

Accuracy estimation of the $^{16}\text{O}_2^+$ transition frequencies targeting the search for the variation in the proton-electron mass ratio

Masatoshi Kajita*

National Institute of Information and Communications Technology, Koganei, Tokyo 184-8795, Japan

(Received 14 November 2016; published 22 February 2017)

We estimate the Stark and Zeeman shifts in the transition frequencies of the $^{16}\text{O}_2^+$ molecular ion as a step in the search for the variation in the proton-to-electron mass ratio μ . The $X^2\Pi v = 21 - a^4\Pi v = 0$ or the $X^2\Pi v = 21 - a^4\Pi v = 1$ transition frequencies (THz region) of the $^{16}\text{O}_2^+$ molecular ion have particularly high sensitivity to the variation in μ . Note also that the Stark shift in the $^{16}\text{O}_2^+$ transition frequencies is expected to be much smaller than that for heteronuclear diatomic molecules. However, the actual systematic uncertainties for the $^{16}\text{O}_2^+$ transition frequencies have never been estimated. We estimated the Stark and Zeeman shifts in the different $^{16}\text{O}_2^+$ transition frequencies. When the molecular ions in a string crystal formed in a linear trap (trap electric field < 0.1 V/cm, and Stark shift $< 10^{-20}$) are used, the $X^2\Pi_{1/2}(v, J) = (0, 1/2) - (v', 1/2) (v' \geq 1)$ transition frequencies are most advantageous for the search for the variation in μ ($\Delta\mu/\mu < 10^{-17}$) because the Zeeman shift is easily suppressed to lower than 10^{-18} and the electric quadrupole shift is zero. On the other hand, the $X^2\Pi_{1/2}(v, J) = (21, 1/2) - a^4\Pi_{1/2}(v, J) = (0, 1/2)$ transition frequency has another merit in that the positive Stark shift induced by the trap electric field can be canceled by the quadratic Doppler shift. Therefore, the measurement using molecular ions in a Coulomb crystal broadened in the radial direction is also possible, when the Zeeman shift is effectively eliminated.

DOI: [10.1103/PhysRevA.95.023418](https://doi.org/10.1103/PhysRevA.95.023418)

I. INTRODUCTION

The standard model of physics is based on the assumption that the fundamental constants are perfectly constant throughout time and space, but Dirac mentioned the possibility of their variation in 1937 [1]. If there are variations in some fundamental constants, the energy structure of atoms and molecules will change. The variation of fundamental constants can be evaluated by measuring the variation in the ratio of two transition frequencies with different sensitivities. The variation in the fine structure constant α has become one of the hottest subjects for researchers since the measurement uncertainties of some atomic transition frequencies were reduced to lower than 10^{-15} [2–6]. Currently, the upper limit of the variation in α is estimated to be less than 10^{-17} /yr [7–9].

The variation in the proton-to-electron mass ratio $\mu = m_p/m_e$ has also been investigated because the ratio of the variations in α and μ provides useful information for grand unification theories [10]. Comparing the Cs hyperfine transition frequency with the $^{171}\text{Yb}^+$ transition frequency, Godun *et al.* and Huntemann *et al.* found that $\Delta\mu/\mu$ cannot be larger than 10^{-16} /yr [8,9]. Note that the variation in this frequency ratio reflects not only the variation in μ but also that in α . To evaluate the model-independent variation in μ , it is preferable to measure the variation in the ratio of the molecular vibrational-rotational transition frequencies to the $^1S_0 - ^3P_0$ transition frequencies of a ^{87}Sr atom or an $^{27}\text{Al}^+$ ion, which have very low sensitivity to μ and α [11] and measurement uncertainty less than 10^{-17} [4–6]. However, molecular transitions have never been measured with an uncertainty lower than 10^{-14} , although a stability of 6×10^{-15} was obtained with an I_2 -stabilized diode laser [12].

The precise measurement of molecular transitions is difficult because the complicated quantum energy structure makes laser cooling and localization in a selected quantum state difficult. Diatomic molecules including an atom without nuclear spin have relatively simple energy structures. The vibrational transition frequencies of M^6Li molecules in an optical lattice [13–15] and MH^+ molecular ions in a linear trap [16,17] are considered to have been measured with uncertainty lower than 10^{-16} , where M is the even isotope of a group II alkaline-earth metal (^{40}Ca , ^{88}Sr , etc.). However, the production of X^6Li molecules with kinetic energy lower than $10 \mu\text{K}$ has never been attained. MH^+ molecular ions have been produced, and the overtone-vibrational transition of a $^{40}\text{CaH}^+$ molecular ion has been observed [18]. The main problem in the case of using MH^+ molecular ions is that they have a large permanent electric dipole moment and their internal states are rearranged through the interaction with black-body radiation (BBR). A cryogenic environment is required to mitigate this effect.

A cryogenic chamber is not required for measurement using homonuclear diatomic molecular ions because there is no electric-dipole ($E1$) transition between different vibrational-rotational states in the electronic ground state. The Stark shift is much smaller than that for heteronuclear diatomic molecules because it is induced only by the coupling with electronic excited states. The N_2^+ ($I = 0$) (v, N) = $(0, 0) \rightarrow (v', 0)$ ($v' \geq 1$) transitions are expected to be measured with uncertainty lower than 10^{-17} (I : nuclear spin, v : vibrational state, N : rotational state) because the Zeeman and quadrupole shifts are zero [19,20]. The $^{14}\text{N}_2^+(v, N) = (0, 0) - (1, 2)$ transition has actually been observed [21]. N_2^+ molecular ions are produced in a selected vibrational-rotational state by resonance-enhanced multiphoton ionization (REMPI) [22]. To prepare the $^{14}\text{N}_2^+$ molecular ion with $I = 0$, high resolution REMPI is required, while I is always 0 for the $^{15}\text{N}_2^+$ molecular ion (natural abundance of 1 ppm) with $N = 0$.

