

# Absolute Frequency Measurement of the $^{40}\text{Ca}^+$ Clock Transition using a LD-based Clock Laser and UTC(NICT)

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**Abstract**— We developed an optical frequency standard using  $^{40}\text{Ca}^+$  with the  $4\ ^2S_{1/2}-3\ ^2D_{5/2}$  electric quadrupole transition. Its absolute transition frequency is 411 042 129 776 390(7) Hz. The uncertainty is limited by the electric quadrupole shift and ambient magnetic field fluctuation. To determine the absolute transition frequency with a better uncertainty, we have observed two pairs of the symmetrically-splitting Zeeman components and measured the transition frequency which is corrected for the electric quadrupole shift. It will be used to determine the absolute transition frequency with respect to the SI base units of time and length. In addition, we are developing a magnetic-shielded ion-trap chamber to reduce the transition-line broadening caused by the magnetic field fluctuation.

## I. INTRODUCTION

Optical frequency standards using new atomic and ionic materials have been proposed for developing more accurate frequency standards than the microwave standards as well as for testing the fundamental constants in physics [1-3]. We have developed an optical frequency standard using single  $^{40}\text{Ca}^+$  ions [4, 5]. One of the advantages of it is all the useful transitions are accessible with existing laser diodes. Partial term energy diagram of  $^{40}\text{Ca}^+$  is shown in Fig. 1. Calcium ions are laser-cooled using both the  $^2S_{1/2}-^2P_{1/2}$  cooling transition at 397 nm and the  $^2P_{1/2}-^2D_{3/2}$  repumping transition at 866 nm. Lifetime of the  $^2D_{5/2}$  state is about 1.2 s (natural linewidth is about 0.2 Hz), which gives a high line-Q to the  $^2S_{1/2}-^2D_{5/2}$  transition at 729 nm. While an odd isotope  $^{43}\text{Ca}^+$  has a merit of

avoiding the first-order Zeeman shift, a complicated light source system is required for laser cooling because of the hyperfine splitting. The first-order Zeeman shift of  $^{40}\text{Ca}^+$  can be canceled by observing a pair of the symmetrically splitting Zeeman components to calculate the average frequency as the transition frequency [6]. Using this method, we measured the clock transition frequency of  $^{40}\text{Ca}^+$  ions with an uncertainty of 7 Hz [7].

In the measurement in [7] we did not measured the electric quadrupole shift. In optical frequency standards using ions with alkaline-earth-metal-like electron structures, its transition frequency from the ground state to a  $D_J$  state is sensitive to the electric field gradient. The atomic quadrupole moment in the electric quadrupole field causes frequency shifts of a few hertz. It is difficult to measure the electric quadrupole field directly. Quadrupole moments were determined for some ions [8, 9] by measuring the change in the transition frequency between the ground state and a metastable  $D_J$  state that depends on a static electric field gradient. From these results, we estimated that the quadrupole shift in our measurement is well smaller than 5 Hz and we counted a frequency error of 5 Hz caused by the quadrupole shift. It contributes largely to the total uncertainty of 7 Hz.

Because the quadrupole shift depends on the magnetic sublevel  $M_J$ , it can be cancelled by measuring the transition frequencies to different  $M_J$  sublevels of the  $D_J$  state [10]. We therefore have observed two pair of the Zeeman components of  $|4\ ^2S_{1/2}, M_J = \pm 1/2\rangle - |3\ ^2D_{5/2}, M_J = \pm 3/2\rangle$  and  $|4\ ^2S_{1/2}, M_J = \pm 1/2\rangle - |3\ ^2D_{5/2}, M_J = \pm 1/2\rangle$  to measure the transition frequency corrected for the quadrupole shift. It will be used to determine the absolute clock transition frequency, in which BIPM Circular T [11] published in May 2009 is utilized.

In this paper, we explain the experimental setup at first, and we explain the transition measurement and the transition frequency estimation. Finally a summary and future plan is described.

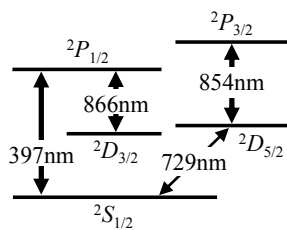


Figure 1. Partial term energy diagram of  $^{40}\text{Ca}^+$  ions.

