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Accuracy estimations of overtone vibrational transition frequencies of optically trapped ^{174}Yb^{6}Li molecules

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The attainable accuracy of the $X\,^2\Sigma(v,N) = (0,0) \rightarrow (v_u,0)$ transition frequencies of optically trapped ^{174}Yb^{6}Li molecules are analyzed ($v_u = 1,2,3,4$) to test the variation in the proton-to-electron mass ratio. We eliminate the Stark shifts induced by the trap and Raman lasers by choosing appropriate frequencies (magic frequencies). For $v_u = 1$ and 2, we obtain more than one experimentally useful magic frequency, thereby leading to more choice in the trap laser. For $v_u = 3$ and 4, the choice in the trap laser is limited. The systematic frequency uncertainty is given by the trap laser frequency detuning from the magic frequency and the fluctuation of the power ratio of the two Raman lasers and can be lower than 10^{-16} for all these transition frequencies. To obtain lower statistical uncertainty, measurement with $v_u = 4$ is more advantageous than that with $v_u = 1 - 3$.

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I. INTRODUCTION

Precise measurements of molecular transitions are useful for testing the variation in the proton-to-electron mass ratio m_p/m_e because of their high sensitivities to m_p/m_e. The variation in m_p/m_e was first discussed on the basis of astronomical measurements, for which the variation over billions of years can be detected [1–4]. Muller *et al.* [4] estimated the upper limit of the variation in (m_p/m_e) in the $z = 0.89$ galaxy located in front of the quasar PKS 1830-211 to be 4×10^{-6}.

In astronomical research, we cannot distinguish between space and time variations. To test for pure time variations in m_p/m_e, one must compare measurements of molecular transitions with those of the atomic transition frequencies in the laboratory. The $^1S_0$-$^3P_0$ transition frequencies of the ^{87}Sr atom [5,6] or the ^{27}Al$^+$ ion [7] are particularly useful as references, because of the high attainable accuracies and low sensitivities to all the dimensionless fundamental constants (m_p/m_e, fine structure constant, etc.). Shelkovnikov *et al.* [8] measured the vibrational transition frequency of SF$_6$ molecules in a thermal beam at an uncertainty level of 10^{-14} using a Cs fountain clock as a reference and obtained $[d(m_p/m_e)/dt]/(m_p/m_e)$ to be $(-3.8 \pm 5.6) \times 10^{-14}$/years.

Several authors have proposed measuring the transition frequencies of cold molecules to test the variation in m_p/m_e [9–15]. Molecules in an optical lattice are particularly advantageous for measuring the transition frequency with low uncertainty because (1) the molecules and probe laser interact for a long time, (2) molecules are localized within the Lamb-Dicke region, (3) the measurement is possible with a large number of molecules, and (4) the collision effect is suppressed (molecules are trapped at different positions in two-dimensional (2D) lattices [6]). The Stark shift induced by the trap laser is also eliminated using the trap laser frequency in which the Stark energy shifts at the upper and lower states are equal (magic trap frequency). The $^1S_0$-$^3P_0$ transition frequency of Sr atoms in the optical lattice was measured with an uncertainty of less than 10^{-16} with this method [5,6]. Zelevinsky *et al.* [16] suggested measuring the $X\,^1\Sigma, v = 27 \rightarrow -3$ transition frequency of ^{88}Sr$_2$ molecules in the optical lattice (v, vibrational quantum number) and Kotochigova *et al.* demonstrated the existence of magic trap frequencies in the quasiresonant regions [17]. However, the Stark shift of the transition frequency is sensitive to slight fluctuations in the trap laser frequency in the quasiresonant region. Therefore, the trap laser frequency must be locked to the magic trap frequency with a very high stability (<1 kHz).

Our latest paper shows the possibility of measuring the $X\,^2\Sigma(v,N) = (0,0) \rightarrow (1,0)$ transition frequency of optically trapped ^{174}Yb^{6}Li molecules eliminating the Stark shift induced by the trap laser [18]. Here, N denotes the rotational quantum number. For the ^{174}Yb^{6}Li vibrational transition frequency, a magic trap frequency also exists in the far-off-resonance region, where the Stark shift is less than 10^{-16} if the trap laser frequency is detuned from the magic trap frequency by ∼1 MHz. The transition can be observed using a Raman transition, eliminating the Stark shift induced by the two Raman lasers by suitably choosing their frequencies (magic Raman frequencies). The Zeeman shifts of the $X\,^2\Sigma(v,N,F,M) = (0,0,3/2,\pm3/2) \rightarrow (1,0,3/2,\pm3/2)$ transitions are estimated to be negligibly small for a magnetic field of 1 G, where F is the quantum number of the hyperfine structure and M is the component of F parallel to the magnetic field [19]. The measurement procedure is as follows.

(1) ^{174}Yb^{6}Li molecules are produced by photoassociation or Feshbach resonance, trapped in a 2D-optical lattice [6]. Groups in Kyoto and Seattle are making progress toward the production of ^{174}Yb^{6}Li molecules via the Feshbach resonance. They have already simultaneous trapped ^{174}Yb and ^{6}Li atoms and observed quantum degenerate states [20–22].

(2) Produced molecules are transformed to the $X\,^2\Sigma(v,N) = (0,0)$ state via stimulated Raman transition, as

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TABLE I. ^{174}Yb^{6}Li $X^2\Sigma(v,N) = (0,0) \rightarrow (v_u,0)$ transition frequency $f_c(v_u)$, the parameter $\lambda(v_u)$ giving the sensitivity of $f_c(v_u)$ to the variation in (m_p/m_e) [defined by Eq. (1)], and the parameter $\kappa(v_u)$ giving the utility of measuring $f_c(v_u)$ to test the variation in (m_p/m_e) [defined by Eq. (5)].

