Optical clock sensitive to variations of the fine-structure constant based on the Ho^{14+} ion

V. A. Dzuba and V. V. Flambaum
School of Physics, University of New South Wales, Sydney 2052, Australia

Hidetoshi Katori
Quantum Metrology Laboratory, RIKEN, Wako-shi, Saitama 351-0198, Japan;
Innovative Space-Time Project, ERATO, Japan Science and Technology Agency, Bunkyo-ku, Tokyo 113-8656, Japan;
and Department of Applied Physics, Graduate School of Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan
(Received 3 November 2014; published 23 February 2015)

We study the Ho^{14+} ion as a candidate for an extremely accurate and stable optical atomic clock which is sensitive to the time variation of the fine-structure constant. We demonstrate that the proposed system has all the desired features including relatively strong optical electric-dipole and magnetic-dipole transitions which can be used for cooling and detection. Zero quadrupole moments for the relevant states in the clock transition allow interrogation of multiple ions to improve the clock stability.

DOI: 10.1103/PhysRevA.91.022119 PACS number(s): 06.20.Jr, 06.30.Ft, 31.15.A−, 32.30.Jc

Theories unifying gravity with other fundamental interactions suggest a possibility for fundamental constants to vary in space or time (see, e.g., Ref. [1]). Searching for variation of the fundamental constants is an important way of testing these theories and finding new physics beyond the standard model. Laboratory measurements limit the rate at which the fine-structure constant α ($\alpha = e^2/\hbar c$) varies in time to about 10^{-17} per year [2,3]. On the other hand, the analysis of quasar absorption spectra shows that the fine-structure constant may vary on an astronomical scale along a certain direction in space forming the so-called α dipole [4]. Earth's movement in the framework of the α dipole (towards areas of bigger α) would lead to the local time variation of α on the scale of 10^{-19} per year [5]. To test the α-dipole hypothesis in terrestrial studies one needs a better accuracy in the laboratory measurements. The current best limit on the local time variation of α has been obtained by comparing Al^+ and Hg^+ optical clocks [2]. The result of this comparison limits the time variation of α to $(\partial\alpha/\partial t)/\alpha = (-1.6 \pm 2.3) \times 10^{-17}$ yr^{-1} [2]), i.e., about 2 orders of magnitude improvement in accuracy is needed to test the α-dipole hypothesis.

The current best optical clocks approach a fractional uncertainty of $\sim 10^{-18}$ [6–8]. However, the transitions used in these clocks are not sufficiently sensitive to the variation of α [9]. If α does change in time, the relative change $\delta\omega/\omega$ of the clock frequencies in any given period of time would be about an order of magnitude smaller than the relative change in $\delta\alpha/\alpha$.

It has been suggested in Ref. [10] to use highly charged ions (HCIs) as extremely accurate atomic clocks to probe possible variation of α. While HCIs are less sensitive to external perturbations due to their compact size, their sensitivity to variation of α is enhanced due to larger relativistic effects. Despite the general trend of increasing energy intervals in HCIs, it is still possible to find clock transitions which are in optical range. This is due to electron energy level crossing while moving from the Madelung level ordering to the Coulomb level ordering with increasing of the ionization degree [11]. A number of optical clock transitions sensitive to variation of α are examined in Refs. [10–17].

Proposals for HCI clocks so far have focused on their high-accuracy aspects, such as the reduced sensitivity to blackbody radiation shift due to a lack of infrared and optical transitions [14]. These proposals, therefore, naturally assume to use quantum logic spectroscopy (QLS) [18] by cotrapping optically accessible ions. From an experimental viewpoint, however, an increase of the number of ions is a pressing need in order to improve clock stability, which is limited by the quantum projection noise (QPN) [19]. Clock stability at the QPN limit is given by $\sigma_y \approx \frac{1}{Q}\frac{1}{\sqrt{N\tau/\tau_c}}$, where $Q = \omega/\Delta\omega$ is the effective quality factor for the interrogated transition and N is the number of ions measured in the clock's cycle time τ_c. Assuming $Q \approx 10^{15}$ and $\tau_c = 1$ s, which are achievable with state-of-the-art lasers [20], a goal uncertainty of, e.g., 1×10^{-18} determines the necessary averaging time of $\tau = 10^6 N^{-1}$ s. In order to achieve this goal within a realistic experimental run time of $\tau \sim 10^4$ s ($\sim$3 h), $N \approx 10^2$ ions need to be interrogated simultaneously. Regrettably, QLS is not applicable to such a number of ions because of difficulties in controlling the degrees of motional states of the ions; therefore electron shelving detection [21] needs to be adopted instead. Moreover, with $N > 1$ ions present, spatially inhomogeneous quadrupole shift originating from Coulomb interactions between ions becomes a major concern.

