A Direct Measurement of the $7s^2S_{1/2} \rightarrow 7p^2P_{3/2}$ Transition Frequency in $^{226}\text{Ra}^+$

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We report a direct measurement of the $7s^2S_{1/2} \rightarrow 7p^2P_{3/2}$ electric-dipole transition frequency in $^{226}\text{Ra}^+$. With a single laser-cooled radium ion we determine the transition frequency to be $785\,722.11(3)$ GHz by directly driving the transition with frequency doubled light and measuring the frequency of the un-doubled light with an iodine reference. This measurement addresses a discrepancy of five combined standard deviations between previously reported values.

Trapped radium ions are appealing for quantum information science [1], searches for new physics beyond the standard model [2, 3], and precision timekeeping [4–6]. $\text{Ra}^+$ is a potential candidate for a transportable optical clock, as the transitions can all be addressed with direct diode lasers, and the ion’s important laser cooling and fluorescence transition at 468 nm is far from the UV compared to most trapped ion optical clock candidates [7], see Fig. 1. The $7s^2S_{1/2} \rightarrow 6d^2D_{5/2}$ optical clock transition at 728 nm, or the narrow $7s^2S_{1/2} \rightarrow 6d^2D_{3/2}$ electric-quadrupole transition at 828 nm, may be used to study radium’s nuclear structure [8, 9], or set bounds on sources of new physics [3].

There is a discrepancy between two previously reported values of the $7s^2S_{1/2} \rightarrow 7p^2P_{3/2}$ transition frequency in $^{226}\text{Ra}^+$: $785\,722.10(3)$ GHz [10] and $785\,721.670(70)$ GHz [6], which is included in a compilation of radium spectroscopy data [11]. The former value was determined from a sum of two direct frequency measurements in $^{226}\text{Ra}^+$ of the $7s^2S_{1/2} \rightarrow 6d^2D_{5/2}$ and $6d^2D_{5/2} \rightarrow 7p^2P_{3/2}$ transitions. The latter value was determined using the transition frequency calculated from a sum of direct measurements in $^{214}\text{Ra}^+$ [6], and the isotope shift between $^{214}\text{Ra}^+$ and $^{226}\text{Ra}^+$ measured in Neu, et al. [12]. In this work we help resolve this discrepancy with direct spectroscopy at 382 nm of the $7s^2S_{1/2} \rightarrow 7p^2P_{3/2}$ transition with a single laser-cooled radium ion. The frequency measurement is calibrated by absorption spectroscopy with known transitions in molecular iodine. The value measured in this work, $785\,722.11(3)$ GHz, agrees with the value from the sum of direct measurements in $^{226}\text{Ra}^+$ [10].

FIG. 1. The Ra$^+$ energy level structure with the transitions driven in the measurement of the $7s^2S_{1/2} \rightarrow 7p^2P_{3/2}$ transition frequency.

FIG. 2. A diagram of the measurement setup. Light at 764-nm (red) from a Ti:Sapphire laser is frequency doubled via second harmonic generation (SHG) to drive the $7s^2S_{1/2} \rightarrow 7p^2P_{3/2}$ transition in Ra$^+$ at 382 nm (purple). An acousto-optic modulator (AOM) is used as a shutter for the 382 nm spectroscopy light. The 764-nm frequency is recorded on a wavemeter. A photodiode (PD) before the iodine cell compensates for laser power drifts. Other beams addressing the ions: Doppler cooling (teal), repump from the $D_{3/2}$ state (gray), and the cleanout beam (dark red).

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The iodine linear absorption spectrum is measured around 764 nm with light from a Ti:Sapphire laser. Frequency doubled light from the same laser drives the $7s\ ^2S_{1/2} \rightarrow 7p\ ^2P_{3/2}$ transition of $^{226}\text{Ra}^+$ at 382 nm, see Fig. 2. From iodine reference lines near 764 nm we can determine the $S_{1/2} \rightarrow P_{3/2}$ transition frequency. During both the radium and iodine spectroscopy the 764-nm laser’s frequency is recorded with a wavemeter (High Finesse WS-8), see Fig. 3.

To measure the $S_{1/2} \rightarrow P_{3/2}$ transition frequency we first scan the iodine spectrum near 764 nm, at half of the transition frequency reported in [10]. We scan over a 20 GHz range that includes two iodine reference lines, 325 and 326 [13]. This is followed by radium spectroscopy and then a second iodine scan to account for wavemeter drift. The radium spectroscopy uses state detection to determine if the population is in a “bright” state, $S_{1/2}$ or $D_{3/2}$, or in the $D_{5/2}$ “dark” state, by collecting $\text{Ra}^+$ fluorescence at 468 nm onto a photomultiplier tube. The $S_{1/2} \rightarrow P_{3/2}$ transition frequency is calculated from the difference between the radium $382\, \text{nm}$ line center and twice the frequency of iodine line 326.