Transition	$f_c(v_u)$(THz)	$\lambda(v_u)$	$\kappa(v_u)$
$v = 0 \rightarrow 1$	4.17	0.473	1
$v = 0 \rightarrow 2$	8.12	0.456	1.88
$v = 0 \rightarrow 3$	11.86	0.444	2.67
$v = 0 \rightarrow 4$	15.37	0.433	3.37
$v = 0 \rightarrow 5$	18.64	0.407	3.84
$v = 0 \rightarrow 6$	21.66	0.369	4.05
$v = 0 \rightarrow 7$	24.42	0.351	4.34
$v = 0 \rightarrow 8$	26.92	0.340	4.64
$v = 0 \rightarrow 9$	29.15	0.318	4.70
$v = 0 \rightarrow 10$	30.97	0.294	4.61
$v = 0 \rightarrow 11$	32.20	0.270	4.41
$v = 0 \rightarrow 12$	33.42	0.246	4.17
$v = 0 \rightarrow 13$	34.39	0.223	3.89

Ni *et al.* [23] and Aikawa *et al.* [24] have done successfully with alkali-alkali molecules. Given the large transition dipole moment between $X\,^2\Sigma$ and $B\,^2\Sigma$ states (see Table I in Ref. [18]), this treatment is also possible for ^{174}Yb^{6}Li molecules.

(3) Two Raman lasers are irradiated to induce the $X\,^2\Sigma(v,N) = (0,0) \rightarrow (1,0)$ transition.

(4) The number of molecules in the $X\,^2\Sigma(v,N) = (1,0)$ state $N(1)$ is monitored by selective photoionization.

(5) The number of molecules in the $X\,^2\Sigma(v,N) = (0,0)$ state $N(0)$ is also monitored. The transition rate is monitored as $N(1)/[N(0) + N(1)]$, eliminating the influence of fluctuations in the number of trapped molecules.

Measuring the overtone vibrational transition frequencies seems to be more advantageous than the $v = 0 \rightarrow 1$ transition frequency for reducing the statistical uncertainty, because of the higher transition frequencies. This paper discuss the usefulness of the ^{174}Yb^{6}Li $X\,^2\Sigma(v,N,F,M) = (0,0,3/2,\pm 3/2) \rightarrow (v_u,0,3/2,\pm 3/2)$ $(v_u \geqslant 1)$ transition frequencies $f_c(v_u)$ with different values of v_u for a test of variation in m_p/m_e. It compares the sensitivities of vibrational transition frequencies to the variation in m_p/m_e and attainable frequency uncertainties (statistical and systematic). Using the ^{174}Yb^{6}Li molecules in an optical lattice, the systematic uncertainty is mainly given by the influence of the detuning of the trap laser frequency from the magic frequency and the fluctuation of the power ratio of the two Raman lasers [18].

We estimated the Stark shifts using the values of transition frequencies and dipole moments obtained via an *ab initio* calculation [18,25,26].

II. TESTING THE VARIATION IN m_p/m_e

A test of variation for (m_p/m_e) is possible when

$$\left|\frac{\Delta f_c(v_u)}{f_c(v_u)}\right| = \lambda(v_u)\left|\frac{\Delta(m_p/m_e)}{(m_p/m_e)}\right| > \frac{\delta f_c(v_u)}{f_c(v_u)} \qquad (1)$$

is satisfied, where $f_c(v_u)$ denotes the $X\,^2\Sigma(v,N) = (0,0) \rightarrow (v_u,0)$ transition frequencies, $\Delta f_c(v_u)$ is the variation in $f_c(v_u)$ induced by the variation in (m_p/m_e), $\Delta(m_p/m_e)$, and $\delta f_c(v_u)$ is the measurement uncertainty of $f_c(v_u)$. Here $\lambda(v_u)$ is the parameter showing the sensitivity of $f_c(v_u)$ to (m_p/m_e), where $\lambda(v_u) = 0.5$ for a pure harmonic vibration.

Table I lists the values of $f_c(v_u)$ and $\lambda(v_u)$ obtained by calculating the variation in $f_c(v_u)$ changing m_p by $\pm 1\,\%$. As v_u becomes higher, $\lambda(v_u)$ decreases, because the unharmonicity of the vibration becomes more significant as v_u increases.

Seeing the astronomical results [3,4], we hope to reduce $[\delta f_c(v_u)/f_c(v_u)]$ to lower than 10^{-16}. The frequency uncertainty is given by

$$\frac{\delta f_c(v_u)}{f_c(v_u)} = \sqrt{\left(\frac{\delta f_c(v_u)}{f_c(v_u)}\right)_A^2 + \left(\frac{\delta f_c(v_u)}{f_c(v_u)}\right)_B^2}, \qquad (2)$$

where $[\delta f_c(v_u)/f_c(v_u)]_A$ and $[\delta f_c(v_u)/f_c(v_u)]_B$ denote the statistical (type A) and systematic (type B) frequency uncertainties, respectively. Sections II A and II B discuss the statistical and systematic uncertainties, respectively.

A. Statistical uncertainty

The statistical frequency uncertainty is estimated by the square root of the two-sample Allan variance [27,28]

$$\left(\frac{\delta f_c(v_u)}{f_c(v_u)}\right)_A \approx \frac{2}{\pi}\frac{1}{f_c(v_u)} \times \sqrt{\frac{\tau_e\{[\delta f_N(v_u)]^2 + D(\tau_p/\tau_e)^2[\delta f_p]^2\}}{\tau N_d}},$$

$$\delta f_N(v_u) \approx \max(\delta f_p, 1/2\pi\tau_p), \qquad (3)$$

where $\delta f_N(v_u)$ is the spectrum linewidth, δf_p is the linewidth of Raman lasers (assumed to be equal for two lasers), N_d is number of ^{174}Yb^{6}Li molecules detected in the $v = v_u$ state after the irradiation of the Raman lasers, τ_e is the time for one measurement cycle, τ_p is the irradiation time of the Raman lasers, τ is the measurement time, and $D(\tau_p/\tau_e)$ is a factor arising from the Dick effect ($D < 1$ with $\tau_p/\tau_e > 0.4$, $D \sim 2.5$ with $\tau_p/\tau_e \sim 0.1$, and $D \sim 10$ with $\tau_p/\tau_e < 0.03$). The irradiation rate $1/\tau_p$ must be higher than the rate at which the coherent interaction is interrupted, for example, by spontaneous emission $\gamma_s(<10^{-3}/s$ [26]) or photon scattering by the trap laser $\gamma_t(0.1 - 2/s$ [18]).