*kajita@nict.go.jp; <http://www.nict.go.jp/en/index.html>

Also the $^{16}\text{O}_2^+$ molecular ion is an attractive homonuclear diatomic molecular ion because the ^{16}O nuclear spin is zero. Hanneke *et al.* proposed measuring the $^{16}\text{O}_2^+ X^2\Pi v = 21 - a^4\Pi v = 0$ or $X^2\Pi v = 22 - a^4\Pi v = 1$ transition frequencies for the reason given below [23]. The energy of the high vibrational state $E_{Xv}/h \approx 1000$ THz is approximately proportional to $\mu^{-0.5}$, while the energy of the $a^4\Pi v = 0, 1$ state E_a has almost no dependence on μ . The variation in $E_\delta/h = (E_a - E_{Xv})/h$ induced by the variation in μ is given by $\Delta E_\delta = -0.5E_{Xv}(\Delta\mu/\mu) = -PE_\delta(\Delta\mu/\mu)$, where $P = 0.5(E_{Xv}/E_\delta)$. The $X^2\Pi v = 21$ and $a^4\Pi v = 0$ ($X^2\Pi v = 22$ and $a^4\Pi$) states are accidentally quasidegenerated and E_δ/h is very sensitive to the variation in μ because $P > 100$. However, the possibility of searching for the variation in μ should be discussed with regard to not only the sensitivity but also the attainable frequency accuracy. The systematic frequency uncertainties for different shifts have never been estimated for the $^{16}\text{O}_2^+$ transition frequencies. In this paper, we discuss the Stark and Zeeman shifts in the different $^{16}\text{O}_2^+$ vibrational-rotational transition frequencies, including the $X^2\Pi v = 21 - a^4\Pi v = 0$ transition frequency. Considering both the sensitivity to the variation in μ and the attainable frequency measurement accuracy, the $X^2\Pi_{1/2}(v, J) = (0, 1/2) - (v', 1/2)(v \geq 1)$ transition frequencies are most advantageous for the search for the variation in μ when molecular ions in a string crystal formed in a linear trap (trap electric field < 0.1 V) are used. Here, J is the total angular momentum given by the electron spin, electron orbital angular momentum, and molecular rotation.

Measurement of the $X^2\Pi_{1/2}(v, J) = (0, 1/2) - (v', 1/2)(v \geq 1)$ transition frequencies can be performed with simpler experimental apparatus than that used for the measurement of the transition frequencies proposed by Hanneke *et al.* [23]. The production of $^{16}\text{O}_2^+$ molecular ions in the desired vibrational rotational state with $v \leq 1$ has already been realized by REMPI [24], but it is more difficult to prepare molecular ions in the highly excited state. The $v = 0 - v'$ transition is probed with a laser in the infrared or optical region, whose frequency stabilization is much easier than that for a THz wave to detect the transitions between accidentally degenerated states. Note also that the $X^2\Pi - a^4\Pi$ transition rate is much lower than that for the vibrational transitions in the $X^2\Pi$ state [23]. The quantum state of the molecular ion after the irradiation of the probe laser is monitored by a quantum logical detection system [25].

II. SENSITIVITY TO THE VARIATION IN FUNDAMENTAL CONSTANTS

When a fundamental constant changes by $X \rightarrow X + \Delta X$, the atomic or molecular transition frequency changes by $f \rightarrow f + \Delta f$. The parameter λ_X used to show the sensitivity of f to the variation in X is defined by

$$\lambda_X = \frac{(\Delta f/f)}{(\Delta X/X)} = \frac{X}{f} \frac{df}{dX}. \quad (1)$$

Values of λ_X are estimated from the change in f obtained by the *ab initio* calculation upon changing the value of X slightly. When f is given as a simple function of X , λ_X can also be obtained from the simple formula for (df/dX) . By measuring the ratio of the two transition frequencies $f_{1,2}$ with

TABLE I. $^{16}\text{O}_2^+$ transition frequencies f and sensitivity parameters for the proton-to-electron mass ratio λ_μ .

Transition	f (THz) [26]	λ_μ
$X^2\Pi_{1/2} v = 0 \rightarrow 1$	56.5	-0.49
$X^2\Pi_{1/2} v = 0 \rightarrow 4$	219.0	-0.48
$X^2\Pi_{1/2} v = 0 \rightarrow 8$	421.9	-0.46
$X^2\Pi_{1/2} v = 21 \rightarrow a^4\Pi_{1/2} v = 0$	2.7	140

different values of $\lambda_X(\lambda_{X1,2})$, the variation in X is obtained by evaluating

$$(\Delta X/X) = \frac{1}{(\lambda_{X1} - \lambda_{X2})} \frac{\Delta(f_1/f_2)}{(f_1/f_2)}. \quad (2)$$

Detection of the variation in X is possible when Δf is larger than the frequency measurement uncertainty δf . Therefore, the minimum detectable value of $(\Delta X/X)$ is estimated as $|\delta f/(\lambda_X f)|$, although Ref. [23] discusses only λ_X .