The pulse sequence for the $S_{1/2} \rightarrow P_{3/2}$ frequency measurement is shown in Fig. 4. All light is linearly polarized to drive symmetric Zeeman transitions with the same amplitude, with a 3 G magnetic field along the trap’s axial axis. We Doppler cool the ion for 500 µs before each pulse sequence. The initial state detection determines if the ion is cooled and if the population is in a bright state (SD1). If the population is not initialized in a bright state, or if the ion is in large orbit the data point is excluded. Population in the $D_{3/2}$ state is then optically pumped for 100 µs with light at 1079 nm to the ground state (P1). The $7s\ ^2S_{1/2} \rightarrow 7p\ ^2P_{3/2}$ spectroscopy transition is then driven with light at 382 nm for 500 µs (P2). Decays from the $P_{3/2}$ state have an 11% probability to be shelved in the $D_{5/2}$ dark state [14]. We use these decays to determine the probability of driving the $S_{1/2} \rightarrow P_{3/2}$ transition at a given laser frequency with a second state detection (SD2) to form a binomial distribution, see Fig. 5. Finally any population that remains in the $D_{5/2}$ state is reset to the bright states by optically pumping with 802 nm light (P3). The pulse sequence is repeated many times as the 382-nm laser is swept over the transition in a ∼100 MHz range. The $7s\ ^2S_{1/2} \rightarrow 7p\ ^2P_{3/2}$ spectroscopy is shown in Fig. 3 along with the corresponding iodine absorption reference spectrum.

FIG. 3. The iodine absorption (gray) and radium spectroscopy (red) data are plotted in terms of the undoubled 764 nm laser frequency that we record on a wavemeter. Data is scaled and vertically offset for clarity. The closest iodine absorption reference spectrum.

| SD1 | P1 | P2 | SD2 | P3 |
|-----|----|----|-----|----|
| 1 ms | 0.1 ms | 0.5 ms | 1 ms | 0.1 ms |
| 468 | 1079 | 382 | 802 |

FIG. 4. The pulse sequence used for the $7s\ ^2S_{1/2} \rightarrow 7p\ ^2P_{3/2}$ spectroscopy. Squiggly lines depict electric dipole allowed decays, straight lines with an arrow indicate optical pumping, and double-arrows indicate optical cycling.

The $S_{1/2} \rightarrow P_{3/2}$ radium measurement data is binned by frequency, and the shelving probability is fit to the exponential of a Lorentzian, see Fig. 5, to account for population depletion of the $S_{1/2}$ state (see Appendix A). The full width at half-maximum of 40(1) MHz gives a lower bound of 4.0(1) ns for the $P_{3/2}$-state lifetime, which is in agreement with the calculated value of 4.73 ns [15]. The 382-nm light is incident on the ion along the trap’s axial axis, see Fig. 2, to minimize micromotion broadening of the transition [16].

The closest iodine reference line to the $^{226}\text{Ra}^+\ ^2S_{1/2} \rightarrow P_{3/2}$ transition is line 326 [13]. We calibrate the 326 line center frequency we measured with a wavemeter to an absolute frequency using IodineSpec5 [17, 18]. We fit the absorption dip of line 326 in the IodineSpec5 data to a Voigt function to determine its frequency doubled line center, 785 734.265(3) GHz.

The frequency difference between the $S_{1/2} \rightarrow P_{3/2}$ line center at 382 nm and twice the value of the iodine line
agree with the reported direct measurement of the frequencies, 785 722 MHz. The Lorentzian fit that accounts for $P_{3/2}$ state depletion gives a FWHM of 40(1) MHz. Error bars are the most likely 68% confidence interval of a binomial distribution.

326 center frequency is 12.381 GHz, see Fig. 3. From this frequency difference we determine the transition frequency to be 785 722 MHz. The uncertainty is $\sigma_{\text{total}} = \sqrt{\sigma_{\text{Ra}}^2 + \sigma_{\text{spec}}^2 + \sigma_{\text{wm}}^2}$, where $\sigma_{\text{Ra}}$ (20 MHz) is half the full width at half-maximum of the fitted Ra$^+$ spectrum, see Fig. 3 to account for possible magnetic field shifts due to Zeeman levels, $\sigma_{\text{spec}}$ (3 MHz) is the iodine spectroscopy fitting uncertainty, and $\sigma_{\text{wm}}$ (20 MHz) is the wavemeter uncertainty.

328 measured in [10]. The discrepancy between the frequencies reported in Núñez, et al. [6] and in Holliman, et al. [10], see Table I. This $^{226}\text{Ra}^+$ frequency measurement also serves as a check for the $7s^2S_{1/2} \rightarrow 6d^2D_{5/2}$ (728 nm), $7s^2S_{1/2} \rightarrow 6d^2D_{3/2}$ (828 nm), $6d^2D_{3/2} \rightarrow 7p^2P_{3/2}$ (708 nm), and $6d^2D_{3/2} \rightarrow 7p^2P_{3/2}$ (802 nm) transition frequencies measured in [10]. The $S_{1/2} \rightarrow P_{3/2}$ transition frequency can be calculated from the sum of the 728- and 802-nm frequencies, 785 722.11(3) GHz, or the 828- and 708-nm frequencies, 785 722.000(4000) MHz. *Frequencies calculated from indirect measurements.