Here we estimate $[\delta f_c(v_u)/f_c(v_u)]_A$ when ^{174}Yb^{6}Li molecules are produced via photoassociation and Feshbach resonance. Of the two methods, photoassociation is advantageous to produce molecules with a short period, but the initial kinetic energy is as high as 100 μK. With Feshbach resonance, the production takes longer but the initial kinetic energy is lower than 1 μK and all the produced molecules can be transformed to the $(v,N) = (0,0)$ state. With Feshbach resonance, we can get more than 2 orders higher value of N_d than with photoassociation. We assume $\delta f_p = 1$ Hz, $\tau_p = 0.3$ s, $\tau_e = 3(15)$ s, and $N_d = 50(5000)$ when ^{174}Yb^{6}Li molecules are produced via the photoassociation (Feshbach resonance). Then $[\delta f_c(1)/f_c(1)]_A = 1.0 \times 10^{-13}/\sqrt{\tau(\text{s})}[8.4\times 10^{-14}/\sqrt{\tau(\text{s})}]$ and $[\delta f_c(4)/f_c(4)]_A = 2.7\times 10^{-14}/\sqrt{\tau(\text{s})}[2.3\times 10^{-14}/\sqrt{\tau(\text{s})}]$ are obtained for molecules produced by photoassociation (Feshbach resonance). Using probe lasers with narrower linewidth, the statistic uncertainty can be reduced significantly.

Seeing Eqs. (1)–(3), the following relation must be satisfied for testing the variation in m_p/m_e:

$$\lambda(v_u)\left|\frac{\Delta(m_p/m_e)}{(m_p/m_e)}\right| > \frac{\delta f_c(v_u)}{f_c(v_u)} > \frac{2\delta f_N(v_u)}{\pi f_c(v_u)}\sqrt{\frac{\tau_e}{N_d\tau}}. \qquad (4)$$

Seeing that $\delta f_N(v_u)$, δf_L, and $D(\tau_L/\tau_e)$ do not depend on v_u, Eq. (4) is rewritten as

$$\left|\frac{\Delta(m_p/m_e)}{(m_p/m_e)}\right| > \frac{1}{\kappa(v_u)}\left(\frac{\delta f_c(1)}{f_c(1)}\right)_A,$$

where

$$\kappa(v_u) = \frac{\lambda(v_u) f_c(v_u)}{\lambda(1) f_c(1)}. \qquad (5)$$

Measuring $f_c(v_u)$ with higher $\kappa(v_u)$ is more advantageous to test the variation in m_p/m_e. As shown in Table I, $\kappa(v_u)$ increases drastically as v_u increases at $v_u \leqslant 4$. At $v_u \geqslant 4$, the increase of $\kappa(v_u)$ is less significant and $\kappa(v_u)$ decreases at $v_u > 9$. This is because both $\lambda(v_u)$ and $[f_c(v_u)/v_u f_c(1)]$ decrease as the unharmonicity of the vibration increases at higher vibrational state (with pure harmonic vibration, $\lambda(v_u) = 0.5$ and $[f_c(v_u)/v_u f_c(1)] = 1$ for any value of v_u).

B. Systematic uncertainty

One should also consider the systematic uncertainty $[\delta f_c(v_u)/f_c(v_u)]_B$ when discussing the utility of measuring $f_c(v_u)$. Now we discuss the systematic uncertainties arising from the Stark shifts induced by trap and Raman lasers etc. We performed the analysis for $v_u = 1$–4, where the Stark shifts are analyzed accurately taking the couplings with seven vibrational states in the electronically excited states (particularly the $A\,^2\Sigma$ and $B\,^2\Sigma$ states, which are specially dominant). Measuring $f_c(v_u)$ with $v_u \geqslant 5$ is presumably not much more useful than measuring $f_c(4)$, considering $\kappa(v_u) < 1.4 \times \kappa(4)$.

1. Optical trap and Stark shift induced by trapping laser light

The second-order Stark shift in the $X\,^2\Sigma(v,N) = (0,0) \rightarrow (v_u,0)$ transition frequency $f_c(v_u)$ of ^{174}Yb^{6}Li molecules trapped by a laser light (power density, I_T; frequency, f_T) is given by

$$\delta f_L(v_u) = \frac{[S_{v_u}(f_T) - S_0(f_T)]}{h}\frac{I_T}{\varepsilon_0 c},$$
$$S_{v_X}(f_T) = -\sum_{\Phi,v}\frac{\mu_{v_X}(\Phi,v)^2}{3h}\frac{f_e(\Phi,v) - f_c(v_X)}{[f_e(\Phi,v) - f_c(v_X)]^2 - f_T^2}, \qquad (6)$$
$$v_X = 0, v_u \quad f_c(0) = 0,$$

where $\Phi = (A\,^2\Sigma, B\,^2\Sigma, C\,^2\Sigma, A\,^2\Pi, B\,^2\Pi, C\,^2\Pi)$ denotes the electronically excited states shown in Fig. 1, and $\mu_{v_X}(\Phi,v)$ is the $X\,^2\Sigma(v = v_X) \rightarrow \Phi(v)$ transition dipole moment. The $N = 0$ states only have dipole couplings with $N = 1$ states and the $X\,^2\Sigma(v_X, N = 0) \rightarrow \Phi(v, N = 1)$ transition dipole matrix elements are $\mu_{v_X}(\Phi,v)/\sqrt{3}$. The $f_e(\Phi,v)$ is the $X\,^2\Sigma(v,N) = (0,0) \rightarrow \Phi(v,1)$ transition frequency. Values of $f_e(\Phi,0)$ and $f_v = f_e(\Phi,1)$–$f_e(\Phi,0)$ for each electronically excited states are shown in Fig. 1.

