Search of the variation in the proton-to-electron mass ratio using two vibrational transition frequencies of molecular ions

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We propose to monitor the variation in the proton-to-electron mass ratio \( \left( \frac{m_p}{m_e} \right) \) from the two vibrational transition frequencies of molecular ions.

We consider the following vibrational transition frequencies \( f(v') \) for example: \( ^{16}\text{O}_2^+ \ X^2\Pi_{1/2} (v,J)=(0,1/2)-(v',1/2) \)

\[
f(v') = f_v v' - x f_v (v' + 1)
\]

\[
Q(v') = \frac{(f(v') - f(2v')/2)/f(v')} = \frac{xf v' / f_v}{f_v}
\]

This represents the ratio between harmonic and unharmonic vibrational terms.

\( Q(v') \) proportional to \( \left( \frac{m_p}{m_e} \right)^{-1/2} \)

\( ^{16}\text{O}_2^+ \ Q(4) \) measured with the uncertainty of \( 1 \times 10^{-18} \)

cancel the frequency shifts satisfying

\[
\frac{\delta f(v')}{f(v')} = \frac{\delta f(2v')}{f(2v')}
\]

(relativistic effects etc.)
Precise measurement of time & frequency

important role for the development of physics beyond
standard model

Atomic transition frequencies

attained the accuracy of $10^{-18}$

$^1S_0-^3P_0$ $^{87}\text{Sr}$ (Ohmae-san’s talk), $^{171}\text{Yb}$, $^{27}\text{Al}^+$

(should be possible also with $^{115}\text{In}^+$ Ohtsubo-san’s poster)

S-F $^{171}\text{Yb}^+$ →sensitive to the variation in the finestructure constant

$(-4.1 \pm 2.5) \times 10^{-18}/\text{yr}$

But molecular transition frequencies has never been measured with the uncertainty lower than $10^{-15}$
Why precise measurement of molecular transitions is useful?

We can observe phenomena, which cannot be observed with atomic transitions

1. **variation in the proton-to-electron mass ratio**
   
   $\text{vibration freq. } \propto (m_p/m_e)^{1/2} \quad \text{rotational freq. } \propto (m_p/m_e)^{-1}$

2. Detection of electron EDM (Abe-san's talk)
3. Symmetry violation of chiral molecules
4. Gravity in the micro size
Which molecular transition is useful for precise measurement?

vibrational transition with

\[ \Delta N = \Delta J = \Delta F = \Delta M = 0 \] (only \( \nu \) changes)

(molecular shape does not change)

\[ \downarrow \]

Stark, Zeeman, electric quadrupole shifts at upper and lower states are almost equal (cancelled)

Molecular figure unchanged

Parallel shift,

Molecular shift changes

Shifts are not parallel
Molecular vibrational transition frequency

\[ \nu = 0 \rightarrow \nu' \]

We can select the convenient transition to prepare the probe laser

Probe laser between 1.3 – 1.5 \( \mu \text{m} \)

linewidth narrower than 10 mHz is possible using cold Si cavity

Natural linewidth of vibrational spectrum of diatomic molecules

- hetero-nuclear: several Hz
- homo-nuclear: < 1 \( \mu \text{Hz} \) (ultra-narrow laser linewidth is useful)
Why precise measurement of molecular transition is difficult?
How can we overcome with molecular ions (co-trapped with atomic ion)?

Complicated energy structure (vibrational-rotationsl states)

Laser cooling is difficult
sympathetic cooling with laser cooled atomic ions

Difficult to localize in a selected state
quantum logical one way transition (sideband transition) \( n, \) normal motion mode
repeat \( |\Phi_i, n=0> -> |\Phi_{i+1}, n=1> \) and \( |n=1> -> |n=0> \)

Difficult to monitor the state by fluorescence
quantum logical detection

<table>
<thead>
<tr>
<th>Molecular ion</th>
<th>Normal motion</th>
<th>Atomic ion</th>
</tr>
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<tbody>
<tr>
<td>( \Phi_0 )</td>
<td>( n = 0 \rightarrow 1 )</td>
<td>( n = 1 )</td>
</tr>
<tr>
<td>( \Phi_1 )</td>
<td>( n = 0 \rightarrow 1 )</td>
<td>( n = 0 )</td>
</tr>
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Fluorescence: OFF