For a model-independent search of the pure variation in μ , the ratios of molecular vibrational-rotational transition frequencies to a reference frequency with small λ_μ and λ_α should be measured. The $^{87}\text{Sr } ^1\text{S}_0 - ^3\text{P}_0$ transition frequency (429.2 THz, 698 nm) is one of the best references because $\lambda_\mu < 10^{-4}$, $\lambda_\alpha = 0.06$ [11], and the frequency uncertainty is on the order of 10^{-18} [4,5].

Table I shows the $^{16}\text{O}_2^+ X^2\Pi_{1/2} v = 0 \rightarrow v'$ ($v' = 1, 4, 8$) transition frequencies f and the corresponding values of λ_μ . These transition frequencies are given by $f = v'f_v - v'(v'+1)xf_v$ with a difference of less than 0.01% from the experimental result [26], where f_v (=57.1 THz) and xf_v (=0.487 THz) are the harmonic and the unharmonic vibrational potential terms, respectively. Since $f_v \propto \mu^{-0.5}$ and $xf_v \propto \mu^{-1}$, λ_μ is approximately given by $[-0.5v'f_v + v'(v'+1)xf_v]/f$. The effect of the variation in the rotational constant on the estimation of λ_μ is negligible for the vibrational transition frequency. The $v = 0 \rightarrow 4$ transition is convenient for cooperative measurement between two laboratories, because the probe laser light (1369 nm) can be transferred to a distant location via an optical fiber and can be compared with a ^{87}Sr lattice clock laser (698 nm) after frequency doubling. The $v = 0 \rightarrow 8$ transition is convenient for direct comparison with a ^{87}Sr lattice clock laser with a frequency difference of 7.3 THz. The values of f and λ_μ are also shown for the $^{16}\text{O}_2^+ X^2\Pi_{1/2} v = 21 \rightarrow a^4\Pi_{1/2} v = 0$ transition, which was proposed by Hanneke *et al.* [23] because of the large value of λ_μ .

III. ESTIMATION OF THE STARK SHIFT

For homonuclear diatomic molecules, the Stark shift is induced only by the coupling with electronically excited states and its dependence on the rotational state is very small. Using the values of the transition frequencies and Einstein coefficients listed in Ref. [27], we obtained the dc quadratic Stark energy shift in each vibrational state in the $X^2\Pi v = 0, 1, 4, 8$, $J = 1/2$ state ($a^4\Pi v = 0$, $J = 1/2$ state) by considering the coupling with the $A^2\Pi v = 0-21$ ($b^4\Sigma v = 0-7$) states. Table II lists the dc quadratic Stark

TABLE II. Stark coefficients induced by a dc electric field, $\delta f_S/E^2$, blackbody radiation $\delta f_{\text{BBR}}/(T/300)^4$, and a probe laser $\delta f_P/I_P$ listed as ratios to $\lambda_\mu f$ to show the utility of searching for the variation in the proton-to-electron mass ratio μ .

Transition	$\delta f_S/[\lambda_\mu f E^2]/[(\text{V}/\text{cm})^2]$	$\delta f_{\text{BBR}}/[\lambda_\mu f [T(\text{K})/300]^4]$	$\delta f_P/[\lambda_\mu f I_P]/[(\text{W}/\text{cm}^2)]$
$X^2\Pi_{1/2} v = 0 \rightarrow 1$	1.1×10^{-19}	7.0×10^{-18}	4.3×10^{-17}
$X^2\Pi_{1/2} v = 0 \rightarrow 4$	6.2×10^{-20}	4.0×10^{-18}	2.4×10^{-17}
$X^2\Pi_{1/2} v = 0 \rightarrow 8$	6.8×10^{-20}	4.3×10^{-18}	3.4×10^{-17}
$X^2\Pi_{1/2} v = 21 \rightarrow a^4\Pi_{1/2} v = 0$	8.9×10^{-20}	5.6×10^{-18}	3.3×10^{-17}

coefficients $\delta f_S/[\lambda_\mu f E^2]$ for each transition frequency (E : electric field). For the molecular ions in a string crystal formed in a linear trap, the trap electric field is less than 0.1 V and $|\delta f_S/[\lambda_\mu f]| < 10^{-20}$ is attained.

A Stark δf_{BBR} is also induced by BBR, which is approximately proportional to T^4 , where T is the ambient temperature. Table II lists $\delta f_{\text{BBR}}/[\lambda_\mu f [(T(\text{K})/300)^4]$. Stabilizing T by replacing it with $T \pm \Delta T$, the uncertainty of $\delta f_{\text{BBR}}/[\lambda_\mu f]$ is reduced by a factor of $4\Delta T/T$.

The Stark shift is also induced by a probe laser and is proportional to the laser intensity I_P . Values of $\delta f_P/[\lambda_\mu f I_P]$, where δf_P is the Stark shift induced by the probe laser, are also shown in Table II. Observing the one-photon quadrupole ($E2$) transition, the probe laser intensity is expected to be less than 10 mW/cm² and $\delta f_P/[\lambda_\mu f] < 10^{-18}$. This shift can be further suppressed by the hyper-Ramsey method [28].

