Sensitive measurement of $m_p/m_e$ variance using vibrational transition frequencies of cold molecules

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Abstract. The pure vibrational transition frequencies of magnetically trapped cold XH molecules are useful to detect the variance in the proton-to-electron mass ratio $\beta$ (X: alkali-earth atom). This paper compares the buffer gas cooling efficiency and accuracies of the vibrational transition frequencies for different XH molecules. $^9$BeH transition appears most advantageous for the detection of variance in $\beta$.

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1. Introduction

The study of possible variations in nature’s fundamental constants is currently a very popular research topic. Calmet and Fritzsch have shown that \((d\beta/dt)/\beta = R_c(d\alpha/dt)/\alpha\), where \(R_c\) denotes a value between 20 and 40 [1]; \(\alpha\), the fine-structure constant; and \(\beta\), the proton-to-electron mass ratio. Variances in \(\alpha\) and \(\beta\) provide very important information for the development of the Grand Unification Theory (GUT), because the actual value of \(R_c\) depends on the details of this theory.

Variance in \(\alpha\) can be detected by measuring the variance in the ratio between different atomic transition frequencies. However, it is difficult to detect the variance in \(\beta\) on the basis of atomic transitions alone, because the ratio of the isotope shift of the atomic transition frequency (effect of the change in nuclear mass with a ratio of several \%) is of the order of \(10^{-5}\). The molecular transition frequencies are useful for the detection of variance in \(\beta\) because the vibrational and rotational transition frequencies are proportional to \(\beta^{-1/2}\) and \(\beta^{-1}\), respectively.

Initially, variances in \(\alpha\) and \(\beta\) were discussed on the basis of astronomical results. Webb et al [2] measured the variance in \(\alpha\) in quasars (the absorption red shift \(z\) was between 1 and 3.5) to be \(\Delta\alpha/\alpha = (-0.72 \pm 0.18) \times 10^{-5}\), whereas \(\Delta\alpha/\alpha = (-0.1 \pm 0.2) \times 10^{-5}\) at \(z < 0.6\). Hudson et al [3] measured the microwave transition frequencies of cold OH molecules within an accuracy of \(3 \times 10^{-9}\), aiming at the measurement of \((d\alpha/dt)/\alpha\) through comparisons with measurements from OH megamasers in interstellar space. The variance in \(\beta\) in quasars with \(z = 2.59\) and \(3.02\) was measured to be \(\Delta\beta/\beta = (2 \pm 0.6) \times 10^{-5}\) [4], whereas \(\Delta\beta/\beta = (0.6 \pm 1.9) \times 10^{-6}\) when \(z = 0.68\) [5]. The upper limit of \(\Delta\beta/\beta\) is presently estimated to be \(-1.2 \times 10^{-16} \text{ years}^{-1}\) [6].

The variance in \(\alpha\) is now measured in the laboratory since the accuracies of atomic clocks have been improved [7]–[11]. Rosenband et al [12] measured the ratio of the Al\(^{+}\) and Hg\(^{+}\) transition frequencies within an accuracy of \(5.2 \times 10^{-17}\) and determined the value of \((d\alpha/dt)/\alpha\) to be \((-1.6 \pm 2.3) \times 10^{-17} \text{ years}^{-1}\). Shelkovnikov et al [13] measured the vibrational transition frequency of SF\(_6\) molecules at the \(10^{-14}\) uncertainty level and obtained \((d\beta/dt)/\beta = (-3.8 \pm 5.6) \times 10^{-14} \text{ years}^{-1}\).

The inversion transition frequencies (exponential dependence on \(\beta\)) of ammonia molecules are much more sensitive to variance in \(\beta\) as compared with vibrational and rotational transitions. Van Veldhoven et al [14] improved the resolution of the ND\(_3\) inversion spectrum by using a decelerated molecular beam. This method specifies that interaction time between molecules and the probing microwave cannot be greater than 0.1 ms (the linewidth cannot be narrower than 10 kHz) with this method. Bethlem et al [15] are in the process of developing a \(^{15}\)NH\(_3\) molecular fountain apparatus with the intention of reducing the uncertainty in the inversion transition frequency. However, it is rather difficult to reduce the frequency uncertainty to below \(10^{-14}\) because of the significant Zeeman and Stark shifts. Flambaum and Kozlov [16] suggested observing the transition frequency between the fine-structure excited state and the vibrational excited state. When these two excited states are quasidegenerate (Cl\(_2\), CuS, IrC, SiBr), the transition frequency is highly sensitive to the variance in \(\alpha\) and \(\beta\). DeMille et al [17] proposed to measure the variance in \(\beta\) using the transition frequencies between a quasidegenerate pair of Cs\(_2\) molecular vibrational levels, each associated with different electronic potentials. However, it must be noted that transitions between quasidegenerate states are also sensitive to the perturbations induced by the Stark or Zeeman effects. These perturbations are complicated to analyze particularly for heavy molecules, whose energy gaps between different quantum states.
are narrow. Zelevinsky et al [18] proposed to measure the variance in $\beta$ using the vibrational transition of the optically trapped transition of $\Sigma_1^+$ molecules that is induced by the Raman transition. In this case, the Stark shift by Raman laser is rather significant (of the order of 100 Hz) and the intensity of Raman laser must be controlled to 0.1%.

To detect the variance in $\beta$, a frequency with high dependence on $\beta$ should be measured with high accuracy. In our last paper [19], we proposed to measure the $|X^2\Sigma, n_v = 0, N = 0, F = 1, M = 1\rangle \rightarrow |X^2\Sigma, n_v = 1 \text{ or } 2, N = 0, F = 1, M = 1\rangle$ transition frequency of XH molecules ($X: {^{40}}Ca$ or $^{24}Mg$), where $n_v$ denotes the vibrational quantum number; $N$, the quantum number of molecular rotation; $F$, the quantum number of hyperfine structure; and $M$, the component of $F$ parallel to the magnetic field. The molecules are cooled by using a buffer gas and trapped by using an inhomogeneous magnetic field, as performed by a Harvard group [20]. Doppler-free spectrums are observed using two-photon absorption by means of two counter-propagating laser beams, whose frequency is half the transition frequency. The frequency uncertainty can potentially be below $10^{-15}$. In another paper [21], we proposed to obtain a terahertz (THz) wave by combining clock lasers with one molecular transition $f(\text{mol})$ (IR region, frequency uncertainty $< 10^{-15}$) and two atomic transitions $f(A, B)$ (optical region, frequency uncertainty $< 10^{-16}$). The frequency of this THz wave $f_p (= f(A) - f(B) \pm f(\text{mol}))$ is much more sensitive to the variance in $\beta$ as compared with $f(\text{mol})$.

In this paper, we provide a much more detailed analysis of the vibrational frequency uncertainties of alkali-earth-hydride molecules, including the $^9$BeH$|X^2\Sigma, n_v = 0, N = 0, F = 5/2, M = 5/2\rangle \rightarrow |X^2\Sigma, n_v = 1 \text{ or } 2, N = 0, F = 5/2, M = 5/2\rangle$ transition. The mass and permanent dipole moment of $^9$BeH molecules are smaller than those of $^{24}$MgH and $^{40}$CaH molecules. It must be noted that $^9$BeH molecules are fermions, whereas $^{24}$MgH and $^{40}$CaH molecules are bosons. Therefore, the frequency shifts caused by the Zeeman shift, ac Stark shift and collision shift are smaller for $^9$BeH transition as compared with those for $^{24}$MgH and $^{40}$CaH transitions. This paper also addresses the effects of the collision with the buffer gas (cooling, collisional frequency shift), which were not discussed in [19]. The $^9$BeH molecule, because of its smaller mass, is more advantageous for He buffer gas cooling as compared with $^{40}$CaH and $^{24}$MgH molecules.