## II. EXPERIMENTAL SETUP

The experimental setup is illustrated by Fig. 2. Because its details were mentioned at other papers [5], we describe here it in brief. It is composed of three parts, which are an ion trap, a cooling laser system, and a clock laser system. An optical frequency comb is also used for frequency measurement of the clock laser [12]. The clock laser and the frequency comb are placed in a different room from the ion-trap room. Light of the clock laser system is distributed to the ion-trap room using a polarization-maintaining (PM) single-mode (SM) fiber of 40 m. To avoid the laser-linewidth broadening by fiber transfer, a phase-noise cancellation is set up for the clock laser system.

To produce  $^{40}\text{Ca}^+$  ions from Ca atoms, a two-step optical excitation method is employed using 423 and 374-nm lights. The 423-nm light is produced by the second harmonics of a power-amplified 846-nm diode laser with a periodically-poled (pp) KTP crystal. The  $^{40}\text{Ca}^+$  ions are confined in a radio-frequency (RF) ion trap consisting of a 0.6-mm-radius ring electrode and two 1.2-mm-diameter end-cap electrodes. A pair of electrodes is used to compensate stray electric field. An RF voltage at 660 V<sub>pp</sub> and 23 MHz is applied to the ring electrode. The vacuum pressure is about  $2 \times 10^{-8}$  Pa.

The trapped  $^{40}\text{Ca}^+$  ions are laser-cooled with Littrow-type extended-cavity diode lasers (ECDLs) at 397 nm (Nichia) and 866 nm (Toptica). A personal-computer (pc) program with a frequency-stabilized He-Ne laser (Melles Griot) and two transfer cavities is employed to stabilize and control the laser frequencies. The Allen variance of  $<10^{-10}$  at averaging time of  $1 - 10^3$  seconds was measured.

We have developed an ultra stable frequency-tunable LD system at 729 nm as the clock laser system [13]. Its frequency is stabilized by Pound-Drever-Hall method to couple its partial output to a high-finesse ( $F = 16 \times 10^4$ ) ultra-low-expansion (ULE) cavity. Measuring the beatnote frequency between outputs from two 729-nm clock lasers, we confirmed that the

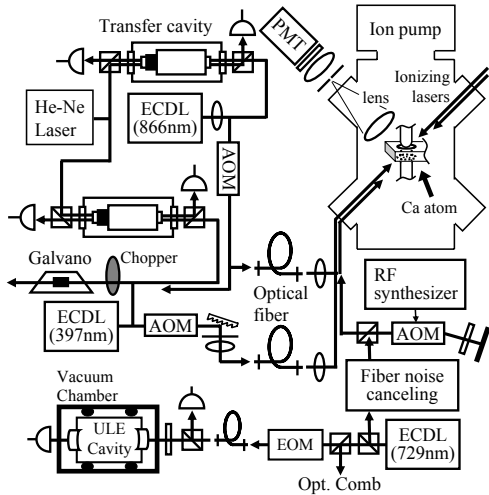


Figure 2. Experimental setup for single  $^{40}\text{Ca}^+$  ions. AOM: acousto-optic modulator; PMT: photo-multiplier tube; Galvano: Galvano tube; EOM: electro-optic modulator. Fiber noise canceling is shown in Fig. 3.

linewidth of the clock laser is  $<25$  Hz. To minimize the long-term drift of frequency, the ULE cavity is put in a vacuum chamber with a three-stage temperature-stabilizing system. As the result of stabilizing the temperature at which coefficient of the thermal expansion is almost zero, we have measured the long-term drift of 0.03 Hz/s.

The clock-laser radiation is distributed to the ion-trap room with a 40-m PM SM fiber. To minimize the phase noise caused by fiber transfer, we employed a cancellation system shown in Fig. 3. We located an AOM in front of the input fiber coupler and located a partial mirror behind the output coupler. Beatnote signal between the direct output light from the clock laser system and the round-trip light passing through the 40-m fiber is observed. Comparing it to a precise local frequency of 160 MHz, the phase noise is extracted as the error signal. It is fed back to the AOM. We have measured a servo bandwidth of the phase lock loop of 2 kHz and the FWHM of the beatnote signal of 1 Hz.