Comparing $\delta f_S/[\lambda_\mu f E^2]$, $\delta f_{\text{BBR}}/[\lambda_\mu f [T(\text{K})/300]^4]$, and $\delta f_P/[\lambda_\mu f I_P]$, there is no significant difference between the different $^{16}\text{O}_2^+$ transition frequencies listed in Table II. However, note that the positive Stark shift induced by the trap electric field can be eliminated by cancellation with the quadratic Doppler shift (see Sec. V) by applying a suitable rf-trap electric field frequency [29]. For the $X^2\Pi_{1/2} v = 21 \rightarrow a^4\Pi_{1/2} v = 0$ transition frequency, δf_S is positive and it can be eliminated by applying the rf-trap electric field with the frequency of 11 MHz. For the $X^2\Pi_{1/2} v = 0 \rightarrow v'$ transition frequencies, δf_S is negative ($\delta f_S/[\lambda_\mu f E^2]$ shown in Table II is positive with negative values of λ_μ) and the cancellation with the quadratic Doppler shift is not possible.

IV. ESTIMATION OF ZEEMAN SHIFT

The Zeeman shift in the $^{16}\text{O}_2^+$ molecular ion in the $X^2\Pi_\Omega(v, J)$ state is estimated by a considerably different method from that in molecules in the Σ state because the electron orbital angular momentum and electron spin are defined with the component parallel to the molecular axis with the quantum numbers Λ and Σ , respectively. Here, $\Omega = \Lambda + \Sigma$ and there is an energy gap A_v between different Ω states at each vibrational state. The molecular rotation is not defined by an independent quantum number (with the Σ state, defined by N), and the rotational energy is given by the total angular momentum J as $B_v [J(J+1) - \Omega^2]$, where B_v is the rotational constant in each vibrational state. With the nonrelativistic approximation, the linear Zeeman energy shift E_Z in the $X^2\Pi_\Omega(v, J)$ state is given by [30]

$$E_Z = \left(\frac{\mu_B}{h}\right) \frac{M}{J(J+1)} \{ \Omega(g_L \Lambda + g_S \Sigma) + g_{R(v, \Omega, J)} [J(J+1) - \Omega^2] \} B, \quad (3)$$

where B is the magnetic field, M is the component parallel to the magnetic field, and μ_B is the Bohr magneton ($\mu_B/h = 1.3996$ MHz/G). The g factors of electron orbital angular momentum, electron spin, and molecular rotation are denoted as $g_L (=1)$, $g_S (=2.002)$, and $g_{R(v, \Omega, J)} (=3.06 \times 10^{-5}$ with $v = 0, \Omega = J = 1/2$), respectively. While g_L and g_S have no dependence on the vibrational state, $g_{R(v, \Omega, J)}$ (estimated by the method shown in Ref. [31]) has a dependence on v, Ω , and J . E_Z does not change with the $\Lambda \rightarrow -\Lambda, \Sigma \rightarrow -\Sigma, \Omega \rightarrow -\Omega$ transforms. The $^{16}\text{O}_2^+$ nuclear spin is zero; therefore, there is no hyperfine structure.

The Zeeman shift in the transition frequency δf_Z is given by the difference between E_Z in the upper and lower states. Considering Ω as a ‘‘good quantum number,’’ (Λ, Σ) is $(1, 1/2)$ in the $X^2\Pi_{3/2}$ state and $(1, -1/2)$ in the $X^2\Pi_{1/2}$ state. E_Z/B in the $X^2\Pi_{3/2}$ state is on the order of ± 1 MHz/G, while it is less than ± 1 kHz/G in the $X^2\Pi_{1/2}$ state. Therefore, $\delta f_Z/B$ in the $X^2\Pi_{1/2} \rightarrow X^2\Pi_{3/2}$ transition frequency is on the order of ± 1 MHz/G and is not suitable for precise measurement. Therefore we only consider the $\Delta\Omega = 0$ transitions.

Table III shows the linear Zeeman coefficients in the $X^2\Pi_{1/2} v = 0 \rightarrow 1$ vibrational-rotational transition frequencies. The Zeeman shift in the $\Delta J = \Delta M = 0$ transition frequency is much less than that in the $\Delta J = 2$ transition frequency because of the cancellation of the shifts in the upper and lower states. To examine the Zeeman shift in the $\Delta\Omega = \Delta J = \Delta M = 0$ transitions, the energy structure should be considered in more detail. There are off-diagonal matrix elements of the Hamiltonian $-B_v \sqrt{J(J+1) - 3/4}$ between the $X^2\Pi_{3/2}(v, J)$ and the $X^2\Pi_{1/2}(v, J)$ states [23], and they induce a mixture of both states (Ω mixture). For the $\Delta J = \Delta M = 0, J \geq 3/2$ transition, the Ω mixture leads the significant dependence of $g_{R(v, \Omega, J)}$ on v, Ω , and J [32]. The dependence of $g_{R(v, \Omega, J)}$ on v is mainly given by the dependence of A_v and B_v on v ($A_0 = 6.00$ THz, $B_0 = 50.4$ GHz, and $A_1 = 5.98$ THz, $B_1 = 49.8$ GHz [26]). Because of the $X^2\Pi_{1/2} - X^2\Pi_{3/2}$ coupling, there is a quadratic Zeeman shift with a coefficient smaller than ± 0.1 Hz/G² for the

 TABLE III. Linear Zeeman coefficients in the $X^2\Pi_{1/2} v = 0 \rightarrow 1$ vibrational-rotational transition frequencies $\delta f_Z/B$ and their ratio to $\lambda_\mu f$.