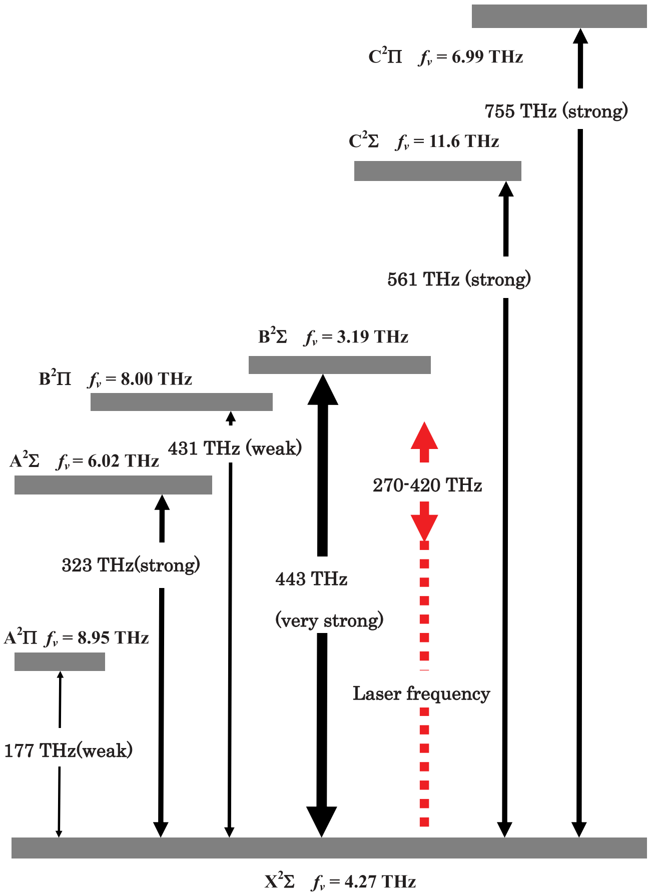

FIG. 1. (Color online) Electronic energy structure of the ^{174}Yb^{6}Li molecule giving the values of the electronic transition frequencies $f_e(\Phi,0)$ and the vibrational frequency $f_v = f_e(\Phi,1) - f_e(\Phi,0)$ at each electronic state. Electronic transition intensities are denoted by "very strong," "strong," and "weak."

To find the solutions for the magic trap frequencies where $\delta f_L(v_u) = 0$, we calculated $\delta f_L(v_u)$ as a function of the trap laser frequency f_T, taking the trap laser power density to be 23 kW/cm^2. The result is shown in Fig. 2 for the range spanning from 270 THz (1.11 μm) to 420 THz (714 nm). The electronic quasiresonant regions have many solutions for the magic trap frequencies [17,18]. However, they are not experimentally useful, because of the high sensitivity of $\delta f_L(v_u)$ to the slight detuning of f_T from the magic frequency and the high rate of photon scattering (electronic transition) [18].

The value of $\delta f_L(v_u)$ is positive (negative) at the far-off-resonant area, where the $X\,^2\Sigma$-$A\,^2\Sigma$ ($X\,^2\Sigma$-$B\,^2\Sigma$) coupling is dominant. This is because the vibrational frequency in the $A\,^2\Sigma$ ($B\,^2\Sigma$) state is higher (lower) than that in the $X\,^2\Sigma$ state (see Fig. 1) [18]. Because the vibrational frequency in the $X\,^2\Sigma$ state is neither highest nor lowest in all electronic states for the ^{174}Yb^{6}Li molecule, there is also a magic frequency in the far-off-resonant area.

Table II lists solutions for the magic trap frequencies, where the conditions $|d[\delta f_L(v_u)/f_c(v_u)]/df_T| < 3 \times 10^{-15}$/MHz and $\gamma/2\pi < 0.5$ Hz (γ being the photon scattering rate) are