## III. SPECTRUM MEASUREMENT AND TRANSITION FREQUENCY ESTIMATION

A computer-aided system is employed for the single  $^{40}\text{Ca}^+$  ion loading, in which lighting time period of a Ca oven and the ionizing LDs is optimized for loading of the single  $^{40}\text{Ca}^+$  ion. When more than one ion are loaded, another program, that reduces the trap potential and blocks the 866-nm light for a fixed time, is run to decrease the number of ions. Usually about 6000 photons are observed for one second from single laser-cooled  $^{40}\text{Ca}^+$  ions. Dc potentials are applied to the compensation electrodes to minimize the excess micromotion. We observe linewidths of  $<30$  MHz for the laser cooling.

Spectra of the  $4\ ^2S_{1/2} - 3\ ^2D_{5/2}$  quadrupole clock transition are observed by means of the electron-shelving method [6]. That is, after applying the clock laser at 729 nm, the ionic quantum state is interrogated by laser cooling; if the clock transition has occurred, the ion does not fluoresce at 397 nm, otherwise, it fluoresces by laser cooling. A measurement time sequence is employed to observe the clock transition spectrum, in which 854-nm light is additionally used to quench the ion from the  $^2D_{5/2}$  state to the ground state. The 397, 866 and 854-nm lasers are blocked while the clock laser is applied to the ion for typically 4 ms. After the interrogation using the 397 and 866-nm lasers, the single ion is initialized to the ground state and laser-cooled using the 397, 866 and 854-nm lasers. Once of the clock transition is recognized when the photon counting rate  $<1000$  counts/s is observed at the interrogation

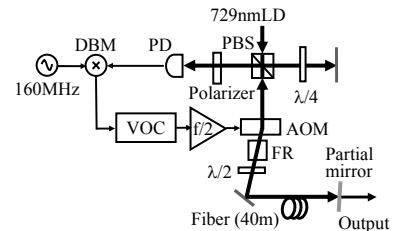


Figure 3. Fiber noise canceling system for fiber distribution of 729-nm light. DBM: double balanced mixer; PD: photo diode; PBS: polarizing beam splitter; VOC: voltage controlled crystal oscillator; FR: Faraday rotator.

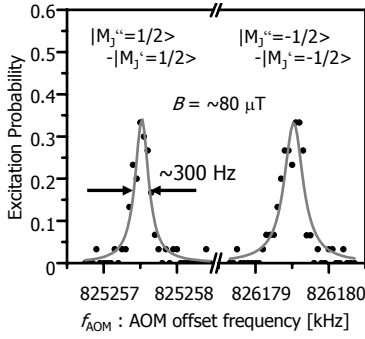


Figure 4. Example of the pair of the  $|4\ ^2S_{1/2}, M_J'=\pm 1/2\rangle - |3\ ^2D_{5/2}, M_J=\pm 1/2\rangle$  transitions of  $^{40}\text{Ca}^+$  ions. The dots showing the observed values are approximated by Lorentz line profiles. The horizontal axis shows offset frequency by an AOM to the transition frequency.

time. This time sequence is repeated for typically 50 times at each clock laser frequency. Dividing the number of the clock transition by the repetition number, the excitation probability is measured. To minimize the transition frequency fluctuation due to the ambient magnetic field fluctuation, mainly caused by the ac electric supply, the lasers are applied synchronously to the 50-Hz phase of the electric power.

#### A. Zeeman Spectrum of the $\Delta M_J = 0$ Components

All the Zeeman components of the  $^{40}\text{Ca}^+ 4\ ^2S_{1/2} - 3\ ^2D_{5/2}$  clock transition are shifted in the magnetic field. Therefore, a compensation of this shift is required to measure the transition frequency. In a stable magnetic field, the first-order Zeeman shift resolves the transition into ten components symmetrically. The relative intensity among the components depends on the polarization vector of the clock laser, its wave vector and the magnetic field vector. Using selection rules of the transition in magnetic field, we observed a symmetrically splitting pair of the Zeeman components of  $|^2S_{1/2}, 1/2\rangle - |^2D_{5/2}, 1/2\rangle$  and  $|^2S_{1/2}, -1/2\rangle - |^2D_{5/2}, -1/2\rangle$  ( $\Delta M_J = 0$  components) because they are the most insensitive to the magnetic fluctuations among the ten components, where  $|^2S_{1/2}$  or  $|^2D_{5/2}, M_J\rangle$  denotes  $M_J$  sublevels. The first-order Zeeman shift can be cancelled by averaging these two transition frequencies.