In [21], we proposed to measure the frequency of the THz-wave $f_p$, obtained from the combination of the ($^{40}$CaH, Ca$^+$, Sr) and ($^{24}$MgH, Al$^+$, Yb) transitions. In these methods, $f_p$ is sensitive not only to the variance in $\beta$, but also to that in $\alpha$. In this paper, we also propose the combination of the ($^9$BeH, Sr, Ca) transitions; this combination is advantageous to detect the pure variance in $\beta$.

2. Experimental procedure

The transition frequency should be measured by using the following procedure:

1. XH molecules are produced by the laser ablation of XH$_2$ ($X: ^9$Be, $^{24}$Mg or $^{40}$Ca). Weinstein et al [20] produced more than $10^{10}$ $^{40}$CaH molecules.
2. XH molecules in the $M_S = 1/2$ ($M_S$: electron spin component parallel to the magnetic field) state are loaded into the magnetic trap area after cooling with the buffer gas. The magnetic field distribution is expressed by $B(R) = PR^n$. This loading takes about 0.4 s. The buffer gas should be quickly extracted ($< 0.3$ s), opening a gate to another chamber.
Table 1. Wavelength ($\lambda_{\text{probe}}$) and saturation power density ($I_s$) of the probe laser, wavelength of the pump laser ($\lambda_d$), and wavelength of observed fluorescence ($\lambda_f$). In this paper, we consider the detection using the transition to the $A^2\Sigma$ state, while the transition to the $B^2\Sigma$ state was considered in [19].

| BeH   | $n_v = 0 \rightarrow 1$ | $10.06$ | $79$ | $555$ [24] | $499$ [24] |
|-------|-------------------------|--------|-----|-----------|-----------|
|       | $n_v = 0 \rightarrow 2$ | $5.37$ | $26$ | $551$ [24] | $499$ [24] |
| MgH   | $n_v = 0 \rightarrow 1$ | $14.02$| $22$ | $562$ [24] | $520$ [24] |
|       | $n_v = 0 \rightarrow 2$ | $7.15$ | $8.9$| $557$ [24] | $517$ [24] |
| CaH   | $n_v = 0 \rightarrow 1$ | $15.87$| $11$ | $760$ [24] | $694$ [24] |
|       | $n_v = 0 \rightarrow 2$ | $8.06$ | $3.4$| $756$ [24] | $692$ [24] |

More than $10^8$ molecules are expected to be trapped [20]. Lambo et al [22] developed an alternate method to load paramagnetic atoms or molecules released from a solid neon matrix.

3. The magnetic gradient is adiabatically reduced ($P = P_i \rightarrow P_f$, $P_i > P_f$), as a result, the molecular trapping energy $E_{\text{trap}} (= \text{kinetic energy} + \text{Zeeman potential energy})$ is reduced by a factor of $(P_f/P_i)^{2/\left(n_B+2\right)}$ (adiabatic cooling). Also evaporative cooling effect is expected in this procedure. Weinstein et al [23] reduced the temperature of magnetically trapped Cr atoms from 1 K down to 10 mK, by means of adiabatic and evaporative cooling. The $^9$BeH molecule is a fermion and the evaporative cooling effect (caused by elastic collision) is suppressed at temperatures below than 1 mK. Further, the molecular density is reduced down to a value for which the collision shift is negligible small. This procedure should take approximately 0.1 s, which is much longer than the period of molecular vibrational motion inside the trap area (of the order of 1 ms).

4. Molecules in vibrationally excited states are transformed to the ground state by irradiating the pump laser. The pump laser is resonant with the $|X^2\Sigma, n_v = 1 \text{ or } 2 \rangle \rightarrow |A^2\Pi, n_v = 0 \text{ or } 1 \rangle$ transition. The wavelengths of pump lasers are listed in table 1. The pump laser power density is greater than 1 mW cm$^{-2}$ and the irradiating time is of the order of 10 $\mu$s. It is preferable to use this procedure to improve the S/N ratio, because $10^{-1} - 10^{-2}$ of trapped molecules are initially in the $n_v = 1$ or 2 states [20].

5. The IR probe laser is irradiated to counterpropagate along two directions for a period longer than $\tau \approx 1/2\pi \Delta f_{N1,2}$, where $\Delta f_{N1,2}$ denote the natural linewidths of the $n_v = 0 \rightarrow 1, 2$ transitions. The wavelengths of the probe laser are listed in table 1. The power density of the probe laser $I$ should be lower than the saturation power density ($I_s$; listed in table 1) so that the light shift of the transition frequency is lower than $10^{-15}$.

6. The pump laser is irradiated again to induce the $|X^2\Sigma, n_v = 1 \text{ or } 2 \rangle \rightarrow |A^2\Pi, n_v = 0 \text{ or } 1 \rangle$ transition. The power density of the pump laser is greater than 1 mW cm$^{-2}$ and the irradiating time is of the order of 10 $\mu$s. The frequency shifted fluorescence is detected by the $|A^2\Pi, n_v = 0 \text{ or } 1 \rangle \rightarrow |X^2\Sigma, n_v = 0 \text{ or } 1 \rangle$ transitions. The wavelengths of the observed fluorescence are shown in table 1 [24].
3. Buffer gas cooling effect

In the procedure (2), XH molecules are loaded into a magnetic trapping area via elastic collision with cold \(^3\)He buffer gas. This section compares the cooling efficiencies of different molecules.

When the temperature of the XH molecule is significantly greater than that of the \(^3\)He buffer gas, the change in kinetic energy of the XH molecules \(K_{XH}\) per unit time is expressed by

\[
\frac{dK_{XH}}{dt} = -\frac{4m_{XH}m_{He}}{3(m_{XH} + m_{He})^2}K_{XH}v_{XH}\sigma_{XH-He} = -\frac{4m_{He}\sqrt{2m_{XH}}}{3(m_{XH} + m_{He})^2}K_{XH}^2/2\eta_{He}\sigma_{XH-He}^e,
\]

where \(m\) denotes the mass; \(n\), the density; \(v\), the velocity; and \(\sigma^e\), the elastic collision cross section. The \(K_{XH}\) at a certain time \(t\) after the buffer gas cooling is expressed by

\[
K_{XH}(t) \approx 36(m_{XH} + m_{He})^4K_{XH}(0)\left(\frac{1}{6(m_{XH} + m_{He})^2 + 4\sqrt{2m_{XH}K_{XH}(0)m_{He}\eta_{He}\sigma_{XH-He}^e}}\right)^2,
\]

equation (2) converges to zero at \(t \rightarrow \infty\), although it should actually converge to the temperature of \(^3\)He buffer gas. This discrepancy is caused because equations (1) and (2) are obtained by considering the initial velocity of \(^3\)He atom to be zero. Equation (2) is actually valid while the temperature of the XH molecule is significantly greater than that of the \(^3\)He buffer gas.

