT simulations suggest that among all electronic excited states, initial states with configurations that contain orbitals have a higher probability of being populated during the neutralization process. Simulations that take these findings into account (by assuming that these 24 states are populated ten times more than every other state) result in an offset parameter of $E_0 = 6.40 \pm 0.03$ eV, which is within the uncertainty of the scenario described above. In this case the isomeric energy is $8.17 \pm 0.05$ eV, corresponding to a wavelength of 151.8 ± 1.0 nm.

To obtain the fit results, a least-squares minimization method is used. The energy determination is not affected by the applied minimization routine; if a different routine resulted in systematic shifts in the deflection point of the measured data, these shifts would be compensated by the reference energy, as it results from the application of the exact same fit to the simulated data.

Data availability

Drawings of the spectrometer are available from the corresponding author on request.

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Author contributions B.S., L.v.d.W. and I.A. performed the experiments. B.S., L.v.d.W., P.V.B., I.A., S.S., C.L., F.L., T.S., C.E.D., A.P. and P.G.T. discussed the experimental results. P.V.B. and A.P. performed the theoretical calculations. The radioactive sources were produced in C.E.D.’s group. C.L. and F.L. performed the DFT calculations. B.S., L.v.d.W. and P.G.T. wrote the manuscript with input from all authors.

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Additional information

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Extended Data Fig. 1 | Sectional view of the focusing and bending electrodes and the collection region. a, Top view. b, Lateral view. Ions are focused by focusing electrodes (labelled ‘1’, ‘2’, ‘3’ and ‘4’) onto graphene. A large fraction (∼50%) of the ions is neutralized. Secondary electrons, as well as ions that are not neutralized, are deflected by bending electrodes and cannot enter the spectrometer collection region. A grid placed at the entrance of the collection region is used to shield electric radiofrequency and d.c. fields. The collection region is accessible via several ports to allow calibration. For the calibration a gas discharge lamp is used and photoelectrons are generated along the line indicated by the arrow (labelled ‘He I radiation’). An MCP detector is used to monitor the ion and atom extraction.
Extended Data Fig. 2 | Sectional view of the magnetic-bottle-type retarding-field electron spectrometer. The retarding-field voltage is applied to the central grid in the retarding-field unit. The outer grids are kept grounded and the electrodes between them are biased via a voltage divider chain.
Extended Data Fig. 3 | Experimental scheme. a–c. A mixed-ion cloud (containing Th$^{2+}$ and Th$^{3+}$ ions) is trapped in a segmented RFQ magnet (blue area). The cloud/bunch (white) is released and injected into the QMS (red area), which serves as an ion guide. The difference in kinetic energy (Th$^{3+}$ ions are faster than Th$^{2+}$ ions) leads to a temporal separation of the two charge states. The ion bunches are then neutralized in graphene and continue their flight as atoms (black). The atoms are counted with an MCP detector (MCP II). A time-of-flight spectrum is shown in b (the corresponding measurement is presented in Extended Data Fig. 4b). The neutralization also triggers the internal conversion decay of the $^{229m}$Th nuclear isomer. When $^{229m}$Th decays inside the collection region of the electron spectrometer, the internal conversion (IC) electron is guided towards MCP I and generates a signal. The time-resolved signal, as well as the time windows that are used to count the internal conversion electrons, are shown in c (a measurement is shown in Extended Data Fig. 4a). cts, number of counts. Dimensions are not to scale.
Extended Data Fig. 4 | Internal conversion electron signal. a, b, Internal conversion electron signal measured with MCP I at two different retarding voltages (a). Th$^{3+}$ (Th$^{5+}$) ions generate a signal at $t \approx 80 \mu s$ ($t \approx 97 \mu s$) from the release of the ion bunch. $10^5$ bunches were recorded for each retarding voltage. The number of counts from neutralized atoms measured with MCP II are shown in b (for $2.25 \times 10^6$ bunches recorded). We note that the ratio of the Th$^{3+}$ and Th$^{5+}$ peaks from a is not reflected in b. This can be explained as follows: in the Th$^{3+}$ charged state, $^{229}$Th and $^{233}$U are extracted from the buffer-gas stopping cell at approximately equal rates, whereas the extraction rate in the Th$^{5+}$ charged state is dominated by $^{228}$Th (see ref. 34). In our setup, thorium cannot be separated from uranium by the time-of-flight method; therefore, it can be expected that only $\sim$50% of the Th$^{3+}$ peak in b results from neutralized $^{229}$Th$^{3+}$ ions. By contrast, the internal conversion electron signal results solely from neutralized $^{229}$Th ions.
Extended Data Fig. 5 | Comparative measurements. Comparative measurement of $^{230}$Th and $^{229(m)}$Th at a blocking voltage of 0 V. For the $^{229(m)}$Th ($^{230}$Th) measurement, 5,000 (>800,000) bunches were recorded. To compare $^{230}$Th with $^{229(m)}$Th, the number of counts was normalized to the number of extracted atoms measured with MCP II (see Extended Data Fig. 3). Constant background has been subtracted in the $^{230}$Th measurement.
Extended Data Fig. 6 | Calibration measurements. Measured (integrated) calibration spectra (red) and their derivatives, shown together with a fitting function (black). For better visualization, data and derivatives are normalized to their respective maxima. The energy scale has been corrected for surface potentials. Measurements were obtained as detailed in ref. 31. a, Typical argon calibration spectrum used in the measurements (electron kinetic energies of 5.46 eV and 5.28 eV). b, Neon calibration spectrum, showing a clear separation of the two lines (electron kinetic energies of 1.52 eV and 1.43 eV). arb., arbitrary units.
Extended Data Fig. 7 | Monitoring of the applied blocking voltages.