An example of the observed spectrum is shown in Fig. 4. The clock laser is applied for 4 ms in the measurement time sequence, which is synchronized to the 50-Hz ac supply, and

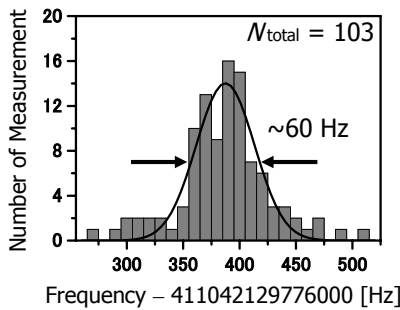


Figure 5. Histogram of all measured transition frequency data. The standard error for the center frequency decision is 3.9 Hz.

we have observed the linewidth of about 300 Hz. Without the synchronization to the electric 50 Hz, the linewidth of about 1 kHz was observed. In addition, we have not observed the much narrower linewidth than 300 Hz even if the clock laser is applied for the longer time than 4 ms. Therefore, the linewidth seems to be limited by not only the transit-time broadening but also residual magnetic fluctuation. The ion trap chamber is not enclosed with a magnetic shield.

#### B. Absolute Frequency Estimation using UTC(NICT)

The first-order Zeeman shift is cancelled by calculating the average frequency of the symmetrically-splitting two Zeeman components. We estimated the absolute transition frequency using the following equation.

$$f = f_{\text{ULE}} + 1/2(f_{\text{AOM:-1/2}} + f_{\text{AOM:1/2}}) + f_{\text{HM-TT}} + f_{\text{SYS}}, \quad (1)$$

where  $f_{\text{ULE}}$  is the 729-nm LD frequency stabilized by the ULE cavity,  $f_{\text{AOM:-1/2}}$  is the offset frequency, which is modulated by a AOM, to the  $|^2S_{1/2}, -1/2\rangle - |^2D_{5/2}, -1/2\rangle$  transition frequency,  $f_{\text{AOM:1/2}}$  is the offset frequency to the  $|^2S_{1/2}, 1/2\rangle - |^2D_{5/2}, 1/2\rangle$  frequency,  $f_{\text{HM-TT}}$  is the frequency correction between our Hydrogen maser and the SI base unit of time on the geoid (TT) through UTC(NICT), and  $f_{\text{SYS}}$  is the systematic frequency shift, respectively. The  $f_{\text{ULE}}$  is measured by an optical frequency comb counter referring to the Hydrogen maser, which is operated simultaneously with the spectrum measurement. Frequency of the reference Hydrogen maser is checked by the UTC(NICT) every hour, and the frequency difference of the UTC(NICT) from the TT is estimated using the BIPM Circular T.

We estimated the systematic frequency shift  $f_{\text{SYS}}$  and its error as follows. To correct the ac Stark shift due to a faint leakage of 397-nm light through the AOM, we measure the transition frequency at different 397-nm light powers. The black body radiation (BBR) shift and the gravitational shift are calculated to be 0.4 (frequency error: 0.1) Hz at the room temperature (300 K) and 3.4 (0.1) Hz, respectively [4, 14]. At the applied magnetic field strength of 80  $\mu\text{T}$  the second-order Zeeman shift is estimated as small as 0.17 Hz. Both of the frequency errors by the ULE cavity drift and the dc magnetic field drift are estimated to be  $<0.2$  Hz. We did not measure the electric quadrupole shift. Because it was reported to be  $<5$  Hz from the single-ion experiments by other groups [15], we estimated a relatively large error of 5 Hz for the quadrupole shift.

We observed such Zeeman spectra as is shown in Fig. 4 more than 100 times. From the measured frequencies and the frequency shift estimation, we have estimated the absolute frequency of the  $^{40}\text{Ca}^+$  clock transition to be 411 042 129 776 390(7) Hz. A histogram of the all the measured transition frequency data is shown in Fig. 5. The standard error of 3.9 Hz, which is the standard deviation divided by the root square of the total measurement number, includes the 397-nm Stark shift error and the statistical error called Type A. This error is smaller than the error estimated for the electric quadrupole shift. Therefore, the total uncertainty of 7 Hz is mainly limited by the quadrupole shift.