$X^2\Pi_{1/2}(v, J, M)$	$\delta f_Z/B$ (Hz/G)	$\delta f_Z/[\lambda_\mu f B]/(\text{G})$
$(0, 1/2, \pm 1/2) \rightarrow (1, 1/2, \pm 1/2)$	∓ 0.14	$\pm 5.1 \times 10^{-15}$
$(0, 3/2, \pm 3/2) \rightarrow (1, 3/2, \pm 3/2)$	∓ 4.3	$\pm 1.6 \times 10^{-13}$
$(0, 5/2, \pm 5/2) \rightarrow (1, 5/2, \pm 5/2)$	∓ 14	$\pm 5.2 \times 10^{-13}$
$(0, 1/2, \pm 1/2) \rightarrow (1, 5/2, \pm 5/2)$	± 1100	$\mp 4.1 \times 10^{-11}$

$J \geq 3/2$ states. The Zeeman shift in the $X^2\Pi_{3/2}(v, J, M) = (0, J', M') \rightarrow (v', J', M')$ transition frequency is $(-1) \times$ (Zeeman shift in the $X^2\Pi_{1/2}(0, J', M') \rightarrow (v', J', M')$ transition frequency).

The Ω -mixture effect does not exist for the $X^2\Pi_{1/2} J = 1/2$ state, and $|(g_{R(1,1/2,1/2)} - g_{R(0,1/2,1/2)})/g_{R(0,1/2,1/2)}| (\approx 0.01)$ is much smaller than $|(g_{R(1,\Omega,J)} - g_{R(0,\Omega,J)})/g_{R(0,\Omega,J)}|$ with $J \geq 3/2$. The relativistic effect leads a dependence of the spin-orbit interaction on v , but this effect is negligibly small (correction ratio $< 10^{-10}$) because the nuclear vibrational motion velocity is less than 2000 m/s. The linear Zeeman coefficient in the $X^2\Pi_{1/2}(v, J, M) = (0, 1/2, \pm 1/2) \rightarrow (v', 1/2, \pm 1/2)$ transition frequency is much smaller than that in the $\Delta J = \Delta M = 0, J \geq 3/2$ transition frequency. The Zeeman shift in the $(J, M) = (1/2, \pm 1/2) \rightarrow (1/2, \pm 1/2)$ transition is strictly linear with the magnetic field, and the Zeeman shift is perfectly eliminated by averaging the $M = \pm 1/2 \rightarrow \pm 1/2$ transition frequencies. Considering that $g_{R(v',1/2,1/2)} - g_{R(0,1/2,1/2)}$ is approximately proportional to v' [31], the change in $\delta f_Z/[\lambda_\mu f B]$ is less than 10% for the $X^2\Pi_{1/2}(v, J, M) = (0, 1/2, \pm 1/2) \rightarrow (v', 1/2, \pm 1/2)$ transition frequencies with $v' = 1-8$.

In the $a^4\Pi$ state, the linear Zeeman coefficient is smallest in the $a^4\Pi_{1/2}$ state, and it is on the order of ± 1 MHz/G in other $a^4\Pi_\Omega$ states. The couplings between different Ω states are much larger than those between the $X^2\Pi_{3/2}$ and $X^2\Pi_{1/2}$ states because of the smaller A_v ($A_0 = -1.4$ THz [23]). This effect is also significant when $J = 1/2$ because of the coupling between the $a^4\Pi_{1/2}$ and $a^4\Pi_{-1/2}$ states. For the $X^2\Pi_{1/2}(v = 21, J = 1/2, M = \pm 1/2) \rightarrow a^4\Pi_{1/2}(v = 0, J = 1/2, M = \pm 1/2)$ transition frequency, $\delta f_Z/B = \pm 1.4$ kHz/G and $\delta f_Z/[\lambda_\mu f B] = \pm 3.8 \times 10^{-12}$ /G. There is also a quadratic Zeeman shift with a coefficient smaller than ± 1 Hz/G². Therefore, the $X^2\Pi_{1/2}(v, J, M) = (0, 1/2, \pm 1/2) \rightarrow (v', 1/2, \pm 1/2)$ transition frequencies are most advantageous in the search for the variation in μ since they suppress the Zeeman shift to less than 10^{-18} .

V. OTHER FREQUENCY UNCERTAINTIES

For the molecular ions in a linear trap, there is a significant electric field gradient and the electric quadrupole shift can be a serious problem in precise measurement. This shift is proportional to $3M^2 - J(J+1)$, and it is zero for the $J = 1/2$ state. Measurement of the $J = 1/2 \rightarrow 1/2$ transition frequency is also advantageous for this reason. For other cases, the electric quadrupole shift should be eliminated by averaging the transition frequencies with different M .

The quadratic Doppler shift δf_{QD} is proportional to the kinetic energy K and $\delta f_{\text{QD}}/fK = -1/(m_i c^2) = -4.4 \times 10^{-18}/\text{mK}$ for all transition frequencies (m_i : mass of molecular ion). Then $\delta f_{\text{QD}}/f\lambda_\mu K = 8.8 \times 10^{-18}/\text{mK}$ for the pure vibrational frequencies and $\delta f_{\text{QD}}/f\lambda_\mu K = -3.1 \times 10^{-20}/\text{mK}$ for the $X^2\Pi_{1/2} v = 21 \rightarrow a^4\Pi_{1/2} v = 0$ transition frequency. A kinetic energy lower than 0.1 mK can be obtained by sideband Raman cooling and $|\delta f_{\text{QD}}/f\lambda_\mu| < 10^{-18}$ can be attained.