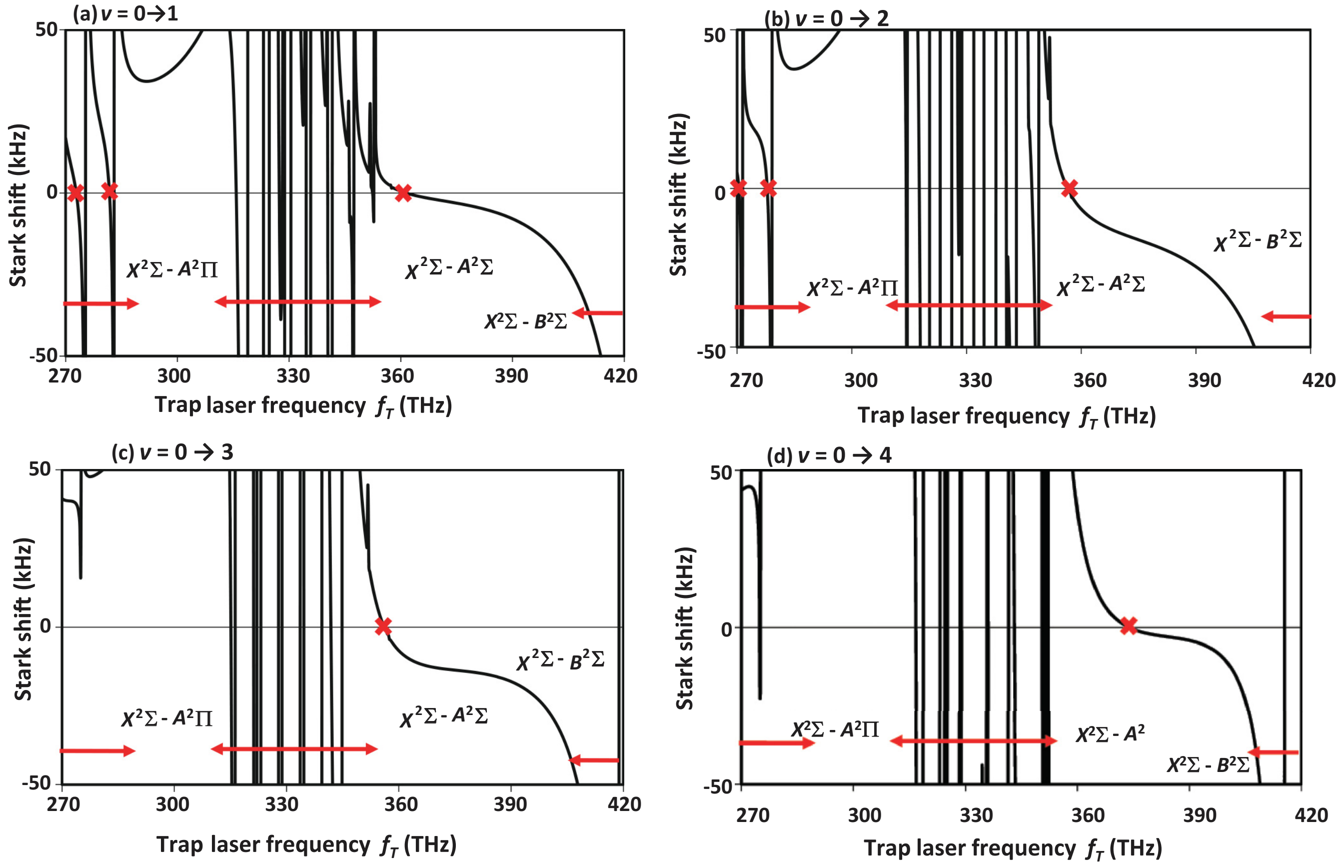

FIG. 2. (Color online) Dependence of the Stark shift of the ^{174}Yb^{6}Li $X^2\Sigma(v,N) = (0,0) \rightarrow (v_u,0)$ transition frequency on the trap laser frequency. Values of v_u are 1, 2, 3, and 4 in panels (a), (b), (c), and (d), respectively. We assume that the laser power density is 23 kW/cm^2. The magic trap frequencies, shown in Table II, are highlighted (red in the color figure online). The arrows (red in the color figure online) denote the frequency regions that are quasiresonant with the $X\,{}^2\Sigma$-$A\,{}^2\Pi$, $X\,{}^2\Sigma$-$A\,{}^2\Sigma$, and $X\,{}^2\Sigma$-$B\,{}^2\Sigma$ transitions.

satisfied with the trap laser power density for a potential depth of 10 μK. These magic trap frequencies will hopefully be used in measurements, because the frequencies of the Ti:sapphire (fiber) laser can be locked within 100 (10) kHz using a reference cavity with a simple structure. With $v_u = 1$ and 2, there are three solutions of magic trap frequencies, where the conditions shown above are satisfied. We can trap molecules with a Ti:sapphire laser with a magic trap frequency in the 360-THz region, and we can also use a fiber laser with magic trap frequencies in the 270- to 280-THz region. With $v_u = 3$ and 4, there is only one solution in the 360-THz region.

TABLE II. Trap laser frequencies f_T, where the Stark shift in the ^{174}Yb^{6}Li $X\,{}^2\Sigma(v,N) = (0,0) \rightarrow (v_u,0)$ transition frequency $[\delta f_L(v_u)/f_c(v_u)]$ is zero (known as the magic trap frequency). This table shows also the trap laser power density to give a potential depth of 10 μK and the slope of the Stark shift against the trap laser frequency $d[\delta f_L(v_u)/f_c(v_u)]/df_T$. This table shows only the solutions for magic trap frequencies that satisfy $d[\delta f_L(v_u)/f_c(v_u)]/df_T < 5 \times 10^{-15}$ with this laser power density.

Transition	f_T (THz)	Power density (kW/cm^2)	$d[\delta f_L(v_u)/f_c(v_u)]/df_T$ (MHz)
$v = 0 \rightarrow 1$	273.0	11.5	-9.0×10^{-16}
	281.8	10.8	-2.5×10^{-15}
	361.4	16.8	-5.8×10^{-17}
$v = 0 \rightarrow 2$	270.5	11.6	-1.1×10^{-15}
	277.9	10.7	-1.2×10^{-15}
	356.7	20.2	-2.4×10^{-16}
$v = 0 \rightarrow 3$	356.1	20.5	-2.0×10^{-16}
$v = 0 \rightarrow 4$	374.2	12.0	-3.2×10^{-17}

Here we discuss the effect of the nonscalar polarizability, which is the Stark shift term that depends on the angle between the polarization of the light field and the vector directions of the molecular rotation and electron-orbit angular momentum. When this effect is significant, the magic trap frequency depends on the polarization of the trap laser and $\delta f_L(v_u)$ cannot be zero simultaneously for all the trapped molecules in a 3D lattice (polarization is not uniform). This problem can be solved by trapping molecules in a 2D lattice with uniform polarization (already applied for the ^{87}Sr ${}^1S_0$-${}^3P_0$ transition frequency [6]). For molecules in the ${}^2\Sigma$ $N = 0$ states (only quantum numbers of electron-spin and Li nuclear-spin are nonzero), the nonscalar polarizability effect is negligibly small compared with the uncertainty of the calculated value of $\mu_{v_X}(\Phi,v)$ (3% [26]), because the electric dipole moments (EDM) of electron and Li nuclear (correlated to the spin) are very small as follows. The electron EDM is less than 10^{-27} $e$cm

(5.3×10^{-19} D) [29] and the electron-spin-dependent Stark shift term is less than 20 mHz with the molecular-internal electric field being lower than 100 GV/cm. Therefore, the electron-spin-dependent Stark shift term is more than 7 orders smaller than the scalar term (0.2 MHz for the potential depth of 10 μK). Also the Li nuclear-spin-dependent Stark shift term is of the same order as the electron-spin-dependent term. Therefore, we ignored this effect during the calculation. There is a significant nonscalar polarizability of the ^{43}Ca$^+$ ion in the $^2D_{5/2}(F = 1\text{–}6)$ state (Table II in Ref. [30]), but it is considered to be zero in the $^2S_{1/2}(F = 3 \text{ and } 4)$ state (Table I in Ref. [30]).