Equation (2) shows that the cooling speed is determined by the product of \(\sigma_{XH-He}^e\) \(v_{XH}/(m_{XH} + m_{He})^2\) and \(n_{He}\). Here, we assume that the elastic collision interaction is dominated by the exchange force (repulsive). The radius of \(He\) atom is significantly smaller than that of the XH molecules; the radius of the XH molecules is roughly estimated from the bonding length \(r_d = (2.0 \times 10^{-8}\text{ cm}, 1.7 \times 10^{-8}\text{ cm} \text{ and } 1.3 \times 10^{-8}\text{ cm}\) for \(^{40}\)CaH, \(^{24}\)MgH and \(^9\)BeH molecules, respectively [24]). Therefore, the values of \(\sigma_{CaH-He}^e, \sigma_{MgH-He}^e\) and \(\sigma_{BeH-He}^e\) are roughly estimated to be \(1.25 \times 10^{-15}\text{ cm}^2, 9.08 \times 10^{-16}\text{ cm}^2\) and \(5.31 \times 10^{-16}\text{ cm}^2\), respectively. To reduce the kinetic energy \(K_{XH}/k_B = 100 \rightarrow 1\) K within 0.4 s, the value of \(n_{He}\) should be higher than \(2.4 \times 10^{13}, 1.5 \times 10^{13}\) and \(1.0 \times 10^{13}\text{ cm}^{-3}\) for \(^{40}\)CaH, \(^{24}\)MgH and \(^9\)BeH molecules, respectively. The \(^9\)BeH molecule is more advantageous for \(He\) buffer gas cooling as compared with \(^{40}\)CaH and \(^{24}\)MgH molecules.

XH molecules can also be loaded into the magnetic trap area by being released from a solid Ne matrix [22]. The experimental apparatus is less complex than that for the buffer gas cooling. This method is useful mainly when \(m_{XH} < m_{Ne}\). Therefore, this method is particularly useful for \(^9\)BeH molecules [22].

4. Frequency shift

This section discusses the shift in the XH(\(^2\)\(\Sigma\), \(n_v = 0, N = 0, F = I(X) + I(H) + 1/2, M_F = F\) → \(^2\)\(\Sigma, n_v = 0, N = 0, F = I(X) + I(H) + 1/2, M_F = F\) (\(q = 1, 2\) transition frequencies \(f_q\)). Here, \(I\) is the nuclear spin \((I^{(40)}Ca) = I^{(24)}Mg = 0, I^{(40)}H = 1/2, I^{(9)}Be = 3/2\). The values of \(f_q\), the vibrational transition dipole moment between \(n_v = 0\) and 1 states \(\mu'\), and the natural linewidth \((\Delta f_{1/2})\) of \(^{24}\)MgH or \(^{40}\)CaH molecules are listed in table 2 [24]–[29]. As shown in appendix B in [19], \(\mu'\) is roughly estimated [30] as follows:

\[
\begin{align*}
\mu' &= \sqrt{\eta}\mu_0, \\
\eta &= \frac{B_{n_v} - B_{n_v+1}}{B_0}.
\end{align*}
\]

The vibrational transition dipole moment \(\langle n_v | \mu | n_v - 1 \rangle\) is expressed by \(\sqrt{n_v}\mu'\).
Table 2. Listed are molecular rotational constants with \( n_v = 0 \) \((B_0)\), change ratio of the rotational constant by changing \( n_v \) \((\eta = (B_{n_v} - B_{n_v+1})/B_0)\), permanent dipole moment with \( n_v = 0 \) \((\mu_0)\), \( n_v = 0 \rightarrow 1 \) vibrational transition dipole moment \((\mu')\), \( n_v = 0 \rightarrow 1 \) transition frequency \((f_1)\), \( n_v = 0 \rightarrow 2 \) transition frequency \((f_2)\), and the natural linewidth of the \( n_v = 0 \rightarrow 1, 2 \) transitions \((\Delta f_{N1,2})\) are shown. The spectrum is observed using two-photon transition given the probe laser frequency, \( f_{1,2}/2 \). Superscript ‘c’ denotes the calculated values. \( \mu' \) is estimated using the values of \( B_0, \eta \) and \( \mu_0 \) with the method described in appendix B in [19]. \( \Delta f_N \) was estimated using the estimated value of \( \mu' \).

| \( B_0 \)(GHz) | \( \eta \) | \( \mu_0 \)(D) | \( \mu' \)(D) | \( f_1 \)(THz) | \( f_2 \)(THz) | \( \Delta f_{N1} \)(Hz) | \( \Delta f_{N2} \)(Hz) |
|----------------|--------|----------------|----------------|----------------|----------------|----------------|----------------|
| \(^{40}\text{CaH}\) | 126.7  | 0.023          | 2.94           | 0.42           | 37.8           | 74.4           | 22.3          | 44.6          |
| \(^{24}\text{MgH}\) | 174.5  | 0.032          | 1.23           | 0.21           | 42.9           | 83.9           | 8.2           | 16.4          |
| \(^{9}\text{BeH}\) | 309.3  | 0.029          | 0.28           | 0.048          | 59.6           | 117.0          | 1.1           | 2.2           |

These transitions are dipole forbidden and can be observed using two-photon absorption by means of two counter-propagating laser lights with a frequency of \( f_{1,2}/2 \); therefore, the observed spectrum is free from the first-order Doppler effect. This section discusses estimates of frequency shifts caused by the Zeeman shift (induced by a trapping magnetic field), second-order Doppler effect, ac Stark shift (induced by the irradiated probe laser and black body radiation), and collision (with molecules of the same species or the buffer gas).

4.1. Zeeman shift

The Zeeman shift in transition frequency is caused by the difference in Zeeman energy shifts in the upper and lower energy states. First, let us consider the Zeeman energy shift \( E_Z \) of trapped molecules, whose energy distribution is at thermal equilibrium with temperature \( T \). We assume that the molecules would only be trapped by the Zeeman trapping force and that the magnetic field is zero at the trap center. When the magnetic field distribution is expressed by \( B \propto R^n \), the mean value of \( E_Z \) is obtained by using the virial law, as \( 2K/n_B = 3k_B T/n_B \) (\( K \) is the mean kinetic energy).

The mean Zeeman shift in the \( |X^2 \Sigma, n_v, C \rangle \rightarrow |X^2 \Sigma, n_v', C' \rangle (|C \rangle = |N, J, F, M_F \rangle) \) transition frequency is expressed as follows:

\[
(\Delta f_{Z})_{\text{ave}} = \left( \frac{E_Z (n_v', C') - E_Z (n_v, C)}{h} \right)_{\text{ave}} = \frac{3k_B T}{h n_B} \left( \frac{E_Z (n_v', C') - E_Z (n_v, C)}{E_Z (n_v, C)} \right)_{\text{ave}}. \tag{4}
\]

Here, let us consider the dependence of \( E_Z (n_v, C) \) on the magnetic field. There is no spin–spin interaction for the molecules in the \( ^2 \Sigma \) state. Therefore, the mixture between different \( N \) states is negligible small when the electric field is lower than 100 V cm\(^{-1} \) [19]. Therefore, we discuss when \( |C \rangle = |C_a \rangle = |N = 0, F = I(X) + I(H) + 1/2, M_F = F \rangle \) (stretching state) ignoring the mixture of the \( N \geq 1 \) states. In this case, the Zeeman energy shift \( E_Z (n_v, C_a) \) is
strictly linear to the magnetic field $B$ with a coefficient

\[
Z_{n_v} = \mu_B \left[ \frac{1}{2} g_S + \frac{1}{2} g_I(H) \right],
\]

for $^{24}\text{MgH}$ and $^{40}\text{CaH}$

\[
Z_{n_v} = \mu_B \left[ \frac{1}{2} g_S + \frac{1}{2} g_I(H) + \frac{3}{2} g_I(\text{Be}) \right],
\]

for $^9\text{BeH}$

where $\mu_B$ denotes the Bohr magneton and $g_{S,I}$ denotes the g-factors for electron spin ($g_S = 2.003$) and nuclear spin ($g_{I(H)} \approx 3.0 \times 10^{-2}$ $g_I(\text{Be}) \approx -4.27 \times 10^{-4}$ [31]), respectively. In fact, the values of $g_S$ and $\mu_B$ are independent of the vibrational state and the value of $(\Delta f_Z)_{ave}$ is very small. Therefore, the $|n_v, C_a \rightarrow |n_v', C_a\rangle$ transition frequency can be measured without significant Zeeman shift, also when molecules are magnetically trapped. The value of $(\Delta f_Z)_{ave}$ is nonzero because of the slight dependence of $g_I$ on the vibrational state, as explained below.