The gravity redshift is given by $\delta f_G/fH = g_a/c^2 = 10^{-18}/\text{cm}$, where H is the altitude and g_a is the acceleration due to gravity. For the pure vibrational transition frequency, $\delta f_G/f\lambda_\mu H = -2 \times 10^{-18}/\text{cm}$, and for

the $X^2\Pi_{1/2} v = 21 \rightarrow a^4\Pi_{1/2} v = 0$ transition frequency, $\delta f_G/f\lambda_\mu H = 7.1 \times 10^{-21}/\text{cm}$.

VI. COMPARISON WITH OTHER HOMONUCLEAR DIATOMIC MOLECULAR IONS

Reference [19] showed that the N_2^+ ($I = 0$) $X^2\Sigma(v, N, J, M) = (0, 0, 1/2, \pm 1/2) \rightarrow (v', 0, 1/2, \pm 1/2)$ transition frequency can be measured with uncertainty lower than 10^{-17} . In this section, we compare this transition frequency with the $^{16}\text{O}_2^+$ $X^2\Pi_{1/2}(v, J, M) = (0, 1/2, \pm 1/2) \rightarrow (v', 1/2, \pm 1/2)$ transition frequency.

The main difference is that the rotational energy is zero in the N_2^+ $N = 0$ state, while it is nonzero with the $^{16}\text{O}_2^+$ $J = 1/2$ state. Because of the zero rotational energy, the N_2^+ transition frequency can be observed without a Zeeman shift, and uncertainty lower than 10^{-17} can be obtained with a single transition. For the $^{16}\text{O}_2^+$ transition frequency, the rotational energy is nonzero, which makes the Zeeman shift nonzero. Uncertainty lower than 10^{-17} can be obtained by averaging the $M = \pm 1/2 \rightarrow \pm 1/2$ transition frequencies. A two-photon transition is required for the N_2^+ transition, while the one-photon $E2$ transition is possible for the $^{16}\text{O}_2^+$ transition.

The preparation of molecular ions with $I = 0$ is necessary for measurement using the N_2^+ molecular ion [20]. For this purpose, high-resolution REMPI is required with $^{14}\text{N}_2^+$. Another method is to use $^{15}\text{N}_2^+$, whose natural abundance is on the order of 1 ppm. The ^{16}O nuclear spin is zero; therefore, the preparation of $^{16}\text{O}_2^+$ molecular ions in $X^2\Pi_{1/2}(v, J) = (0, 1/2)$ by REMPI is possible using a simple laser system and natural O_2 gas [24]. Therefore, measurement using $^{16}\text{O}_2^+$ molecular ion is possible with a simpler apparatus than that with N_2^+ .

Measurement of the vibrational transition frequencies of H_2^+ , D_2^+ , and HD^+ molecular ions is useful to obtain the absolute values of μ and other parameters because they can be calculated by solving the Schrödinger and Dirac equations analytically [33,34]. The energy structures of H_2^+ and D_2^+ molecular ions are the same as those of the $^{15}\text{N}_2^+$ and $^{14}\text{N}_2^+$ molecular ions, respectively. However, the measurement of the vibrational transition frequencies with uncertainty lower than 10^{-17} is difficult, mainly because of the significant quadratic Doppler shift (for a kinetic energy of 1 mK, 7.0×10^{-17} for H_2^+ and 3.5×10^{-17} for D_2^+). For the measurement of the HD^+ transition frequency, the complicated hyperfine structure makes it difficult to localize the molecular ion in a selected quantum state.

VII. CONCLUSION

This paper discussed the possibility of searching for the variation in the proton-to-electron mass ratio μ via precise measurement of the transition frequencies of $^{16}\text{O}_2^+$ molecular ions, considering both the sensitivity parameter for the variation in μ (λ_μ) and the attainable accuracy ($\delta f/f$). Using molecular ions in a string crystal formed in a linear trap (trap electric field < 0.1 V/cm, and Stark shift $< 10^{-20}$), the $^{16}\text{O}_2^+$ $X^2\Pi_{1/2}(v, J, M) = (0, 1/2, \pm 1/2) \rightarrow (v', 1/2, \pm 1/2)$ transition frequencies are most advantageous

in searching for the variation in μ with $\Delta\mu/\mu < 10^{-17}$, because the Zeeman shift is strictly linear with small coefficients ($\delta f_Z/\lambda_\mu f B = \pm 5.1 \times 10^{-15}$ /G) and can be eliminated perfectly by averaging the $M = \pm 1/2 \rightarrow \pm 1/2$ transition frequencies. Note also that the electric quadrupole shift is zero.

The $X^2\Pi_{1/2}(v, J, M) = (21, 1/2, \pm 1/2) \rightarrow a^4\Pi_{1/2}(v, J, M) = (0, 1/2, \pm 1/2)$ transition has a large value of λ_μ , as proposed in Ref. [23]. However, it is not an advantageous transition for obtaining a low $[\delta f/\lambda_\mu f]$, because the linear Zeeman shift is much larger than that for the $X^2\Pi_{1/2}(v, J) = (0, 1/2) \rightarrow (v', 1/2)$ transition frequencies ($\delta f_Z/\lambda_\mu f B = \pm 83 \times 10^{-12}$ /G) and also the quadratic Zeeman shift exists. However, this transition has the merit that the Stark shift induced by the trap electric field is positive and can cancel with the quadratic Doppler shift when the rf-trap electric field frequency is 11 MHz [29]. Therefore, measurement using molecular ions in a string crystal is not required. Also, the electric quadrupole shift is zero for this transition frequency.