For these reasons we relax the condition of having a simple electron structure and search for ions which have relatively strong electric-dipole ($E1$) or magnetic-dipole ($M1$) optical transitions from both ground and clock states. The criteria for a suitable system are the following.

(i) Clock transition has a high sensitivity to the variation of α (e.g., it is a $5s$ to $4f$ or $5p$ to $4f$ transition).

(ii) It is optical transition (230 nm $< \lambda <$ 2000 nm or 5000 $cm^{-1} < \hbar\omega <$ 43 000 cm^{-1}) for existing narrow-linewidth lasers to access.

(iii) It is a transition between long-lived states with a lifetime between 100 and 10^4 s.

(iv) There are other relatively strong optical transitions (equivalent lifetime, $\tau \leqslant 1$ ms).

(v) Clock transition is not sensitive to the gradients of the electric field (e.g., there is no electric-quadrupole moment in both states).

Note that blackbody radiation shift is not a limiting factor for HCI clocks, since trapping of HCIs for more than

TABLE I. Highly charged ions with optical clock transitions sensitive to variation of α satisfying the criteria discussed in the text.

Ion	Ground state		Clock state		Energy (cm^{-1})
Er^{14+}	$4f^7 5s$	$J=4$	$4f^6 5s^2$	$J=0$	18 555
Dy^{10+}	$4f^7 5p$	$J=3$	$4f^6 5p^2$	$J=0$	20 835
Ho^{14+}	$4f^6 5s$	$J=0.5$	$4f^5 5s^2$	$J=2.5$	23 800

a day requires an ultrahigh vacuum of $\sim 10^{-12}$ Pa that is achievable with cryogenic pumps, which naturally cools the environmental temperature to ~ 10 K. Here we assume a typical collision cross section of $\sim 10^{-14}$ cm^2 between HCIs and residual gases [22].

Clock transitions for some HCIs that satisfy all these criteria are presented in Table I. All these ions have complicated electronic structures with six to eight electrons in open $4f$, $5s$, and $5p$ shells. The analysis is done by the many-electron version of the configuration interaction (CI) method developed in Ref. [23]. Breit and quantum radiative corrections are also included as has been described in Refs. [24,25]. The precision of this analysis is limited, which means that the clock frequencies calculated in Table I may differ from real ones by up to an estimated value of 10 000 cm^{-1}. Even with this shift most of the presented transitions remain in the optical range.

We now discuss in more detail the Ho^{14+} ion which currently appears as the best candidate for an optical clock. Its level structure is shown in Fig. 1. Table II shows low-lying energy levels of Ho^{14+}. For the $4f^6 5s\ {}^8F_{1/2}$ ground state, the $4f^5 5s^2\ {}^6H^o_{5/2}$ state can be taken as the clock state. Only levels which are connected to the ground or clock state by electric-dipole ($E1$) or magnetic-dipole ($M1$) transitions are shown in Table II. The total number of states in the considered energy interval is much larger. For each fine-structure multiplet, $N_s = \min(2S+1, 2L+1)$ gives the number of states, where

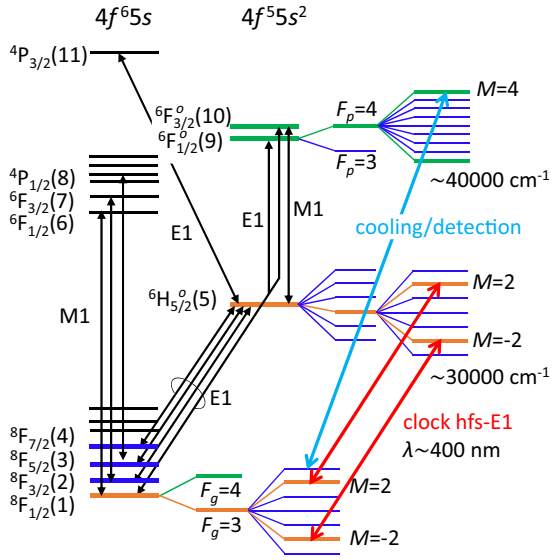

FIG. 1. (Color online) Low-lying energy levels of Ho^{14+}. Numbers in parentheses correspond to those in Tables II and IV to denote electronic states.