Here we consider also the utility of this estimation using the calculated values of $\mu_{v_X}(\Phi,v)$ and $f_e(\Phi,v)$, which have uncertainties of 3% and 1%, respectively [26]. We calculated the shift of the magic trap frequencies changing the $X\,^2\Sigma$-$B\,^2\Sigma$ coupling intensity by 10% [$\mu_{v_X}(B\,^2\Sigma,v)$ by 5%]. The shift of the magic trap frequencies is less than 3 THz and there is no significant change of $d[\delta f_L(v_u)/f_c(v_u)]/df_T$. Note also that the coupling with the continuum state was not taken into account, which can give the influence for the polarizability in electronically excited states. The influence of the continuum state can give the a 10% change of the static polarizability of the Sr atom in the electronically excited ($^3P_0$) state, but it is less than 1% in the ground ($^1S_0$) state [31]. Also for the ^{43}Ca$^+$ ion, the tail contribution in the ground ($^2S_{1/2}$) state is less than 0.01% of the total polarizability, while it is 5% in the excited ($^2D_{5/2}$) state [30]. In estimating the magic trap frequencies for ^{87}Sr [32] and ^{171}Yb [33] $^1S_0$-$^3P_0$ transitions ignoring the coupling with continuum state, no significant discrepancies were found in the experimental results. The contribution to the Stark energy shift due to the coupling with the continuum state is less than 2%, which gives an uncertainty of the magic trap frequency of less than 0.6 THz. The uncertainties of the magic trap frequencies shown in Table II are less than 4 THz, dominated by the uncertainties of the calculated values of $\mu_{v_X}(\Phi,v)$ and $f_e(\Phi,v)(\Phi = A\,^2\Sigma \text{ and } ^2\Sigma)$.

Here we estimate the fourth-order Stark shift [34] that is significant when the $X\,^2\Sigma(v_X,N=0) \leftrightarrow \Phi''(v',N=0,2)$ transition frequency is quasiresonant at $2f_T$. This coupling between $X\,^2\Sigma(v_X,N=0)$ and $\Phi'(v',N=0,2)$ is nonzero because the wave functions of $\Phi(v,N=1)$ states are mixed with the $X\,^2\Sigma(v_X,N=0)$ and $\Phi'(v',N=0,2)$ states. The frequency shift induced by this effect is given by

$$\begin{aligned}
\delta f_{QL}(v_u) &= \frac{\left[S_{Qv_u}(f_T) - S_{Q0}(f_T)\right]}{h}\left(\frac{I_T}{\varepsilon_0 c}\right)^2,\\
S_{Qv_X}(f_T) &= \sum_{\Phi,\Phi',v,v'} \frac{1}{4h[f_e(\Phi',v') - f_c(v_X) - 2f_T]}\\
&\quad\times\left(\frac{\mu_{v_X}(\Phi,v)\langle\Phi,v|\mu|\Phi',v'\rangle}{3}\right)^2\\
&\quad\times\left\{\frac{1}{h^2[f_e(\Phi,v) - f_c(v_X) - f_T]^2}\right.\\
&\quad\left.+\frac{1}{h^2[f_e(\Phi',v') - f_e(\Phi,v) - f_T]^2}\right\},\\
v_X &= 0,v_u, \qquad f_c(0) = 0,
\end{aligned} \tag{7}$$

where $\langle\Phi,v|\mu|\Phi',v'\rangle$ denotes the transition dipole moment between (Φ,v) and (Φ',v') states. For simplicity, we consider only one pair of Φ and Φ' states where $|f_e(\Phi,0) - f_T|$ and $|f_e(\Phi',0) - 2f_T|$ are minimum. Assuming $[f_e(\Phi,0) - f_T] \approx [f_e(\Phi',0) - f_e(\Phi,0) - f_T]$ and $\mu_{v_X}(\Phi,v_X) \approx \langle\Phi,v_X|\mu|\Phi',v_X\rangle \gg \mu_{v_X}(\Phi,v)$, $\langle\Phi,v_X|\mu|\Phi',v'\rangle(v,v' \neq v_X)$, Eq. (7) is simplified as

$$\begin{aligned}
S_{Qv_X}(f_T) &= \frac{1}{2h[f_e(\Phi',v_X) - f_c(v_X) - 2f_T]}\\
&\quad\times\left(\frac{\mu_{v_X}(\Phi,v_X)\langle\Phi,v|\mu|\Phi',v_X\rangle}{3h^2[f_e(\Phi,v_X) - f_c(v_X) - f_T]}\right)^2\\
&\approx \frac{S_{v_X}^2}{2h[f_e(\Phi',v_X) - f_c(v_X) - 2f_T]},\\
f_T &= 350\text{–}370\ \text{THz}, \quad \Phi = B\,^2\Sigma, \quad \Phi' = C\,^2\Pi,\\
f_T &= 270\text{–}290\ \text{THz}, \quad \Phi = A\,^2\Sigma, \quad \Phi' = C\,^2\Sigma.
\end{aligned} \tag{8}$$

Here we consider taking $(S_0 I_T/\varepsilon_0 ch) = (S_{v_u} I_T/\varepsilon_0 ch) \approx$ 0.2 MHz (trap potential of 10 μK). When f_T is 350 − 360 THz, $[f_e(C\,^2\Pi,0) - 2f_T] \approx 30$ THz and $|\delta f_{QL}(v_u)/f_c(v_u)|$ is estimated to be on the order of 3×10^{-17}. When f_T is 270–290 THz, $[f_e(C\,^2\Sigma,0) - 2f_T] \approx$ 2–20 THz with present calculation uncertainty) and $|\delta f_{QL}(v_u)/f_c(v_u)|$ is estimated to be on the order of 1×10^{-16}–3×10^{-15}. When molecules are trapped by a laser in the 270–290 THz region, $f_c(v_u)$ without a fourth-order Stark shift should be extrapolated by measuring with different trap laser power densities.