Measurement of the $X^2\Pi v = 0 - v'$ transition frequencies is much easier than that for the $X^2\Pi v = 21 \rightarrow a^4\Pi v = 0$ or $X^2\Pi v = 22 \rightarrow a^4\Pi v = 1$ transition frequencies because (1) the preparation of $^{16}\text{O}_2^+$ molecular ions in the $X^2\Pi v = 0, J = 1/2$ state is much easier than that in the highly excited state [24], (2) frequency stabilization of the probe laser in the infrared or optical region is much easier than that for a THz wave to induce the transition between accidentally degenerated states, and (3) the vibrational transition rate is much higher than that of the $X^2\Pi - a^4\Pi$ transition.

ACKNOWLEDGMENTS

I greatly appreciate my fruitful discussions with C. Shi and P. O. Schmidt (PTB). This research was supported by a Grant-in-Aid for Scientific Research (B) (Grant No. JP25287100), a Grant-in-Aid for Scientific Research (C) (Grant No. JP16K05500), and a Grant-in-Aid for Exploratory Research (Grant No. JP15K13545) from the Japan Society for the Promotion of Science (JSPS).

-
- [1] P. A. M. Dirac, The cosmological constants, *Nature (London)* **139**, 323 (1937).
- [2] S. Bize, S. A. Diddamus, U. Tanaka, C. E. Tanner, W. H. Oskay, R. E. Drullinger, T. E. Parker, T. P. Heavner, S. R. Jefferts, L. Hollberg, W. M. Itano, and J. C. Bergquist, Testing the Stability of Fundamental Constants with the $^{199}\text{Hg}^+$ Single-Ion Optical Clock, *Phys. Rev. Lett.* **90**, 150802 (2003).
- [3] N. Huntemann, C. Sanner, B. Lipphardt, Chr. Tamm, and E. Peik, Single-Ion Atomic Clock with 3×10^{-18} Systematic Uncertainty, *Phys. Rev. Lett.* **116**, 063001 (2016).
- [4] I. Ushijima, M. Takamoto, M. Das, T. Ohkubo, and H. Katori, Cryogenic optical lattice clocks, *Nat. Photon.* **9**, 185 (2015).
- [5] T. L. Nicholson, S. L. Campbell, R. B. Hutson, G. E. Marti, B. J. Bloom, R. L. McNally, W. Zhang, M. D. Barrett, M. S. Safronova, G. F. Strouse, W. L. Tew, and J. Ye, Systematic evaluation of an atomic clock at 2×10^{-18} total uncertainty, *Nat. Commun.* **6**, 6896 (2015).
- [6] C. W. Chou, D. B. Hume, J. C. J. Koelemeij, D. J. Wineland, and T. Rosenband, Frequency Comparison of Two High-Accuracy Al^+ Optical Clock, *Phys. Rev. Lett.* **104**, 070802 (2010).
- [7] T. Rosenband, D. B. Hume, P. O. Schmidt, C. W. Chou, A. Brusch, L. Lorini, W. H. Oskay, R. E. Drullinger, T. M. Fortier, J. E. Stalnaker, S. A. Diddamis, W. C. Swan, N. R. Newbery, W. M. Itano, D. J. Wineland, and J. C. Bergquist, Frequency ratio of Al^+ and Hg^+ single-ion optical clocks; Metrology at the 17th decimal place, *Science* **319**, 1808 (2008).
- [8] R. M. Godun, P. B. R. Nisbet-Jones, J. M. Jones, S. A. King, L. A. M. Johnson, H. S. Margolis, K. Szymaniec, S. N. Lea, K. Bongs, and P. Gill, Frequency Ratio of Two Optical Clock Transitions in $^{171}\text{Yb}^+$ and Constraints on the Time Variation of Fundamental Constants, *Phys. Rev. Lett.* **113**, 210801 (2014).
- [9] N. Huntemann, B. Lipphardt, C. Tamm, V. Gerginov, S. Weyers, and E. Peik, Improved Limit on a Temporal Variation of m_p/m_e from Comparisons of Yb^+ and Cs Atomic Clocks, *Phys. Rev. Lett.* **113**, 210802 (2014).
- [10] X. Calmet and H. Fritzsche, The cosmological evolution of the nucleon mass and electroweak coupling constants, *Eur. Phys. J. C* **24**, 639 (2002).
- [11] E. J. Angstmann, V. A. Dzuba, and V. V. Flambaum, Relativistic effects in two valence-electron atoms and ions and search for variation of the fine-structure constant, *Phys. Rev. A* **70**, 014102 (2004).
- [12] C. Philippe, R. L. Tragat, D. Holleville, M. Lours, T. Minh-Pham, J. Hrabina, F. D. Burck, P. Wolf, and O. Acef, Frequency triplet 1.5 μm telecom laser diode stabilized to iodine hyperfine line in the 10^{-15} range, in *Proceedings of the European Frequency and Time Forum (EFTF)* (IEEE, Piscataway, NJ, 2016).
- [13] M. Kajita, G. Gopakumar, M. Abe, and M. Hada, Elimination of Stark shift from the vibrational transition frequency of optically trapped $^{174}\text{Yb}^6\text{Li}$ molecules, *Phys. Rev. A* **84**, 022507 (2011).
- [14] M. Kajita, G. Gopakumar, M. Abe, and M. Hada, Accuracy estimation of overtone vibrational transition frequencies of optically trapped $^{174}\text{Yb}^6\text{Li}$ molecules, *Phys. Rev. A* **85**, 062519 (2012).
- [15] M. Kajita, G. Gopakumar, M. Abe, and M. Hada, Sensitivity of vibrational spectroscopy of optically trapped $^{88}\text{Sr}^6\text{Li}$ and $^{40}\text{Ca}^6\text{Li}$ molecules to variations in m_p/m_e , *J. Phys. B* **46**, 025001 (2013).
- [16] M. Kajita and Y. Moriwaki, Proposed detection of variation in m_p/m_e using a vibrational transition frequency of a CaH^+ ion, *J. Phys. B* **42**, 154022 (2009).
- [17] M. Kajita, M. Abe, M. Hada, and Y. Moriwaki, Estimated accuracies of XH^+ (X: even isotope of group II atoms) vibrational transition frequencies: Toward the test of the variance in m_p/m_e , *J. Phys. B* **44**, 025402 (2011).
- [18] N. B. Khanyile, G. Shu, and K. Brown, Observation of vibrational overtones by single-molecule resonant photodissociation, *Nat. Commun.* **6**, 7825 (2015).
- [19] M. Kajita, G. Gopakumar, M. Abe, and M. Keller, Test of m_p/m_e changes using vibrational transitions in N_2^+ , *Phys. Rev. A* **89**, 032509 (2014).