TABLE II. Low-lying states of Ho^{14+}, their energies (cm^{-1}), g factors, and lifetimes (s). Not all states are shown but only the ground state, the clock state (at $E = 23\,823$ cm^{-1}), and states which have relatively strong $E1$ or $M1$ transitions to either of the two states. Electronic states are numerated as $n = 1,2,3\ldots$ from the lowest state.

n	State		Energy (cm^{-1})	g factor	Lifetime (s)
1	$4f^6 5s$	${}^8F_{1/2}$	0	3.94	
2		${}^8F_{3/2}$	1013	1.99	8.2
3		${}^8F_{5/2}$	2499	1.71	2.3
4		${}^8F_{7/2}$	4298	1.61	1.4
5	$4f^5 5s^2$	${}^6H^o_{5/2}$	23 823	0.286	37
6	$4f^6 5s$	${}^6F_{1/2}$	30 199	−0.17	0.10
7		${}^6F_{3/2}$	31 713	1.22	0.14
8		${}^4P_{1/2}$	34 285	2.96	0.01
9	$4f^5 5s^2$	${}^6F^o_{1/2}$	37 351	−0.63	0.002
10	$4f^5 5s^2$	${}^6F^o_{3/2}$	37 771	1.05	0.005
11	$4f^6 5s$	${}^4P_{3/2}$	38023	1.80	0.01

S is the total spin and L is the total orbital angular momentum. The values of S and L and the corresponding names of the multiplets are found from the values of the g factors (see Table II):

$$g = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}. \qquad (1)$$

For example, the ground state is the lowest state of the ${}^8F$ multiplet which has seven levels with total angular momentum J ranging from $J = 1/2$ to $J = 13/2$. The corresponding nonrelativistic value of the g factor (1) is $g = 4.0$, while the value obtained in the CI calculations is $g = 3.94$.

The clock transition can go as a magnetic-quadrupole ($M2$) or electric-octupole ($E3$) transition. Corresponding rates are 8×10^{-14} and 4×10^{-12} s^{-1}. However, the transition rate is dominated by the electric-dipole ($E1$) transition mediated by the magnetic-dipole hyperfine-structure (hfs) interaction. The holmium atom has a single stable isotope, ^{165}Ho, with a nuclear spin of $I = 7/2$, a nuclear magnetic moment of $\mu = 4.173\mu_N$ [26], and a nuclear electric-quadrupole moment of $Q = 3.58$b [27] (1 b $= 10^{-28}$ m^2). Calculated hfs constants A and B are presented in Table III.

The largest contribution to the hfs-mediated $E1$ clock transition moment is given by

$$d_{\text{hfs-}E1} = \frac{\langle 4f^6 5s\ {}^8F_{1/2}|\hat{H}_{\text{hfs}}|4f^6 5s\ {}^8F_{3/2}\rangle}{\Delta E} \times \langle 4f^6 5s\ {}^8F_{3/2}|E1|4f^5 5s^2\ {}^6H^o_{5/2}\rangle, \qquad (2)$$

TABLE III. Magnetic-dipole and electric-quadrupole hfs constants A and B for the ground and clock states of $^{165}Ho^{14+}$.

State		A (GHz)	B (GHz)
$4f^6 5s$	${}^8F_{1/2}$	96.5	0
$4f^5 5s^2$	${}^6H^o_{5/2}$	3.53	−6.04

where $\hat{H}_{\rm hfs}$ is the magnetic-dipole hfs Hamiltonian, $E1$ is the electric-dipole operator, and $\Delta E = 1013$ cm^{-1} is the energy interval between the ground state and the dominating intermediate state. This term dominates due to small energy denominator. The hfs matrix element is equal to 1.94×10^{-5} a.u. The $E1$ matrix element is related to the electric-dipole transition amplitude between $n = 2$ and 5 states (see Table II) by an angular coefficient. Its value (10^{-5} a.u.) is small due to the absence of the single-electron electric-dipole transition between leading configurations (the $5s \to 4f$ transition cannot go as $E1$). The amplitude is not zero due to configuration mixing.