Nuclei imbedded in the molecules are subject to the magnetic shielding effect, and the value of $g_I(X,H)$ is slightly different from those for bare nuclei (chemical shift). The chemical shift $\rho_A (= (g_I(A) - S^0_{I(A)})/g^0_{I(A)}; g^0_{I(A)}$ is $g_I(A)$ for $A$ atom) in each vibrational state is expressed as follows [32]:

\[
\rho_A(n_v) = \rho_A(0) - \rho_A' r_d(n_v) - r_d(0).
\]

Using $[r_d(n_v) - r_d(0)]/r_d(0) = \eta/2$ (see appendix B in [19]),

\[
g_{I(A)}(n_v) - g_{I(A)}(0) = -\frac{\rho_A' \eta n_v}{2} g_{I(A)}(0)
\]

and

for $^{24}\text{MgH}$ and $^{40}\text{CaH}$

\[
Z_{n_v} - Z_0 \approx -\frac{1}{2 (g_S + g_{I(H)}(0))} \rho_H' \eta n_v g_{I(H)}(0)
\]

for $^9\text{BeH}$

\[
Z_{n_v} - Z_0 \approx -\frac{1}{2 (g_S + g_{I(H)}(0) + 3 g_{I(\text{Be})}(0))} \left( \rho_H' \eta n_v g_{I(H)}(0) + 3 \rho_{\text{Be}}' \eta n_v g_{I(\text{Be})}(0) \right)
\]

are derived. To our knowledge, the values of $\rho_{I}'$ for $^{40}\text{CaH}$, $^{24}\text{MgH}$ or $^9\text{BeH}$ molecules have not been measured or calculated. In fact, $\rho_{I}' \approx \rho_{I}(0)$ for HF molecule [32]; this relation is assumed to be valid for all XH molecules. Here, let us estimate the Zeeman frequency shift by using the value of $\rho_{I}(0)$ for HF ($3.7 \times 10^{-5}$ [32]), OH ($1.3 \times 10^{-5}$ [33]), and CH ($3.5 \times 10^{-6}$ [33]) molecules. Considering that the chemical shift of the XH molecule becomes more significant as the difference between the electronegativities of the X and H atoms increases, $\rho_{I}' < 1 \times 10^{-5}$ is expected for $^{40}\text{CaH}$ and $^{24}\text{MgH}$ molecules and $\rho_{I}' < 5 \times 10^{-6}$ is expected for $^9\text{BeH}$ molecules. For $^9\text{BeH}$ molecules, the values of $\rho_{\text{Be}}'$ should also be considered; this value is expected to be less than $4 \rho_{I}'$ (4: electron number).
The difference in the Zeeman coefficient $Z_{1,2}$ as compared with $Z_0$ is expressed as follows:

$^{40}$CaH

$$\left| \frac{Z_1 - Z_0}{Z_0} \right| < 1.7 \times 10^{-10} \left| \frac{Z_2 - Z_0}{Z_0} \right| < 3.4 \times 10^{-10},$$

$^{24}$MgH

$$\left| \frac{Z_1 - Z_0}{Z_0} \right| < 2.4 \times 10^{-10} \left| \frac{Z_2 - Z_0}{Z_0} \right| < 4.8 \times 10^{-10},$$

$^9$BeH

$$\left| \frac{Z_1 - Z_0}{Z_0} \right| < 2.9 \times 10^{-10} \left| \frac{Z_2 - Z_0}{Z_0} \right| < 5.8 \times 10^{-10}.$$

The mean Zeeman shift in the $|n_v = 0, C_a \rangle \rightarrow |n_v = 1 \text{ or } 2, C_a \rangle$ transition frequency, $(\Delta f_{Z1,2})_{ave}$, is expressed as follows:

$^{40}$CaH

$$\left| \frac{\Delta f_{Z1,2}}{f_{1,2}} \right|_{ave} < 2.9 \times 10^{-13} \frac{T(K)}{n_B},$$

$^{24}$MgH

$$\left| \frac{\Delta f_{Z1,2}}{f_{1,2}} \right|_{ave} < 3.3 \times 10^{-13} \frac{T(K)}{n_B},$$

$^9$BeH

$$\left| \frac{\Delta f_{Z1,2}}{f_{1,2}} \right|_{ave} < 2.8 \times 10^{-13} \frac{T(K)}{n_B}. $$

To obtain a conservative estimation, we assumed $\rho_H' g_{I(H)} \rho_{Be} g_{I(Be)} > 0$. Presumably $\rho_H' g_{I(H)} \rho_{Be} g_{I(Be)}$ is actually negative, because $\rho_A' \rho_0' > 0$ is shown for all XY molecules in [32] and $g_{I(H)} g_{I(Be)} < 0$ [31]. If $\rho_H' g_{I(H)} \rho_{Be} g_{I(Be)} < 0$, the Zeeman frequency shift of the $^9$BeH transition frequency is significantly less as compared with that estimated from equation (11).

The Zeeman frequency shift is lower than $10^{-15}$ when the molecular temperature is lower than 3 mK. The uncertainty in the Zeeman frequency shift can be further reduced by measuring the transition frequencies under different trapping conditions.

4.2. Second-order Doppler effect

When the $^{40}$CaH, $^{24}$MgH, $^9$BeH molecules are cooled down to 10 mK, their velocities $v$ are of the order of 2 m s$^{-1}$, 2.8 m s$^{-1}$ and 4.7 m s$^{-1}$ respectively. The second-order Doppler shift is expressed as following:

$$\Delta f_{1,2}^{SD} = - \left( \frac{v^2}{2c^2} \right) f_{1,2}$$

and $|\Delta f_{1,2}^{SD}/f_{1,2}| \leq 1.2 \times 10^{-16}$.

4.3. ac Stark effect

When an ac electric field is applied, the Stark energy shifts in $|n_v, N = 0 \rangle$ states are induced by coupling with the $|n_v, N = 1 \rangle$ and $|n_v \pm 1, N = 1 \rangle$ states. The off-diagonal matrix elements
of the couplings with the A\textsuperscript{2}Π and B\textsuperscript{2}Σ states were taken into account, which were not considered in [19]. The Stark energy shifts in $E$, $E = S$, $S$ ($S$), $S$ = $E$, $E$ $(0)$, $E$ $(1)$ $\approx$ $\sqrt{n_v + 1}$, and $\langle n_v, N = 0 | \mu | n_v, N = 1 \rangle \approx \sqrt{n_v}$, $\mu'$/$\sqrt{3}$, and $\langle n_v, N = 0 | \mu | n_v, N = 1 \rangle \approx \sqrt{n_v}$, $\mu'/\sqrt{3}$. In this paper, also the effects of the couplings with the A\textsuperscript{2}Π and B\textsuperscript{2}Σ (the B\textsuperscript{2}Σ state does not exist for BeH molecule) states were taken into account, which were not considered in [19]. The Stark energy shifts in $E$, $E = S$, $S$ $(n_v)$, are expressed as follows [34]:

$$E_S(0) = -\frac{2 B_0 \mu_0 E^2}{3h (4 B_0^2 - f_{ac}^2)} - \frac{(f_1 + 2 B_1) \mu^2 E^2}{3h [(f_1 + 2 B_1)^2 - f_{ac}^2]} - \frac{\mu_A^2 E^2}{3h [F_A^2 - f_{ac}^2]} - \frac{\mu_B^2 E^2}{3h [F_B^2 - f_{ac}^2]}$$

$$E_S(1) = -\frac{2 B_1 \mu_1 E^2}{3h (4 B_1^2 - f_{ac}^2)} + \frac{(f_1 - 2 B_0) \mu^2 E^2}{3h [(f_1 - 2 B_0)^2 - f_{ac}^2]} - \frac{2 (f_2 - f_1 + 2 B_2) \mu^2 E^2}{3h [(f_2 - f_1 + 2 B_2)^2 - f_{ac}^2]}$$

$$E_S(2) = -\frac{2 B_2 \mu_2 E^2}{3h (4 B_2^2 - f_{ac}^2)} + \frac{2 (f_2 - f_1 - 2 B_1) \mu^2 E^2}{3h [(f_2 - f_1 - 2 B_1)^2 - f_{ac}^2]} - \frac{(f_3 - f_2 + 2 B_3) \mu^2 E^2}{h [(f_3 - f_2 + 2 B_3)^2 - f_{ac}^2]}$$

where $f_{ac}$ denotes the frequency of the ac electric field; $B_{n_v}$, the rotational constant in the X\textsuperscript{2}Σ $n_v$ state; $f_{n_v}$, the $n_v = 0 \rightarrow n_u$ transition frequency in the X\textsuperscript{2}Σ state; $f_{n_v}^{A\Pi,B\Sigma}$, the $n_v = 0 \rightarrow n_u$ transition frequency in the A\textsuperscript{2}Π and B\textsuperscript{2}Σ states; $F_A$, $F_B$, the (X\textsuperscript{2}Σ, $n_v = 0 \rightarrow A\textsuperscript{2}Π$ or B\textsuperscript{2}Σ, $n_v = 0$) transition frequency; and $\mu_{A\Pi(n_v), B\Sigma(n_v)}^\Sigma$ the transition dipole matrix element between (X\textsuperscript{2}Σ, $n_v$) and (A\textsuperscript{2}Π, $n_v$) and (X\textsuperscript{2}Σ, $n_v$) states. Values of $F_A$, $F_B$, and $\mu_{A\Pi(n_v), B\Sigma(n_v)}^\Sigma$ are shown in Table 3 [35, 36].

$\mu_{A\Pi(n_v), B\Sigma(n_v)}^\Sigma \approx 0.985$ and $\mu_{A\Pi(n_v), B\Sigma(n_v)}^\Sigma \approx 0.96$ for 40CaH molecules.

Table 3. Listed are the X\textsuperscript{2}Σ, $n_v = 0 \rightarrow A\textsuperscript{2}Π$ or B\textsuperscript{2}Σ transition frequencies ($F_{A\Pi,B\Sigma}$), $n_v = 0 \rightarrow 1, 2$ transition frequencies ($f_{1,2}$) in the A\textsuperscript{2}Π and B\textsuperscript{2}Σ states, dipole matrix elements (X\textsuperscript{2}Σ, $n_v = 0 | \mu | A\textsuperscript{2}Π$ or B\textsuperscript{2}Σ, $n_v = 0$) ($\mu_{A\Pi,B\Sigma(n_v)}$) for 40CaH, 24MgH and 9BeH molecules. The value of $\mu_{B\Sigma(n_v)}$, for 24MgH molecule was roughly estimated assuming that the value of $\mu_{B\Sigma(n_v)}$ for the 40CaH molecule is also valid for the 24MgH molecule. The coupling effect with the B\textsuperscript{2}Σ states is actually much less than that with A\textsuperscript{2}Π states and the detailed value of $\mu_{B\Sigma(n_v)}$ does not give a significant effect on the actual Stark shift.

| $40\text{CaH A}^{2}\Pi$ | $40\text{CaH B}^{2}\Sigma$ | $24\text{MgH A}^{2}\Pi$ | $24\text{MgH B}^{2}\Sigma$ | $9\text{BeH A}^{2}\Pi$ |
|------------------------|------------------------|------------------------|------------------------|------------------------|
| $F_{A\Pi,B\Sigma}$ (THz) | 432.3 [24] | 472.9 [24] | 576.8 [24] | 672.3 [24] | 601.0 [24] |
| $f_1$ (THz) | 38.8 [24] | 37.4 [24] | 46.1 [24] | 24.1 [24] | 60.2 [24] |
| $f_2$ (THz) | 76.4 [24] | 73.5 [24] | 90.2 [24] | 47.6 [24] | 118.1 [24] |
| $\mu_{A\Pi,B\Sigma(n_v)}$ (D) | 3.9 [35] | 2.8 [36] | 3.8 [35] | 2.8 | 2.2 [35] |
Here, we assume that relation roughly holds also for $^{24}$MgH and $^9$BeH molecules. The Stark shifts in the $n_v = 0 \rightarrow 1$ and 2 transition frequencies are expressed by

$$
\Delta f_{S1} = \frac{E_S(1) - E_S(0)}{\hbar},
$$

(14)

$$
\Delta f_{S2} = \frac{E_S(2) - E_S(0)}{\hbar}.
$$

The ac electric field is induced by the blackbody radiation and the probing laser light. As shown below, the estimated ac Stark shift is much larger than the values shown in [19], where the couplings with $A^2\Pi$ and $B^2\Sigma$ states were not taken into account.

4.3.1. Blackbody radiation. The blackbody radiation shift is analyzed in much more detail compared with the analysis in [19]. The blackbody radiation has a broad distribution of $f_{ac}$; therefore, equation (13) is rewritten as

$$
E_S(0) = \int \rho_{BB}(f_{ac}) E_S(0, f_{ac}) df_{ac},
$$

$$
E_S(1) = \int \rho_{BB}(f_{ac}) E_S(1, f_{ac}) df_{ac},
$$

$$
E_S(2) = \int \rho_{BB}(f_{ac}) E_S(2, f_{ac}) df_{ac},
$$

(15)

$$
\rho_{BB}(f_{ac}) = \frac{8\pi h f_{ac}^3}{c^5} \frac{1}{\exp(h f_{ac}/k_B T_C) - 1},
$$

where $T_C$ denotes the temperature of the chamber. Figure 1 shows the blackbody radiation shifts in the $n_v = 0 \rightarrow 1$ and 2 transition frequencies as a function of $T_C$. The blackbody radiation shifts at $T_C = 300$ K are $1 \times 10^{-15}$ for the $^{40}$CaH and $3 \times 10^{-16}$ for $^{24}$MgH transitions. For the $^9$BeH transition, the blackbody radiation shift is less than $10^{-16}$ when $T_C < 300$K.

4.3.2. Light shift. $n_v = 0 \rightarrow 1$ transition. When the $n_v = 0 \rightarrow 1$ transition is observed, the light shift, $\Delta f_{L1}$, is estimated calculating equation (13) taking $f_{ac} = f_1/2$. In this case, the influence of the coupling with the $A^2\Pi$ and the $B^2\Sigma$ states is larger than that of the coupling between rotational or vibrational states inside the $X^2\Sigma$ state. Taking a typical value of $E$ ($E_{sat}$), at which the two-photon transition rate is equal to the spontaneous emission rate from the $n_v = 1$ state $2\pi \Delta f_{N1}$, the light shift $\Delta f_{L1}$ with a given value of electric field $E$ or power density of probe laser ($I$) is obtained as follows:

$$
\Delta f_{L1} \approx \Delta f_{L1}^{Sat} \left( \frac{E}{E_{sat}} \right)^2 = \Delta f_{L1}^{Sat} \frac{I}{I_S}
$$

(16)

where $I_S$ denotes saturation power density and $\Delta f_{L1}^{Sat}$ is the light shift with $I = I_S$. 