2. Stark shift induced by Raman lasers

The $X\,^2\Sigma(v,N) = (0,0) \to (v_u,0)$ transition frequency can be measured by probing the two-photon Raman transition using two lasers (power densities I_{R0} and I_{Rv_u} and frequencies f_{R0} and f_{Rv_u}). To induce the Raman transition, the following relation must be satisfied:

$$f_{Rv_u} = f_{R0} - f_c(v_u). \tag{9}$$

In this case, the Rabi frequency $\Omega_R(v_u)/2\pi$ is given by

$$\frac{\Omega_R(v_u)}{2\pi} = \frac{\sqrt{I_{R0} I_{Rv_u}}}{3\varepsilon_0 c h^2} \sum_{\Phi,v} \frac{\mu_0(\Phi,v)\mu_{v_u}(\Phi,v)}{f_e(\Phi,v) - f_{R0}}, \tag{10}$$

and the Stark shift induced by the lasers for the Raman transition is given by

$$\begin{aligned}
\delta f_R(v_u) &= \delta f_{R0}(v_u) + \delta f_{Rv_u}(v_u),\\
\delta f_{Rn}(v_u) &= \frac{[S_{v_u}(f_{Rn}) - S_0(f_{Rn})]}{h}\frac{I_{Rn}}{\varepsilon_0 c} \quad (n = 0, v_u).
\end{aligned} \tag{11}$$

As shown in Fig. 3, $\delta f_R(v_u)$ becomes zero if we choose Raman laser frequencies such that the Stark shifts induced by the two Raman lasers cancel each other (magic Raman frequencies) [18,35]. However, the Stark shift is significant when the ratio of power densities of the two Raman lasers I_{R0}/I_{Rv_u} fluctuates. Table III lists the solutions for the magic Raman frequencies taking $I_{R0} = I_{Rv_u}$. In these solutions, the Stark shifts induced by one Raman laser $|\delta f_{R0}(v_u)/f_c(v_u)|(=|\delta f_{Rv_u}(v_u)/f_c(v_u)|)$ are less than 10^{-13} for laser power densities with $\Omega_R/2\pi = 1$ Hz. Therefore, $|\delta f_R(v_u)/f_c(v_u)| < 10^{-16}$ is also satisfied when I_{R0}/I_{Rv_u} fluctuates with an order of 0.1%. For $v_u = 1, 2,$ and 4,

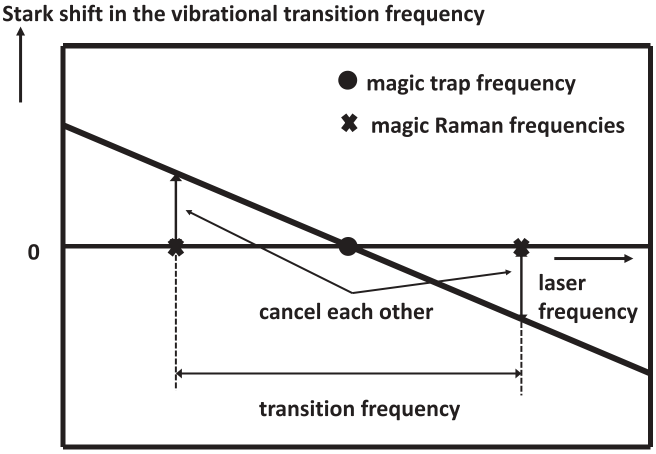

FIG. 3. Elimination of the Stark shift induced by Raman lasers. One of the two Raman laser frequencies is higher and the other lower is than the magic trap frequency. One laser gives a positive Stark shift and the other a negative one; so the total Stark shift can be zero. We assume that the power densities of the two Raman lasers are equal.

there are solutions of magic Raman frequencies where a fluctuation of I_{R0}/I_{Rv_u} with an order of 1% does not give a Stark shift with an order of 10^{-16}. For the solutions of Raman magic frequencies in Table III, the influence of the frequency detuning from the magic Raman frequencies with an order of 1 MHz is less than 10^{-18} and $\gamma_t/2\pi$ is less than 1 mHz, because the power densities of the Raman lasers are more than 4 orders smaller than that of trap lasers. The fourth-order Stark shift induced by the Raman lasers is proportional to $(I_{R0}^2 + I_{Rv_u}^2)$, and it is much less than 10^{-22}.

3. *Other frequency shifts*

TABLE III. Magic Raman frequencies f_{R0} and $f_{Rv_u}[=f_{R0} - f_c(v_u)]$ for which the Stark shift in the ^{174}Yb^{6}Li $X\,^2\Sigma(v,N) = (0,0) \rightarrow (v_u,0)$ transition frequency $[\delta f_R(v_u)/f_c(v_u)]$ is zero, when the power densities of the two lasers are equal. This table shows also the power densities of both lasers, where the transition Rabi frequency $\Omega_R/2\pi$ is 1 Hz, and the Stark shift with one laser $|\delta f_{R0}(v_u)|/f_c(v_u)$ with this power density. This table lists only the magic Raman frequencies for which the Stark shift with one laser is less than 10^{-13} when the transition Rabi frequency is 1 Hz.

Transition	f_{R0} (THz)	f_{Rv_u} (THz)	Power density (W/cm^2)	$\|\delta f_{R0}(v_u)\|/f_c(v_u)$
$v = 0 \rightarrow 1$	274.3	270.1	0.25	5.8×10^{-14}
	278.8	274.6	0.23	6.1×10^{-14}
	282.6	278.4	0.23	6.4×10^{-14}
	316.6	312.4	0.12	6.4×10^{-14}
	364.3	360.1	0.60	4.8×10^{-15}
$v = 0 \rightarrow 2$	277.9	269.8	0.26	8.8×10^{-15}
	362.2	354.1	1.20	5.2×10^{-14}
$v = 0 \rightarrow 3$	365.4	353.5	0.67	2.7×10^{-14}
$v = 0 \rightarrow 4$	385.8	370.4	0.67	5.7×10^{-15}

TABLE IV. This table lists Stark shifts induced by black-body radiation with a surrounding temperature of 300 K, $\delta f_{B0}(v_u)/f_c(v_u)$, and a stray dc electric field of 1 V/cm, $\delta f_{\rm dc0}(v_u)/f_c(v_u)$, in the ^{174}Yb^{6}Li $X\,^2\Sigma(v,N) = (0,0) \rightarrow (v_u,0)$ transition frequency.