### C. Electric Quadrupole Shift

The electric quadrupole moment of the  $D_J$  state interacts with the electric fields and that causes an energy shift of a few hertz. The shift of the  $M_J$  sublevel of the  $D_J$  state is estimated using

$$\hbar\Delta\nu_Q = \frac{dE_z}{dz} \Theta(D, J) \frac{J(J+1)-3M_J^2}{4J(2J-1)} (3\cos^2\beta-1), \quad (2)$$

where  $dE_z/dz$  is the electric field gradient along the symmetry axis of the trap potential ( $z$ ),  $\beta$  is the angle between the axis  $z$  and the magnetic field, and  $\Theta(D, J)$  is the strength of the quadrupole moment in terms of a reduced matrix element. From the  $M_J$  dependence of the quadrupole shift, it can be cancelled by averaging the transition frequencies to all the  $M_J$  levels. However, because the transition linewidth is broadened by residual magnetic fluctuation and transition frequencies of the  $|^2S_{1/2}, \pm 1/2\rangle \rightarrow |^2D_{5/2}, \pm 5/2\rangle$  components are much more sensitive to the magnetic fluctuation than the  $|^2S_{1/2}, \pm 1/2\rangle \rightarrow |^2D_{5/2}, \pm 1/2\rangle$  and the  $|^2S_{1/2}, \pm 1/2\rangle \rightarrow |^2D_{5/2}, \pm 3/2\rangle$  components, it is not practicable to average the transition frequencies to all the  $M_J$  levels. Because of the observed linewidths of the  $\Delta M_J = 0$  components of about 300 Hz, the linewidths of the  $|^2S_{1/2}, \pm 1/2\rangle \rightarrow |^2D_{5/2}, \pm 3/2\rangle$  components was expected to be about 600 Hz. From Eq. (2), the ratio of the quadrupole shifts of the  $\pm 1/2$  level to the  $\pm 3/2$  level is 4:1. We therefore have measured the  $|^2S_{1/2}, \pm 1/2\rangle \rightarrow |^2D_{5/2}, \pm 1/2\rangle$  and  $|^2S_{1/2}, \pm 1/2\rangle \rightarrow |^2D_{5/2}, \pm 3/2\rangle$  components and calculated the transition frequency corrected for the quadrupole shift using the following equation

$$f_Q = (4/3)f_{\pm 3/2} - (1/3)f_{\pm 1/2}, \quad (3)$$

where  $f_{\pm 3/2}$  is the average of transition frequencies of  $|4\ ^2S_{1/2}, 1/2\rangle \rightarrow |3\ ^2D_{5/2}, 3/2\rangle$  and  $|4\ ^2S_{1/2}, -1/2\rangle \rightarrow |3\ ^2D_{5/2}, -3/2\rangle$ ,  $f_{\pm 1/2}$  is the average of transition frequencies of  $|4\ ^2S_{1/2}, 1/2\rangle \rightarrow |3\ ^2D_{5/2}, 1/2\rangle$  and  $|4\ ^2S_{1/2}, -1/2\rangle \rightarrow |3\ ^2D_{5/2}, -1/2\rangle$ .

### D. Zeeman Spectrum to the $3\ ^2D_{5/2}$ ( $M_J = \pm 1/2, \pm 3/2$ ) Levels

We have observed two pairs of the symmetrically splitting Zeeman components. The spectra are observed using the same method to the spectra of the  $\Delta M_J = 0$  components mentioned already. An example of the spectra is shown in Fig. 6. To

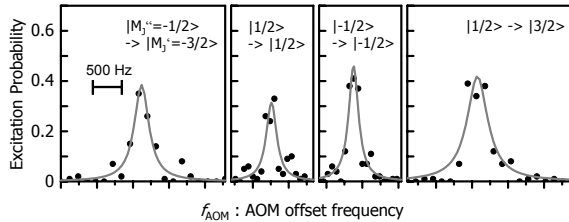


Figure 6. Example of the two Zeeman pairs of the  $|4\ ^2S_{1/2}, M_J' = \pm 1/2\rangle \rightarrow |3\ ^2D_{5/2}, M_J' = \pm 3/2\rangle$  and  $|4\ ^2S_{1/2}, M_J' = \pm 1/2\rangle \rightarrow |3\ ^2D_{5/2}, M_J' = \pm 1/2\rangle$  transitions of  $^{40}\text{Ca}^+$  ions. The dots showing the observed values are approximated by Lorenz line profiles. A scale of 500 Hz is available to estimate linewidths of four Zeeman components.