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Figure 1. Blackbody radiation shift of the (a) $n_v = 0 \rightarrow 1$ and (b) $n_v = 0 \rightarrow 2$ transition frequencies of $^{40}$CaH, $^{24}$MgH and $^9$BeH molecules as a function of the temperature of the setup.

$E_{\text{sat}}$ is estimated as follows:

$$E_{\text{sat}}^2 = \frac{2\pi \langle n_v = 0, N = 0 | \mu | n_v = 0, N = 1 \rangle \langle n_v = 0, N = 1 | \mu | n_v = 1, N = 0 \rangle}{\hbar^2 (f_1/2 - 2B_0)} = 2\pi \Delta f_{N1},$$

(17)

Values of $I_S$ are listed in table 2. Values of $\Delta f_{L2}^{\text{Sat}}/f_1$ are of the order of $8.8 \times 10^{-14}$, $1.0 \times 10^{-13}$ and $4.1 \times 10^{-14}$ for the $^{40}$CaH, $^{24}$MgH and $^9$BeH transitions, respectively. The fraction of molecules excited to the $n_v = 2$ state is of the order of $(I/I_S)^2$. Therefore, the laser power density should be selected as a trade off between a low light shift and high S/N ratio. Taking $(I/I_S) = 1/100$, $\Delta f_{L2}^{\text{Sat}}/f_1$ becomes lower than $10^{-15}$ and 1% of molecules are excited to the $n_v = 1$ state.

$n_v = 0 \rightarrow 2$ transition. When the $n_v = 0 \rightarrow 2$ transition is observed, $f_{ac} = f_2/2$. Taking a typical value of $E$ ($E_{\text{sat}}$), at which the two-photon transition rate is equal to the spontaneous emission rate from the $n_v = 2$ state $2\pi \Delta f_{N2}$, the light shift $\Delta f_{L2}$ with a given value of electric

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field $E$ or power density of probe laser $(I)$ is obtained as follows:

$$\Delta f_{12} \approx \Delta f_{12}^{\text{Sat}} \left( \frac{E}{I_{\text{Sat}}} \right)^2 = \Delta f_{12}^{\text{Sat}} \frac{I}{I_{\text{Sat}}},$$

(18)

where $I_{\text{Sat}}$ denotes saturation power density and $\Delta f_{12}^{\text{Sat}}$ is the light shift with $I = I_{\text{Sat}}$.

$E_{\text{sat}}$ is estimated as follows:

$$2\pi (n_v = 0, N = 0|\mu|n_v = 1, N = 1) (n_v = 1, N = 1|\mu|n_v = 2, N = 0) \frac{r^2}{(f_1 - f_2/2)} \approx \frac{3h^2(f_1 - f_2/2)}{2\mu^2} \Delta f_{N2},$$

(19)

$\Delta f_{N2}$ is reduced by taking a lower value of $I/I_{\text{sat}}$. When $E = E_{\text{sat}}$, the value of $\Delta f_{12}^{\text{Sat}}/f_2$ is $1.3 \times 10^{-13}$, $4.1 \times 10^{-14}$ and $1.0 \times 10^{-14}$ for $^{40}\text{CaH}$, $^{24}\text{MgH}$ and $^9\text{BeH}$ molecules, respectively.

### 4.4. Collision shift

When molecules approach other atoms or molecules, intermolecular interactions cause energy shift $E_c$. The collision shift of $f_{12}$ ($\Delta f_{c12}$) is caused by the difference in $E_c$ in the vibrational ground and excited states.

The collision shift is expressed as follows:

$$\Delta f_{c12} = nv\sigma_{12},$$

(20)

where $n$ denotes the collision partner; $v$, the mean relative velocity; and $\sigma_{12}$, the cross sections of the collision shift. As the collision partner, we consider not only the molecules of the same species but also the buffer gas, which was not considered in [19].

### 4.4.1. Collision between same species

Intermolecular interactions are actually dominated by electric dipole-induced dipole interactions. The collision shift cross sections $\sigma_{12}$ between molecules of the same species are expressed as follows [37]:

For $^{40}\text{CaH}$ and $^{24}\text{MgH}$ (boson)

$$\sigma_{12} = \frac{2\pi}{k^2} \sum_{L=\text{even}} (2L + 1) \frac{\chi_{12}}{|\chi_{12}|} \frac{2\gamma_L k^{2L+1}}{1 + \gamma_L^2 k^{4L+2}},$$

for $^9\text{BeH}$ (fermion)

$$\sigma_{12} = \frac{2\pi}{k^2} \sum_{L=\text{odd}} (2L + 1) \frac{\chi_{12}}{|\chi_{12}|} \frac{2\gamma_L k^{2L+1}}{1 + \gamma_L^2 k^{4L+2}},$$

$$\gamma_{L=0} = \left( \frac{m_{\text{XH}}|\chi_{12}|}{16\hbar^2} \right)^{1/4} \frac{\Gamma(3/4)}{\Gamma(5/4)},$$

$$\gamma_{L>1} = \frac{L}{(L+1)(2L-1)!} \frac{1}{(2L+1)!} \left[ \frac{3m_{\text{XH}}|\chi_{12}|}{\hbar^2 L(L+1)} \right]^{(2L+1)/4},$$

$$\chi_{12} = \frac{\mu_{0}^2}{96\pi^2 e_0^2 \hbar} \left( \frac{\mu_0^2}{B_0} - \frac{\mu_{12}^2}{B_1} \right) (1 + 3 \cos^2 \xi),$$

$\mu_{0,12}$ are the magnetic dipole moments and $B_0, B_1$ are the magnetic fields. $m_{\text{XH}}$ is the reduced mass of the heteronuclear molecules. $\hbar$ is the reduced Planck constant.
Figure 2. Collision shift cross sections of the vibrational transition frequencies of $^{40}$CaH, $^{24}$MgH and $^9$BeH molecules as a function of collision kinetic energy. In this figure, the collisions between molecules of the same species are considered. The collision shift cross sections in the $n_v = 0 \rightarrow 1$ and $n_v = 0 \rightarrow 2$ transitions are shown in (a) and (b), respectively. The collisional frequency shift is actually negative.

using $\mu^2_{n_v} = (1 + n_v \eta) \mu^2_0$ and $B_{n_v} = (1 - n_v \eta) B_0$ (see appendix B in [19]),

$$
\chi_1 \approx - \frac{\mu^4_0}{48 \pi^2 \varepsilon_0^2 h B_0} \eta(1 + 3 \cos^2 \xi),
$$

$$
\chi_2 \approx - \frac{\mu^4_0}{24 \pi^2 \varepsilon_0^2 h B_0} \eta(1 + 3 \cos^2 \xi),
$$

$$
k = \frac{\pi m_{\text{XH}} v}{h},
$$

where $\xi$ denotes the angle between the vectors of the dipole moment and the molecular relative position. Figure 2 shows $\sigma_{1,2}$, calculated by taking $L \leq 8$ into account, as a function of the collision kinetic energy $K$. When $K/k_B$ is lower than 1 mK, the collision cross sections between same boson molecules ($^{40}$CaH, $^{24}$MgH) are inversely proportional to $v$. Therefore, $\Delta f_{C1,2}$ does not depend on $K$, and $\Delta f_{C1}/n$ and $\Delta f_{C2}/n$ are roughly estimated to be of the order
of $-1.3 \times 10^{-10}$ and $-1.5 \times 10^{-10} (-9.7 \times 10^{-11} \text{ and } -1.1 \times 10^{-10}) \text{ Hz cm}^3$, respectively, for $^{40}\text{CaH} (^{24}\text{MgH})$ molecules at $K/k_B < 1 \text{ mK}$. Assuming $n = 10^9 \text{ cm}^{-3}$, $|\Delta f_{c1}/f_1|$ and $|\Delta f_{c2}/f_2|$ are of the order of $3.5 \times 10^{-15}$ and $2.0 \times 10^{-15} (2.3 \times 10^{-15} \text{ and } 1.3 \times 10^{-15})$, respectively, for $^{40}\text{CaH} (^{24}\text{MgH})$ molecular transition.