- [20] M. Kajita, N_2^+ quadrupole transitions with small Zeeman shift, *Phys. Rev. A* **92**, 043423 (2015).
- [21] M. Germann, X. Tong, and S. Willitsch, Observation of electric-dipole-forbidden infrared transitions in cold molecular ions, *Nat. Phys.* **10**, 820 (2014).
- [22] X. Tong, A. H. Winney, and S. Willitsch, Sympathetic Cooling of Molecular Ions in Selected Rotational and Vibrational States Produced by Threshold Photoionization, *Phys. Rev. Lett.* **105**, 143001 (2010).
- [23] D. Hanneke, R. A. Carollo, and D. A. Lane, High sensitivity to variation in the proton-to-electron mass-ratio in O_2^+ , *Phys. Rev. A* **94**, 050101(R) (2016) (Supplementary Material is given in [arXiv:1607.06825v1](https://arxiv.org/abs/1607.06825v1)).
- [24] A. Dochain and X. Urbain, Production of a rovibrationally selected O_2^+ beam for dissociative recombination studies, *EPJ Web Conf.* **84**, 05001 (2015).
- [25] M. Schulte, N. Loerch, I. D. Leroux, P. O. Schmidt, and K. Hammerer, Quantum Algorithmic Readout in Multi-Ion Clocks, *Phys. Rev. Lett.* **116**, 013002 (2016).
- [26] Y. Song, M. Evans, C. Y. Ng, C.-W. Hsu, and G. K. Jarvis, Rotational resolved pulsed ionization photoelectron bands of O_2^+ ($X^2\Pi_{1/2,3/2g}$, $v^+ = 0 - 38$) in the energy range of 12.5–18.15 eV, *J. Chem. Phys.* **111**, 1905 (1999).
- [27] F. R. Gilmore, R. R. Laher, and P. J. Espy, Franck-Condon factors, r-centroids, electronic transition moments, and Einstein coefficients for many nitrogen and oxygen band systems, *J. Phys. Chem. Ref. Data* **21**, 1005 (1992).
- [28] V. I. Yudin, A. V. Taichenachev, C. W. Oates, Z. W. Barber, N. D. Lemke, A. D. Ludlow, U. Sterr, Ch. Lisdat, and F. Riehle, Hyper-Ramsey spectroscopy of optical clock transitions, *Phys. Rev. A* **82**, 011804 (2010).
- [29] P. Dube, A. A. Madej, M. Tibbo, and J. E. Bernard, High-Accuracy Measurement of the Differential Scalar Polarizability of a $^{88}\text{Sr}^+$ Clock Using the Time-Dilation Effect, *Phys. Rev. Lett.* **112**, 173002 (2014).
- [30] C. H. Townes and A. L. Schawlow, in *Microwave Spectroscopy* (Dover, New York, 1955), p. 284.
- [31] J. Ph. Karr, V. I. Korobov, and L. Hilico, Vibrational spectroscopy of H_2^+ : Precise evaluation of the Zeeman effect, *Phys. Rev. A* **77**, 062507 (2008).
- [32] S. P. A. Sauer, A relation between the rotational g-factor and the electric dipole moment of a diatomic molecule, *Chem. Phys. Lett.* **297**, 475 (1998).
- [33] J. Ph. Karr, L. Hilico, J. C. Koemeij, and V. I. Korobov, Hydrogen molecular ions for improved determination of fundamental constants, *Phys. Rev. A* **94**, 050501(R) (2016).
- [34] S. Schiller, D. Bakalov, and V. I. Korobov, Simplest Molecules as Candidates for Precise Optical Clock, *Phys. Rev. Lett.* **113**, 023004 (2014).