The spontaneous emission rate corresponding to the hfs-$E1$ transition moment [see Eq. (2)] is the same as that for the usual $E1$ transition (we use atomic units):

$$A_{\text{hfs-}E1} = \frac{4}{3}(\omega\alpha)^3 \frac{d^2_{\text{hfs-}E1}}{2F_c + 1}, \tag{3}$$

where $\omega = 0.092$ a.u. is the frequency of the clock transition, $d_{\text{hfs-}E1}$ is the reduced matrix element, and F_c is the total angular momentum of the clock state ($\mathbf{F} = \mathbf{I} + \mathbf{J}$). The emission rate from the clock state with $F_c = 3$ is 7.5×10^{-7} s^{-1}. Note that this transition rate gives negligible contribution to the clock state lifetime, which is dominated by the $E1$ transitions to three first excited states of the ground state configuration.

The Rabi frequency $\Omega = d_{\text{hfs-}E1}\mathcal{E}$ for the $4f^6 5s\ {}^8F_{1/2} \to 4f^5 5s^2\ {}^6H^o_{5/2}$ clock transition is estimated from Eq. (2) and the laser electric field $\mathcal{E}$. For a laser intensity of 16 mW/cm^2, the Rabi frequency is estimated to be 1 Hz. The corresponding frequency shift of the clock transition is about 10^{-3} Hz.

The ${}^6H^o_{5/2}$ clock state is split by the hfs interaction into six levels with $F_c = 1, \ldots, 6$. Similarly, the ${}^8F_{1/2}$ ground state is split into $F_g = 3$ and 4. We consider $F_c = F_g = 3$ with $M = 2$ states as a clock transition, because it is insensitive to the electric-field gradients that couple to atomic quadrupole moments and cause quadrupole shift. Since the quadrupole moment is proportional to $3M^2 - F(F+1)$ (M is a projection of F), choosing $F = 3$ and $M = \pm 2$ eliminates quadrupole frequency shift. Note that the ground state has no quadrupole moment because of the total electron angular momentum $J = 1/2$.

Optical pumping to the desired M states can be performed by employing strong $E1$ transitions from the ground state as given in Table IV. In the presence of a bias magnetic field, by applying σ^+-polarized light resonant to the $4f^5 5s^2\ {}^6F^o_{1/2}(F_p = 4)$ pump state (denoted by $n = 9$), ions are spin polarized in the $F_g = M = 3$ state, which is then transferred to the $F_g = 3$, $M = 2$ state by a stimulated Raman adiabatic passage (STIRAP) via the pump state. The STIRAP allows, in principle, a complete population transfer between two states [28]. This $E1$ line can be used for the electron-shelving detection [21]. With σ^+-polarized light resonant to this pump transition, the ground state population is swept into the $F_g = M = 3 \to F_p = M = 4$ quasicyclic transition, where four recycling lasers may depopulate the $F_g = 4$ state as well as $F = 3$, 4, and 5 states in the ${}^8F_{3/2}$ manifold. The same scheme as above can be conveniently used to sideband cool a chain of ions. Here we assume a linear Paul trap where multiple Ho^{14+} ions are cooperatively cooled by coolant ions such as Be^+ whose mass-charge ratio ($A/q = 9$) is similar to that of Ho^{14+} ($A/q \approx 11.8$). Because of the moderate charge state, Ho^{14+} ions can be produced relatively easily by, for instance, a compact electron beam ion trap (CoBIT) [29]. Its magnetic field may be turned off during the clock spectroscopy of Ho^{14+} ions in the linear Paul trap to avoid introducing Zeeman shift.

TABLE IV. Electric-dipole ($E1$) and magnetic-dipole ($M1$) transitions involving ground and clock states including spontaneous emission rates from upper states (n_U) to lower states (n_L), where numeration of the states corresponds to Table II. Numbers in square brackets represent powers of ten.