a. Time-resolved behaviour of the applied retarding voltages. Retarding voltages between $-0.5$ V and $-3.5$ V are applied in steps of $-0.1$ V. Each retarding voltage is held for 1,000 bunches (about 100 s). Before incrementing the voltage, it is set to 0 V to make the measurement independent from the order in which the voltages are applied.

b. Distribution of an exemplary retarding voltage over three days of measurement. The stability is better than 10 mV and limited by temperature fluctuations.
Extended Data Fig. 8 | Single-electron orbital energies for thorium. 
Single-electron (Kohn–Sham) orbital energies for a thorium atom as a function of the distance from the topmost carbon layer, located at \( z = 0 \) Å. Screening of the core by the target’s electrons leads to distance-dependent shifts of the orbital energies. The 6\( s \) and 6\( p \) states (asymptotic energies of about \(-40\) eV and \(-20\) eV, respectively) remain atomic in graphene, whereas higher orbitals (7\( s \), 6\( d \), 5\( f \)) become resonant with the graphene valence bands (overlapping red and green shaded areas, indicating the region of high electron density in the target) at different distances. In the target, a prevalence of states with \( f \) characteristic (purple symbols) is observed. \( E_F \) denotes the Fermi energy.
Extended Data Fig. 9 | Summary of internal conversion electron rates. Bottom, possible values for $\text{IP} - E_i + E_f$ given by the internal conversion selection rules for even (blue) and odd (red) initial electronic states of Th. Initial states are numbered according to their state index (given in Extended Data Table 1). The ionization potential of the Th atom is shown by the black dashed line. The size of the symbols indicates the transition rate from an initial state to a final state. Top, projection of the data shown in the lower panel onto the horizontal axis (energy bin, 0.1 eV).
| even states | odd states |
|-------------|------------|
| State index | $E_i$ [cm$^{-1}$] | State index | $E_i$ [cm$^{-1}$] |
| 1           | 0          | 1           | 7795.275     |
| 2           | 2558.057   | 2           | 8243.601     |
| 3           | 2869.259   | 3           | 10141.136    |
| 4           | 3687.987   | 4           | 10526.544    |
| 5           | 3865.475   | 5           | 10783.154    |
| 6           | 4961.659   | 6           | 11197.031    |
| 7           | 5563.142   | 7           | 11241.730    |
| 8           | 6362.396   | 8           | 11877.839    |
| 9           | 7280.124   | 9           | 12114.366    |
| 10          | 7502.288   | 10          | 13175.113    |
| 11          | 8111.005   | 11          | 13945.307    |
| 12          | 8800.251   | 12          | 14032.085    |
| 13          | 9804.807   | 13          | 14206.917    |
| 14          | 11601.031  | 14          | 14243.993    |
| 15          | 11802.934  | 15          | 14247.307    |
| 16          | 12847.971  | 16          | 14465.222    |
| 17          | 13088.563  | 17          | 14481.869    |
| 18          | 13297.434  | 18          | 15166.901    |
| 19          | 13847.771  | 19          | 15490.077    |
| 20          | 13962.522  | 20          | 15618.984    |
| 21          | 14204.264  | 21          | 15736.969    |
| 22          | 14226.822  | 22          | 16217.482    |
| 23          | 15493.221  | 23          | 16346.651    |
| 24          | 15863.891  | 24          | 16783.847    |
| 25          | 15970.095  | 25          | 17224.303    |
| 26          | 16351.943  | 26          | 17354.639    |
| 27          | 16554.245  | 27          | 17411.224    |
| 28          | 17073.811  | 28          | 17501.176    |
| 29          | 17166.108  | 29          | 17847.077    |
| 30          | 17398.398  | 30          | 18011.380    |
| 31          | 17959.898  | 31          | 18053.617    |
| 32          | 18431.686  | 32          | 18069.065    |
| 33          | 18549.405  | 33          | 18382.826    |
| 34          | 18574.608  | 34          | 18614.338    |
| 35          | 18699.623  | 35          | 18809.887    |
| 36          | 19273.279  | 36          | 18930.293    |
| 37          | 19532.419  | 37          | 19039.153    |
| 38          | 19713.031  | 38          | 19227.336    |
| 39          | 19832.116  | 39          | 19503.144    |
| 40          |            | 40          | 19516.981    |
| 41          |            | 41          | 19588.362    |
| 42          |            | 42          | 19817.182    |
| 43          |            | 43          | 19948.395    |
| 44          |            | 44          | 19986.166    |

List of all thorium states with wavenumbers below 20,000 cm$^{-1}$ that were considered in the analysis. The full dataset is available in ref. $^{44}$. 


Extended Data Table 2 | Uncertainty of the data analysis

| Number of excited states (n) | $E_0$         | Width of the distribution $\sigma$ |
|-----------------------------|---------------|-----------------------------------|
| 2                           | $6.56\pm0.02$ | 0.22                              |
| 4                           | $6.517\pm0.003$ | 0.18                             |
| 5 *                         | $6.506\pm0.001$ | 0.16                             |
| 10                          | $6.504\pm0.001$ | 0.12                             |
| 20                          | $6.492\pm0.001$ | 0.09                             |
| 30                          | $6.494\pm0.001$ | 0.06                             |
| 40                          | $6.493\pm0.001$ | 0.05                             |

Influence of the number $n$ of initially excited electronic states on the systematic uncertainty of the data analysis. Whereas the centroid of the distribution ($E_0$) stays almost constant, the systematic uncertainty ($\sigma$) decreases with increasing $n$. The calculations were performed assuming an energy of 8.3 eV.

*The values obtained for $n = 5$ are used for the energy determination.