When $K/k_B$ is lower than $100 \text{ mK}$, the collision cross section between $^9\text{BeH}$ molecules (fermion) is proportional to $v$. Therefore, $\Delta f_{c1,2}$ are proportional to $K$, and $\Delta f_{c1}/n$ and $\Delta f_{c2}/n$ are roughly estimated to be of the order of $-7.5 \times 10^{-11}$ and $1.26 \times 10^{-10} \times K(\text{K})$ Hz cm$^3$, respectively. Assuming $n = 10^9 \text{ cm}^{-3}$ and $K/k_B = 0.1 \text{ K}$, $|\Delta f_{c1}/f_1|$ and $|\Delta f_{c2}/f_2|$ are of the order of $1.2 \times 10^{-16}$ and $1.1 \times 10^{-16}$, respectively.

4.4.2. Collision with buffer gas. Molecules are loaded into the magnetic trap area through the stage of $^3\text{He}$ buffer gas cooling. Although most of the $^3\text{He}$ buffer gas is extracted after the loading, collisions occur with remaining $^3\text{He}$; these collisions cause the shift in the transition frequency. The collision shift cross sections between particles of different species (XH molecule and $^3\text{He}$ buffer gas) $\sigma_{1,2}^{\text{He}}$ are expressed as follows:

$$
\sigma_{1,2}^{\text{He}} = \frac{\pi}{k^2} \sum_L (2L + 1) \frac{\chi_{1,2}}{|\chi_{1,2}|} \frac{2\gamma_L k_{\text{He}}^L}{1 + \gamma_L^2},
$$

$$
\gamma_{L=0} = \left[ \frac{m_{\text{XH}} m_{\text{He}} |\chi_{1,2}|}{8\hbar^2 (m_{\text{XH}} + m_{\text{He}})} \right]^{1/4} \frac{\Gamma(3/4)}{\Gamma(5/4)},
$$

$$
\gamma_{L\geq1} = \frac{L}{(L+1)(2L-1)!!(2L+1)!!} \left[ \frac{6m_{\text{XH}} m_{\text{He}} |\chi_{1,2}|}{\hbar^2 L (L+1)(m_{\text{XH}} + m_{\text{He}})} \right]^{(2L+1)/4},
$$

(22)

where $\alpha_{\text{He}}$ denotes the polarizability of the $^3\text{He}$ atom ($= 2 \times 10^{-25} \text{ cm}^3$). Figure 3 shows $\sigma_{1,2}^{\text{He}}$, calculated taking $L \leq 5$ into account, as a function of the collision kinetic energy $K$. When $K/k_B$ is lower than $200 \text{ mK}$, $\Delta f_{c1,2}$ does not depend on $K$ and $\Delta f_{c1}/n$ ($\Delta f_{c2}/n$) are roughly estimated to be of the order of $-3.93 \times 10^{-11}$ ($-6.46 \times 10^{-11}$), $-1.85 \times 10^{-11}$ ($-2.20 \times 10^{-11}$) and $-9.39 \times 10^{-12}$ ($-1.12 \times 10^{-11}$) Hz cm$^3$ for $^{40}\text{CaH}$, $^{24}\text{MgH}$ and $^9\text{BeH}$ molecules, respectively. Assuming $n = 10^9 \text{ cm}^{-3}$, $|\Delta f_{c1}/f_1|$ ($|\Delta f_{c2}/f_2|$) are of the order of $1.0 \times 10^{-15}$ ($6.2 \times 10^{-16}$), $4.3 \times 10^{-16}$ ($2.6 \times 10^{-16}$) and $1.6 \times 10^{-16}$ ($9.6 \times 10^{-17}$) for $^{40}\text{CaH}$, $^{24}\text{MgH}$ and $^9\text{BeH}$ transitions, respectively. Therefore, $^3\text{He}$ buffer gas should be extracted after the molecules are magnetically trapped, so that the density of remaining $^3\text{He}$ gas is lower than $10^9 \text{ cm}^{-3}$.

When molecules are loaded from a Ne matrix [22], we must consider the collision with Ne gas. The collisional shift cross section with Ne is calculated from equation (22) by substituting $m_{\text{He}} \rightarrow m_{\text{Ne}}$ and $\alpha_{\text{He}} \rightarrow \alpha_{\text{Ne}} (= 4 \times 10^{-25} \text{ cm}^3)$. When $K/k_B$ is lower than $200 \text{ mK}$, $\Delta f_{c1}/n$ ($\Delta f_{c2}/n$) are roughly estimated to be of the order of $-1.41 \times 10^{-11}$ ($-1.68 \times 10^{-11}$), $-7.58 \times 10^{-12}$ ($-9.02 \times 10^{-12}$), and $-5.04 \times 10^{-12}$ ($-5.99 \times 10^{-12}$) Hz cm$^3$ for $^{40}\text{CaH}$, $^{24}\text{MgH}$ and $^9\text{BeH}$ molecules, respectively. Assuming $n = 10^9 \text{ cm}^{-3}$, $|\Delta f_{c1}/f_1|$ ($|\Delta f_{c2}/f_2|$) are of the
order of $3.7 \times 10^{-16}$ ($2.3 \times 10^{-16}$), $1.7 \times 10^{-16}$ ($1.1 \times 10^{-16}$) and $8.5 \times 10^{-17}$ ($5.1 \times 10^{-17}$) for $^{40}$CaH, $^{24}$MgH and $^9$BeH transitions, respectively.

5. Improvement of the sensitivity to the variance in $\beta$

The vibrational frequencies of XH molecules are expressed by

$$f_{1,2}(XH) = G_{1,2}(XH)\beta^{-1/2},$$

where $G$ is a constant. The subscripts 1 and 2 denote the $n_v = 0 \to 1$ and $2$ transitions, respectively. The atomic (neutral or ion) electronic transition frequencies are approximately expressed by

$$f(\text{atom}) \approx G(\text{atom})\alpha^{\lambda_{\text{atom}}}.$$
Table 4. Atomic transition frequencies $f$ and the parameters $\lambda$ that denote the dependence of $f$ on fine-structure constant $\alpha$. For a given value of $\lambda$, the variance in $f$ is expressed by the formula $(df/df) / f = \lambda (d\alpha/d\alpha) / \alpha$.

| $f$ (THz) | $\lambda$ |
|-----------|------------|
| Ca$^{1\,}\text{S}_0 \rightarrow ^3\text{P}_1$ | 456.0 | 0.030 [38] |
| Sr$^{1\,}\text{S}_0 \rightarrow ^3\text{P}_0$ | 429.2 | 0.061 [39] |
| Yb$^{1\,}\text{S}_0 \rightarrow ^3\text{P}_0$ | 518.24 | 0.283 [39] |
| Al$^{+\,}\text{S}_0 \rightarrow ^3\text{P}_0$ | 1120.71 | 0.0076 [39] |
| Ca$^{+\,}\text{S}_{1/2} \rightarrow ^2\text{D}_{3/2}$ | 411.0 | 0.152 [40] |
| Sr$^{+\,}\text{S}_{1/2} \rightarrow ^2\text{D}_{3/2}$ | 444.8 | 0.384 [38] |
| Yb$^{+\,}\text{S}_{1/2} \rightarrow ^2\text{D}_{3/2}$ | 689.2 | 0.840 [38] |
| Hg$^{+\,}\text{S}_{1/2} \rightarrow ^2\text{D}_{3/2}$ | 1064.7 | -3.19 [38] |