Fluorescence: ON
Molecular ion in a linear trap
(Sympathetically cooled with atomic ion)

For homonuclear molecular ion, there is no electric dipole coupling between different states in the electric ground state

\[\downarrow\]

1. No measurement perturbation by blackbody radiation
2. Stark is very small
\[ ^{16}\text{O}_2^+ \ X^2\Pi_{1/2}(\nu,J,M) = (0,1/2,\pm1/2) - (\nu',1/2,\pm1/2) \] transition frequency

\( \nu \): vibrational state  \( J \): total angular momentum  \( M \): component of \( J \) parallel to the magnetic field

**Electric quadrupole shifts**

**Zeeman shift**

strict linear with coefficients of \( 3 \times 10^{-15}\) G

(much smaller than \( \text{Al}^+ \) clock, Sr and Hg lattice clocks)

Eliminated perfectly averaging \( M = \pm 1/2-\pm1/2 \)

**DC Stark shift**

\(-3.1 \times 10^{-20} \) / \( \text{(V/cm)}^2 \)

**Blackbody radiatin shift** (300 K)

\(-2.0 \times 10^{-18} \)

(same order with \( \text{Al}^+ \), much smaller than Sr and Hg lattice clocks)

**One photon forbidden -> two photon absorption**

\( \nu' = 4 \) light shift = \(-1.4 \times 10^{-14} \) with 1 Hz Rabi Freq. (800 W/cm\(^2\))

\( \nu' = 8 \) light shift = \(-1.2 \times 10^{-14} \) with 1 Hz Rabi Freq. (800 W/cm\(^2\))

using Hyper Ramsey, supressed to \(< 10^{-18} \)

Systematic uncertainty \(< 10^{-18} \)
Statistic uncertainty with $^{16}\text{O}_2^+$ $(\nu,J) = (0,1/2) \rightarrow (8,1/2)$

Spectrum linewidth is given by probe laser (1.41 $\mu$m) linewidth

$\rightarrow$ narrower than 10 mHz can be attained stabilizing with cold Si cavity

**Statistic uncertainty assuming**

single molecular ion

linewidth of 100 mHz (Rabi freq. 0.1 Hz and light shift $1.2 \times 10^{-15}$)

statistic uncertainty $6.6 \times 10^{-19}$ with one day measurement

Attainable accuracy is higher than lattice clocks

Useful to monitor the variation in $m_p/m_e$ using an atomic clock (Sr lattice?) for reference
Can we search without the atomic clock for reference?

Using atomic clock at a distant place, earth tide gives a fluctuation.
Search of the variation in $m_p/m_e$ using $Q(v') = [f(v')-f(2v')/2]/f(v')$

$f(v') = v'f_v - v'(v' + 1)xf$

$f_v \propto (m_p/m_e)^{-1/2}$ harmonic term

$xf \propto (m_p/m_e)^{-1}$ unharmonic term

$Q(v') = [f(v') - f(2v')/2]/f(v') = xf v'/f_v \propto (m_p/m_e)^{-1/2}$

Precise measurement of $Q(v')$ is useful for search the variation in $(m_p/m_e)$

Current upper limit of $m_p/m_e$ $10^{-16}$/yr
Frequency shift in $Q(v')$

$$\delta Q(v') = \{f(2v')/[2f(v') - f(2v')]\} \times [\delta f(v')/f(v') - \delta f(2v')/f(2v')]$$

No shift in $Q(v')$ for the shifts with $\delta f(v')/f(v') = \delta f(2v')/f(2v')$

(1) **Quadratic Doppler shift** + **Gravity red shift** canceled perfectly
   
   (limit of the accuracy of Al$^+$ clock)