| Transition       | [19] | [6] | [10] | This work |
|------------------|------|-----|-----|-----------|
| $S_{1/2} \rightarrow P_{3/2}$ | 1000(4000) | 330(70)* | 100(30)* | 110(30) |

This work measures a transition that was last directly measured nearly a century ago [19], and addresses a discrepancy between the frequencies reported in Núñez, et al. [6] and in Holliman, et al. [10], see Table I. This $^{226}\text{Ra}^+$ frequency measurement also serves as a check for the $7s^2S_{1/2} \rightarrow 6d^2D_{5/2}$ (728 nm), $7s^2S_{1/2} \rightarrow 6d^2D_{3/2}$ (828 nm), $6d^2D_{3/2} \rightarrow 7p^2P_{3/2}$ (708 nm), and $6d^2D_{3/2} \rightarrow 7p^2P_{3/2}$ (802 nm) transition frequencies measured in [10]. The $S_{1/2} \rightarrow P_{3/2}$ transition frequency can be calculated from the sum of the 728- and 802-nm frequencies, 785 722.11(3) GHz, or the 828- and 708-nm frequencies, 785 722.000(4000) MHz. Both values derived from [10] agree with the reported direct measurement of the $S_{1/2} \rightarrow P_{3/2}$ transition frequency. We verify the self-consistency of these sets of measurements in Appendix B.

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**APPENDIX A: DEPLETION ANALYSIS**

If a large proportion of the population is driven out of the $S_{1/2}$ state during driving to the $P_{3/2}$ state, the expected Lorentzian line shape of the spectroscopy distorts due to decays from the $P_{3/2}$ state to the meta-stable $D_{3/2}$ and $D_{5/2}$ states. If the $P_{3/2}$ state only decayed to the $S_{1/2}$ state, the $P_{3/2}$ state population in equilibrium, $P_{0,P}(\omega)$, would be

$$P_P = P_{0,P}(P_P + P_S)$$

$$= P_{0,P}(1 - P_D)$$

where $P_P$ is the population in the $P_{3/2}$ state, $P_S$ is the population $S_{1/2}$ state, and $P_D$ is the total population in both the $D_{3/2}$ and $D_{5/2}$ states. Because the lifetime of the $P_{3/2}$ state is much much shorter than the probe time (P2 in Fig. 4), we can approximate the decay into the $D$ states as

$$\frac{dP_D}{dt} = \frac{P_P(1 - r)}{\tau}$$

where $\tau$ is the lifetime of the $P_{3/2}$ state and $r$ is the branching fraction of the $P_{3/2}$ state to the $S_{1/2}$ state. Under the assumption that the population is always initialized to the $S_{1/2}$ state this gives

$$P_D = 1 - \exp\left(-\frac{P_{0,P}(1 - r)}{\tau}\right).$$

The final dark state population, $P_{D_{3/2}}$, is determined from the branching fractions of the $P_{3/2}$ state to the $D_{3/2}$ state, $s$, and to the $D_{3/2}$ state, $t$,

$$P_{D_{3/2}} = \frac{s}{s + t} P_D$$

which gives the fitting function

$$P_{D_{3/2}} = \frac{s}{s + t} \left[1 - \exp\left(-\frac{a}{(\omega - \omega_0)^2 + \Gamma^2}\right) + c\right]$$

where $a$, $\Gamma$, $\omega$ and $c$ are fitting parameters and the $s$ and $t$ branching fractions are from [14].
APPENDIX B: RADIUM ION FREQUENCY SUMMARY

To verify that the measurements are self-consistent we perform an energy level optimization with the reported \( S_{1/2} \rightarrow P_{3/2} \) transition frequency and other Ra\(^{+} \) transition frequencies reported in [4, 10], see Table II. If we fix the ground state at zero energy, there are seven transitions between four excited states which give three degrees of freedom. We use the energy level optimization code package, LOPT [20], to find the energy values that best agree with our reported frequencies. We calculate the residual sum of squares to be 0.14, which, being less than one, indicates that the measured frequencies are consistent with each other, and the uncertainties were estimated conservatively.

### TABLE II. Summary of \( ^{226}\text{Ra}^{+} \) transition frequency measurements. All units are GHz. *Frequencies calculated from a sum of direct measurements in \( ^{226}\text{Ra}^{+} \).

| Transition                  | This work, [4,10] |
|-----------------------------|-------------------|
| \( S_{1/2} \rightarrow P_{3/2} \) | 785 722.11(3)    |
| \( S_{1/2} \rightarrow P_{1/2} \) | 640 096.63(6)    |
| \( D_{3/2} \rightarrow P_{3/2} \) | 423 444.39(3)    |
| \( S_{1/2} \rightarrow D_{5/2} \) | 412 007.701(18)  |
| \( D_{5/2} \rightarrow P_{3/2} \) | 373 714.40(2)    |
| \( S_{1/2} \rightarrow D_{3/2} \) | 362 277.68(5)    |
| \( D_{3/2} \rightarrow P_{1/2} \) | 277 818.95(8)*   |

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