Some values of $f$(atom) and $\lambda_{\text{atom}}$ are listed in table 4 [38]–[40]. In fact, all frequencies are measured as a ratio to a certain standard frequency. When $f_{1,2}(\text{XH})$ is measured by using $f$(atom) as the standard frequency,

$$\frac{df_{1,2}(\text{XH}) / f(\text{atom})}{df_{1,2}(\text{XH}) / f(\text{atom})} = \frac{1}{2} \frac{d\beta}{d\alpha} - \frac{1}{2} \frac{d\alpha}{d\alpha} \frac{d\alpha}{d\alpha}.$$

We propose a method to improve the sensitivity on $\beta$, as shown below.

When we obtain a THz-wave $f_p = f(A) - f(B) \pm f_{1,2}(\text{XH})/2$ using clock lasers of atoms A and B and the molecule XH (observed with two photon absorption), its frequency can be measured by using an optical frequency comb, which is controlled by $f(B)$. In this case,

$$\frac{f_p}{f(B)} = \frac{f(A) \pm f_{1,2}(\text{XH})/2}{f(B)} - 1,$$

$$\frac{df_p/f(B)}{df_p/f(B)} = \frac{(\lambda_A - \lambda_B) f(A) \pm \lambda_B f_{1,2}(\text{XH})/2}{f_p} \frac{d\alpha}{d\alpha} \pm \frac{f_{1,2}(\text{XH})}{4f_p} \frac{d\beta}{d\beta}.$$

While measuring the variance in $f_p$, the variance in $\beta$ is detected with higher sensitivity as compared with measuring $f_{1,2}(\text{XH})$ with a factor of $[f_{1,2}(\text{XH})/2f_p]$.

As an example, we consider the case in which the Ca$^{+\,\text{S}_{1/2} \rightarrow ^2\text{D}_{3/2}}$, Sr$^{1\,}\text{S}_0 \rightarrow ^3\text{P}_0$, and 40CaH $n_v = 0 \rightarrow 1$ transition frequencies are used. Note that the uncertainty in $f$(Sr) is now already lower than $10^{-15}$ [11] and it can potentially be lower than $10^{-17}$. The uncertainty in $f$(Ca$^+$) is currently of the order of $10^{-14}$–$10^{-15}$ and can also potentially be lower than $10^{-16}$ [41, 42]. Here, we consider

$$f_{p1} = f(\text{Ca}^+) + \frac{f_{1,2}(\text{NaH})}{2} - f(\text{Sr}) = 0.71 \text{ THz}.$$

Using the values of $\lambda_{\text{Ca}^+}$ and $\lambda_{\text{Sr}}$ listed in table 4,

$$\frac{df_{p1}/f(\text{Sr})}{df_{p1}/f(\text{Sr})} = 56.95 \frac{d\alpha}{d\alpha} - 13.5 \frac{d\beta}{d\beta}.$$

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Next, we consider the case in which the $\text{Al}^+ \ ^1S_0 \rightarrow ^3P_0$, $\text{Yb} \ ^1S_0 \rightarrow ^3P_0$, and $\text{MgH} \ n_v = 0 \rightarrow 2$ transition frequencies are used. The uncertainty in $f(\text{Al}^+)$ is now already of the order of $10^{-17}$ [12]. Further, the uncertainty in $f(\text{Yb})$ can potentially be lower than $10^{-17}$ [43]. Note that the clock laser of the $\text{Al}^+$ transition is obtained by doubling the frequency of a laser with the frequency $f(\text{Al}^+)/2$. Here, we consider

$$f_{p2} = \frac{f(\text{Al}^+)}{2} - f(\text{Yb}) - \frac{f_2(\text{MgH})}{2} = 0.17 \text{THz}.$$ 

Therefore,

$$\frac{d}{dt} \left[ \frac{f_{p2}/f(\text{Yb})}{f_{p2}/f(\text{Yb})} \right] = -889 \frac{d\alpha}{\alpha dt} + 63.56 \frac{d\beta}{\beta dt}. \quad (26)$$

We also consider the case in which the Ca $^1S_0 \rightarrow ^3P_1$, Sr $^1S_0 \rightarrow ^3P_0$, and $\text{BeH} \ n_v = 0 \rightarrow 1$ transition frequencies are used. Here, we consider

$$f_{p3} = f(\text{Ca}) - f(\text{Sr}) - \frac{f_1(\text{BeH})}{2} = 3.04 \text{THz}.$$ 

Therefore,

$$\frac{d}{dt} \left[ \frac{f_{p3}/f(\text{Sr})}{f_{p3}/f(\text{Sr})} \right] = -5.22 \frac{d\alpha}{\alpha dt} + 4.9 \frac{d\beta}{\beta dt}, \quad (27)$$

By comparing equations (25)–(27), variances in $f_{p1–3}$ are given by both variances in $\alpha$ and $\beta$. To measure the variances in fundamental constants with high sensitivity, $f_{p2}$ is most advantageous. However, from the theoretical relation $(d\beta/dt)/\beta = R_c (d\alpha/dt)/\alpha$ ($20 < R_c < 40$) [1], it is difficult to estimate the pure variance in $\beta$ from the variance in $f_{p2}$. The variance in $f_{p3}$ is mostly dominated by that in $\beta$; therefore $f_{p3}$ is convenient for measuring the pure variance in $\beta$.

6. Conclusion

The Zeeman shifts on the $^{40}\text{CaH}$ and $^{24}\text{MgH}$ $|n_v = 0, N = 0, F = 1, M = 1 \rangle \rightarrow |n_v = 1 \text{ or } 2, N = 0, F = 1, M = 1 \rangle$ transition frequencies and the $^{9}\text{BeH}$ $|n_v = 0, N = 0, F = 5/2, M = 5/2 \rangle \rightarrow |n_v = 1 \text{ or } 2, N = 0, F = 5/2, M = 5/2 \rangle$ transitions are very small. Therefore, the uncertainty in transition frequency can be lower than $10^{-15}$ when magnetically trapped cold molecules are used.

$^{9}\text{BeH}$ molecules are more advantageous than $^{40}\text{CaH}$ and $^{24}\text{MgH}$ molecules for the loading to the magnetic trap and the precise measurement because of (i) higher buffer gas cooling efficiency, (ii) higher vibrational transition frequency, (iii) smaller ac Stark shift and (iv) smaller collision frequency shift.

The measured vibrational transition frequency is useful to detect the variance in the proton-to-electron mass ratio $\beta$. By combining a molecular transition frequency with two atomic transition frequencies in the optical region, the sensitivity to the variance in $\beta$ is increased. To measure the pure variance in $\beta$, the combination of the $^{9}\text{BeH}$, Ca and Sr transitions is more advantageous than those introduced in [21].

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The precise measurement of the vibrational transition frequencies of diatomic molecules (particularly including H atoms) is useful not only for the detection of the variance in $\beta$, but also for advancement in theoretical molecular physics. With decrease in the uncertainty of vibrational transition frequencies, estimation techniques more detailed than the Born–Oppenheimer approximation will be necessary.

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