(2) Light shift induced by the probe laser ($\delta f_L(v')$) $\propto$ laser power density $I_p(v')$
   
   the light shift is eliminated optimizing $I_p(v')/I_p(2v')$ so that $\delta f_L(v')/f(v') = \delta f_L(2v')/f(2v')$

   if the sign of the light shift is the same for $f(v')$ and $f(2v')$

   for O$_2^+$ transition, $\delta f_L(v')$ is always negative

   Hyper Ramsey is useful to eliminate the effect of the fluctuation in $I_p(v')/I_p(2v')$
Other frequency shift in $Q(v')$ with $O_2^+ \ 2\Pi_{1/2}(v, J) = (0,1/2)\rightarrow(v',1/2)$

Electric quadrupole shift: zero

Zeeman shift: perfect linear with $\pm 1.6 \times 10^{-14}/G$

(eliminated averaging $M = \pm 1/2\rightarrow\pm 1/2$)

DC Stark: $Q(1) -2.4 \times 10^{-18}/(V/cm)^2$ $Q(2) -2.5 \times 10^{-19}/(V/cm)^2$

$Q(4) 8.5 \times 10^{-21}/(V/cm)^2$ (string crystal is not definitely required)

Blackbody radiation shift (300 K): $Q(1) -1.5 \times 10^{-16}$ $Q(2) -1.6 \times 10^{-17}$

$Q(4) 5.4 \times 10^{-19}$

Accuracy of $10^{-18}$ is attainable

We don‘t need an atomic clock for reference
Statistical uncertainty of $O_2^+ Q(4)$

Spectrum linewidth is given by the laser linewidth (natural linewidth $< 1 \, \mu m$)

$O_2^+ \; v = 0 \rightarrow 8$ two photon absorption of $1.41 \, \mu m$ laser

(linewidth $< 10 \, \text{mHz}$ is attainable using cold Si cavity)

$v = 0 \rightarrow 4$ two photon absorption of $2.74 \, \mu m$ laser

or

two photon absorption of signal and idler waves ($f_s$ and $f_i$) of optical parametric oscillator (OPO) pumped by $1.37 \, \mu m$

(pump laser is stabilized within $10 \, \text{mHz}$ using cold Si cavity)

(no effect with the fluctuation of $f_s \rightarrow f_s + \delta f$, $f_i \rightarrow f_i - \delta f$)

Statistical uncertainty with a single molecular ion with the linewidth of $100 \, \text{mHz}$

$6 \times 10^{-18}$ with two weeks

Measurement with multi-molecular ion is also possible
The proposed method is applicable also with other molecular ions satisfying

(1) $\Delta J = 0$ with $J = 0$ or $1/2$ \textit{(electric quadrupole shift zero)}
(2) Transition between stretched states \textit{(Zeeman shift is linear)}
(3) Sign of light shift is the same with $f(v')$ and $f(2v')$ \textit{(light shift is eliminated by optimizing the intensity ratio of two probe lasers)}

Applicable also \((v,J) = (0,0) \rightarrow (v',0)\) with CaH$^+$, SrH$^+$ etc.
Not applicable with $^{15}$N$_2^+$ \((v,N,J) = (0,0,1/2) \rightarrow (v',0,1/2)\) \textit{(sign of light shift depends on $v'$)}
Conclusion

We propose to measure the variation in the proton-to-electron mass ratio \( \frac{m_p}{m_e} \) using two vibrational transition frequencies of molecular ion

Example: We consider \( f(v') \) with

\[
^{16}\text{O}_2^+ ~ ^2\Pi_{1/2} (v,J) = (0,1/2)-(v',1/2)
\]

electric quadrupole shift zero

Zeemaan shift eliminated perfectly

\[
Q(v') = \frac{f(v') - f(2v')/2}{f(v')} \propto \left( \frac{m_p}{m_e} \right)^{-1/2}
\]

elimination of relativistic effects

light shift induced by probe laser

supression of DC Stark shift

blackbody radiation shift

useful for the search of the variation in \( \left( \frac{m_p}{m_e} \right) \)

atomic clock for reference is not necessary
Publications

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