Transition	$\delta f_{B0}(v_u)/f_c(v_u)$	$\delta f_{\rm dc0}(v_u)/f_c(v_u)$
$v = 0 \rightarrow 1$	1.1×10^{-14}	-1.9×10^{-15}
$v = 0 \rightarrow 2$	7.8×10^{-15}	-8.4×10^{-15}
$v = 0 \rightarrow 3$	9.6×10^{-15}	-8.9×10^{-15}
$v = 0 \rightarrow 4$	8.6×10^{-15}	-9.2×10^{-15}

In this section, we consider the frequency shifts induced by effects, except for the Stark shift induced by the trap and the Raman lasers. The Stark shift induced also by blackbody radiation (BBR), whose power density with a surrounding temperature T(K) at each frequency component f is given by

$$I_{\rm BBR}(f)df = \frac{8\pi h f^3}{c^2}\frac{df}{\exp(hf/k_B T) - 1}, \tag{12}$$

and the total power density $\int I_{\rm BBR}(f)df$ is proportional to T^4. Actually the frequency component of BBR is much higher than the vibrational and rotational transition frequencies and much lower than the electronic transition frequencies. Therefore, the Stark shift induced by BBR is given by

$$\begin{aligned}\frac{\delta f_B(v_u)}{f_c(v_u)} &\approx \frac{1}{f_c(v_u)}\int \frac{S_{v_u}(f) - S_0(f)}{h}\frac{I_{\rm BBR}(f)}{\varepsilon_0 c}df \\ &\approx \frac{1}{f_c(v_u)}\frac{S_{v_u}(0) - S_0(0)}{h\varepsilon_0 c}\int I_{\rm BBR}(f)df \propto T^4. \end{aligned}\tag{13}$$

The value of the Stark shift for $T = 300$ K, $[\delta f_{B0}(v_u)/f_c(v_u)]$ is shown in Table IV. The polarization of BBR is totally random and the nonscalar polarizability effect is zero. The uncertainty of the BBR shift is lower than 10^{-16} when a cryogenic chamber with temperature lower than 80 K is used or the surrounding temperature is stabilized (within ±1 K for 300 K).

The Stark effect in the $X\,^2\Sigma(v,N) = (v_X,0)$ $(v_X = 0,v_u)$ states induced by a stray dc electric field is mainly induced by the couplings with the $X\,^2\Sigma(v,N) = (v_X,1)$ state and the couplings with electronically excited states contribute slightly. The effects of the couplings between different vibrational states in the $X\,^2\Sigma$ state are negligibly small, because of the small vibrational transition dipole moments [26]. Therefore, the Stark shifts in $f_c(v_u)$ induced by the stray dc electric field $E_{\rm dc}$ are given by

$$\frac{\delta f_{\rm dc}(v_u)}{f_c(v_u)} = \frac{E_{\rm dc}^2}{f_c(v_u)}\left[\frac{\mu_0^2}{6hB_0} - \frac{\mu_{v_u}^2}{6hB_{v_u}} + \frac{S_{v_u}(0) - S_0(0)}{h}\right], \tag{14}$$

where $\mu_0(\mu_{v_u})$ and $B_0(B_{v_u})$ denote the permanent dipole moment and rotational constant in the $X\,^2\Sigma, v = 0(v = v_u)$ state, respectively [25,26]. The nonscalar polarizability effect in the $^2\Sigma N = 0$ state is negligibly small, as discussed in Sec. II B1. Table IV lists the Stark shift induced by a dc electric field of 1 V/cm, $[\delta f_{dc0}(v_u)/f_c(v_u)]$. When the stray dc electric field is kept lower than 0.1 V/cm, $|\delta f_{\rm dc}(v_u)/f_c(v_u)|$ is less than 10^{-16}.

We estimated the Zeeman shift of the $X\,^2\Sigma(v,N,F,M) = (0,0,3/2,\pm3/2) \rightarrow (v_u,0,3/2,\pm3/2)$ transition frequencies to be $\mp5 \times 10^{-17}$/G. Both transitions are observed as an overlapped spectrum that is independent of the Zeeman shift [19].

The second-order Doppler shift and collision shift are lower than 10^{-19} when molecules with kinetic energy lower than 10 μK are trapped in a 2D lattice [6].

III. CONCLUSION

In this paper, we discussed the possibility of testing the variation in the proton-to-electron mass ratio m_p/m_e by measuring the $X\,^2\Sigma(v,N,F,M) = (0,0,3/2,\pm3/2) \to (v_u,0,3/2,\pm3/2)$ transition frequency $f_c(v_u)$ of ^{174}Yb^{6}Li molecules in an optical lattice ($v_u = 1$–4). A large number of molecules are trapped at different positions in a 2D lattice with uniform polarization of the light field. Therefore, we can measure the spectrum with high signal-to-noise ratio and suppress the collision shift. The second-order Stark shifts of the transition frequency induced by the trap and Raman lasers are eliminated by stabilizing the laser frequencies at the special frequency, where the Stark energy shifts at the upper and lower states are equal (magic frequencies).

There is a solution of the experimentally useful magic frequency in the 360-THz region for $v_u = 1$–4. For $v_u = 1$ and 2, there are other solutions in the 270- to 280-THz region. The systematic frequency uncertainties $[\delta f_c(v_u)/f_c(v_u)]_B$ are given by the influence of the trap laser frequency detuning from the magic frequency and the fluctuation of the power ratio of the two Raman lasers. The second-order Stark shift induced by the trap laser is lower than 10^{-16} if the laser frequency fluctuation is less than 50 kHz. For the magic trap frequencies in the 270- to 280-THz region, the fourth-order Stark shift can be of the order of 10^{-15}. Therefore, this effect should be estimated by measuring with different trap laser power densities.

Also the Stark shift induced by the two Raman lasers is less than 10^{-16} if the power ratio of both lasers is stabilized within 0.1% (with some solutions 1%). We have also compared the sensitivity of the transition frequency to the variation in m_p/m_e, $\lambda(v_u)$, and the statistical frequency uncertainty with a given measurement time, $[\delta f_c(v_u)/f_c(v_u)]_A$. Measuring with $v_u = 4$ seems more advantageous than with $v_u = 1$–3 for testing the variation in m_p/m_e. Measuring with $v_u \geqslant 5$ is presumably not much more advantageous than with $v_u = 4$ because $\kappa(v_u) < 1.4 \times \kappa(4)$ (see Table I).

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