minimize time difference in observation of the center parts of the four components, after a data acquisition of one component at a single clock laser frequency, the laser frequency is tuned to one of other components, and we acquired the excitation probability data one after the other among the four Zeeman components. The clock laser was applied for 4 ms at every measurement sequence, which is synchronized with the electric 50 Hz. The linewidth of the  $|^2S_{1/2}, \pm 1/2\rangle \rightarrow |^2D_{5/2}, \pm 3/2\rangle$  components is almost twice of the  $|^2S_{1/2}, \pm 1/2\rangle \rightarrow |^2D_{5/2}, \pm 1/2\rangle$  components because of the difference in the sensitivity of the transition frequency shift to the residual magnetic fluctuation.

### E. Absolute Frequency Estimation

We observed such spectra as is shown in Fig. 6 more than 100 times. The distribution of all the measured transition frequency data is shown in Fig. 7. They are not corrected for the frequency difference between the UTC(NICT) and the TT using BIPM Circular T, which will be published in May 2009. The standard error of 3.6 Hz includes the 397-nm Stark shift error, the quadrupole shift cancellation error and Type A error. The frequency difference between the UTC(NICT) and the TT is usually a few hertz and its error is  $<1$  Hz. Therefore, we hope that by the correction using the Circular T the absolute frequency will be determined with a total error of  $<4$  Hz. In this case, its relative uncertainty will be at the  $10^{-15}$  level. The Innsbruck university and LNE-SYRTE group has measured the clock transition frequency of  $^{40}\text{Ca}^+$  ions to be 411 042 129 776 393.2(1.0) Hz [16]. Although our measurement has a larger uncertainty, the both measurements are consistent.

## IV. SUMMARY AND FUTURE PLAN

Calcium ion is very attractive for application in optical frequency standards because its  $4\ ^2S_{1/2} - 3\ ^2D_{5/2}$  clock transition can be measured with existing LDs. By using LD-based light sources and a small ion trap, we are developing a robust and compact optical frequency standard. The measured optical clock frequency of  $^{40}\text{Ca}^+$  ions is 411 042 129 776 390(7) Hz, which corresponds to  $1.7 \times 10^{-14}$  relative uncertainty. Because the error in the frequency-shift estimation of the electric quadrupole shift contributes largely to the total error of 7 Hz, we have measured the transition frequency corrected for the quadrupole shift by observing two pairs of the symmetrically splitting Zeeman components. We will correct the measured

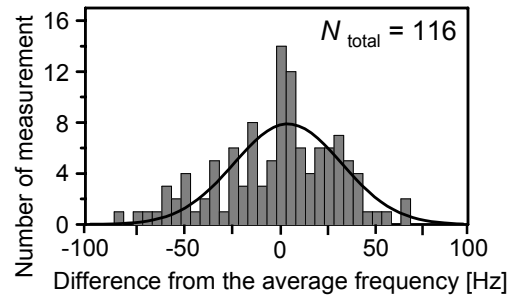


Figure 7. Distribution of all the measured transition frequency data. The standard deviation of the measured frequency (SD) is 38.4 Hz, and the standard error, SD divided by the root square of  $N_{\text{total}}$ , is 3.6 Hz.



Figure 8. The two-layer magnetic shield for ion trap of  $^{40}\text{Ca}^+$  ions. In the magnetic shield (right side), there are a vacuum chamber (70-mm cube) and three pairs of magnetic coils.

transition frequency for the frequency difference between the UTC(NICT) and the TT to determine the absolute frequency with a relative uncertainty of  $< 10^{-14}$ .

At present the spectral linewidth is limited to about 300 Hz because of the residual ambient magnetic fluctuation. Even if we irradiate the ion with the clock laser for a longer time than 4 ms, the magnetic fluctuation for the irradiation time causes a larger line broadening than 300 Hz. We therefore develop a magnetic-shielded ion-trap chamber, which is shown in Fig. 8. The vacuum pressure is attainable to be  $10^{-9}$  Pa level. The magnetic strength is reduced to  $< 1/20$  in the shield. We expect that some improvements, including the magnetic shielding and more stable cooling and clock laser system, will make it possible to determine the clock frequency with a relative uncertainty of  $< 5 \times 10^{-15}$ .

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