Transition		Frequency	Amplitude	Rate
$n_U \to n_L$	Type	(cm^{-1})	(10^{-3} a.u.)	(s^{-1})
a. Transitions to ground state ($n_L = 1$)				
$2 \to 1$	$M1$	1013	15	0.12
$6 \to 1$	$M1$	30 199	0.48	6.4
$7 \to 1$	$M1$	31 713	0.29	1.4
$8 \to 1$	$M1$	34 285	0.67	18
$9 \to 1$	$E1$	37 351	2.81	410
$10 \to 1$	$E1$	37 771	2.18	130
$11 \to 1$	$M1$	38 023	0.49	6.7
b. Transitions from and to clock state ($n_{U/L} = 5$)				
$5 \to 2$	$E1$	22 810	5.1 [−2]	1.0 [−2]
$5 \to 3$	$E1$	21 324	4.3 [−3]	6.0 [−5]
$5 \to 4$	$E1$	19 525	8.1 [−2]	1.6 [−2]
$10 \to 5$	$M1$	13 948	4.6 [−1]	0.29
$11 \to 5$	$E1$	14 200	7.1 [−2]	7.0 [−3]

The lifetime of the clock state is about 37 s. It is mainly due to electric dipole transitions to the first three excited states in the ground state configurations (see Table IV). The table also lists $E1$ and $M1$ transitions that can be used for electronic state manipulation as well as laser cooling of ions. In particular, the ${}^6H^o_{5/2} \to {}^6F^o_{3/2}$ ($M1$) transition followed by an $E1$ decay to the ground state may be conveniently used to depopulate the clock state. The amplitudes are given by reduced matrix elements of the electric-dipole ($e\mathbf{r} \cdot \mathbf{E}$) and magnetic-dipole ($\mu \cdot \mathbf{H}$) operators. The $M1$ amplitudes include the electron magnetic moment μ, which in atomic units is equal to $\alpha/2 = 3.65 \times 10^{-3}$ (Gaussian-based atomic units). Spontaneous emission rates for both $E1$ and $M1$ transitions are given by Eq. (3) with F_c replaced by J.

The clock transition is sensitive to variation of the fine-structure constant since it is a $4f$ to $5s$ transition [11]. It is convenient to present frequency dependence on α in the form

$$\omega(x) = \omega_0 + qx, \text{ where } x = \left[\left(\frac{\alpha}{\alpha_0}\right)^2 - 1\right]. \tag{4}$$

The sensitivity coefficient q is found in atomic calculations by varying the value of α in computer codes. In our calculations $q = -186\,000$ cm^{-1} and the variation of the clock frequency is related to the variation of the fine structure constant by

$$\frac{\delta\omega}{\omega} = -18\frac{\delta\alpha}{\alpha}. \tag{5}$$

As it has been mentioned above the precision of present calculations based on the version of the CI method developed in Ref. [23] is limited. The main problem is the energy interval between states of different configurations. Precision for energy intervals within one configuration is better and is on the level of 10% to 20%. Therefore, to start with, it is important to spectroscopically investigate transitions between different configurations using, e.g., CoBIT [30], whose spectral resolution of ~ 2 cm^{-1} will determine the fine structures. The best candidates are the $E1$ transitions from the ground state to the $^6F^o_{1/2,3/2}$ states located at $\sim 4 \times 10^4$ cm^{-1}. Once this frequency is measured, it helps to adjust the calculations and improves significantly all other predictions. Note that even significant change in the frequency of the clock transition of Ho^{14+} leaves it in the optical range, making the ion an attractive candidate for experimental study.

The work was supported by the Australian Research Council and by the Competitive Program for Creative Science and Technology Pioneering Projects, Riken. H.K. would like to thank M. Wada, N. Nakamura, and K. Okada for discussions on trapping HCIs.

[1] J.-P. Uzan, Rev. Mod. Phys. **75**, 403 (2003).
[2] T. Rosenband *et al.*, Science **319**, 1808 (2008).
[3] N. Leefer, C. T. M. Weber, A. Cingöz, J. R. Torgerson, and D. Budker, Phys. Rev. Lett. **111**, 060801 (2013).
[4] J. K. Webb, J. A. King, M. T. Murphy, V. V. Flambaum, R. F. Carswell, and M. B. Bainbridge, Phys. Rev. Lett. **107**, 191101 (2011).
[5] J. Berengut and V. V. Flambaum, EPL **97**, 20006 (2012).
[6] N. Hinkley, J. A. Sherman, N. B. Phillips, M. Schioppo, N. D. Lemke, K. Beloy, M. Pizzocaro, C. W. Oates, and A. D. Ludlow, Science **341**, 1215 (2013).
[7] B. J. Bloom, T. L. Nicholson, J. R. Williams, S. L. Campbell, M. Bishof, X. Zhang, W. Zhang, S. L. Bromley, and J. Ye, Nature (London) **506**, 71 (2014).
[8] I. Ushijima, M. Takamoto, M. Das, T. Ohkubo, and H. Katori, arXiv:1405.4071 [Nature Photonics (to be published)].
[9] E. J. Angstmann, V. A. Dzuba, and V. V. Flambaum, Phys. Rev. A **70**, 014102 (2004).
[10] J. C. Berengut, V. A. Dzuba, and V. V. Flambaum, Phys. Rev. Lett. **105**, 120801 (2010).
[11] J. C. Berengut, V. A. Dzuba, V. V. Flambaum, and A. Ong, Phys. Rev. A **86**, 022517 (2012).
[12] J. C. Berengut, V. A. Dzuba, V. V. Flambaum, and A. Ong, Phys. Rev. Lett. **106**, 210802 (2011).
[13] J. C. Berengut, V. A. Dzuba, V. V. Flambaum, and A. Ong, Phys. Rev. Lett. **109**, 070802 (2012).
[14] A. Derevianko, V. A. Dzuba, and V. V. Flambaum, Phys. Rev. Lett. **109**, 180801 (2012).
[15] V. A. Dzuba, A. Derevianko, and V. V. Flambaum, Phys. Rev. A **86**, 054502 (2012).
[16] M. S. Safronova, V. A. Dzuba, V. V. Flambaum, U. I. Safronova, S. G. Porsev, and M. G. Kozlov, Phys. Rev. Lett. **113**, 030801 (2014).
[17] M. S. Safronova, V. A. Dzuba, V. V. Flambaum, U. I. Safronova, S. G. Porsev, and M. G. Kozlov, Phys. Rev. A **90**, 042513 (2014).
[18] T. Rosenband, P. O. Schmidt, D. B. Hume *et al.*, Phys. Rev. Lett. **98**, 220801 (2007).
[19] W. M. Itano, J. C. Bergquist, J. J. Bollinger, J. M. Gilligan, D. J. Heinzen, F. L. Moore, M. G. Raizen, and D. J. Wineland, Phys. Rev. A **47**, 3554 (1993).
[20] T. Kessler, C. Hagemann, C. Grebing, T. Legero, U. Sterr, F. Riehle, M. J. Martin, L. Chen, and J. Ye, Nature Photonics **6**, 687 (2012).
[21] W. Nagourney, J. Sandberg, and H. Dehmelt, Phys. Rev. Lett. **56**, 2797 (1986).
[22] J. Vancura, V. J. Marchetti, J. J. Perotti, and V. O. Kostroun, Phys. Rev. A **47**, 3758 (1993).
[23] V. A. Dzuba and V. V. Flambaum, Phys. Rev. A **77**, 012514 (2008).
[24] V. A. Dzuba, V. V. Flambaum, and M. S. Safronova, Phys. Rev. A **73**, 022112 (2006).
[25] V. V. Flambaum and J. S. M. Ginges, Phys. Rev. A **72**, 052115 (2005).
[26] http://www.webelements.com/holmium/isotopes.html.
[27] P. Raghavan, At. Data Nucl. Data Tables **42**, 189 (1989).
[28] K. Bergmann, H. Theuer, and B. W. Shore, Rev. Mod. Phys. **70**, 1003 (1998).
[29] N. Nakamura, H. Kikuchi, H. A. Sakaue, and T. Watanabe, Rev. Sci. Instrum. **79**, 063104 (2008).
[30] A. Komatsu, J. Sakoda, M. Minoshima, H. A. Sakaue, X.-B. Ding, D. Kato, I. Murakami, F. Koike, and N. Nakamura, Plasma Fusion Res. **7**, 1201158 (2012).