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Prospect of molecular clocks

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While uncertainties of some of the atomic transition frequencies have been reduced to the level of 10^{-8}, the molecular transition frequencies are currently difficult to be measured with the uncertainty below 10^{-15}. This is mainly because of the complicated energy levels of the molecules having the vibrational-rotational states. This paper lists some molecular transition frequencies, which can be measured with the uncertainties lower than $10^{-16.}$ © Anita Publications. All rights reserved.

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1 Introduction

Since 1967, the standard of Time & Frequency has been given based on the ^{133}Cs hyperfine transition frequency (9 192 631 770 Hz) [1]. The measured ^{133}Cs transition frequency is actually not in accordance with the definition, because of interaction with the electric and magnetic fields (causing Stark and Zeeman shifts), and the relativistic effects (giving quadratic Doppler, gravity red etc. shifts). Using atoms in a thermal beam, the obtained accuracy was 5×10^{-15} after accounting corrections to the estimated frequency shifts [1]. Today accuracies in the measurements are improved drastically using the laser cooled techniques. After the development of an atomic fountain apparatus, the uncertainty of ^{133}Cs atomic transition has been reduced to lower than 10^{-15} [2].

To get low ratio of the frequency uncertainty to the transition frequency, it is preferable to consider large transition frequencies. Some transition frequencies of atoms are in the optical region that can be better suitable for the frequency standards than the ^{133}Cs hyperfine transition frequency. However, there lies a problem as the frequency in the optical region cannot be measured with a frequency counter. Development of the frequency comb has solved this problem [3], and the accuracies of atomic transition frequencies in the optical region have been improved drastically in the 21st century.

Confinement of atoms in an area narrower than the wavelength of probe light is also an important subject to observe the spectrum without encountering the first order Doppler effects. The idea using an ion trapped by rf-electric field was given by Dehmelt [4]. The motion of a single ion in a Paul trap is the quasi-harmonic oscillation around the center, where the electric field is zero. Its amplitude is reduced by laser cooling down to much smaller than the wavelength of the probe light and the Stark shift induced by the trap electric field is negligibly small. With linear electrode (rf-trapping in radial directions and dc trapping in the longitudinal direction), the trap electric field is zero on the node but the electric field gradient in the longitudinal direction is significant. Therefore, the Stark shift can be negligible with several ions in the string crystal, but the electric quadrupole shifts can be significant for ions with large electric quadrupole moments. The ^{27}Al^{+} and ^{171}Yb^{+} transition frequencies have been measured with uncertainties lower than 10^{-17} [5, 6].

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Another method is the measurement with neutral atoms, cooled down to 1-3 mK and trapped by a standing wave of laser light (optical lattice). Measurement with many atoms, trapped in an area smaller than the half of the wavelength of trap laser, makes it possible to observe the spectrum with high signal-to-noise (*S/N*) ratio. The trap laser induces Stark shift in the transition, which depends on the trap laser frequency. This problem is solved by using a trap laser with a certain frequency (magic frequency), where the Stark shifts of the upper and lower states are equal and the differential Stark shift in the transition frequency is zero. Using this technique, transition frequency in ^{87}Sr has been measured with an uncertainty lower than 10^{-17} [7, 8].

Precise measurements of atomic transition frequencies are also immensly useful in the studies of fundamental physics; for example testing variation of the fine-structure constant [9-11]. The precise measurement of the molecular vibrational-rotational transition frequencies is also required to test the variation in the proton-to-electron mass ratio.

Precise measurements of molecular transition frequencies have been considered to be much more difficult than that of the atomic transitions. This is because the energy structure with vibrational-rotational states is much more complicated than that of atoms, and it is difficult to localize a molecule in a selected quantum state. The complicated energy structure makes it also difficult to reduce the kinetic energy by laser cooling.

However, cold molecules has been obtained with different methods in the 21st century. Measurements of some of the molecular vibrational transition frequencies seem to be feasible within the uncertainties of 10^{-16}. This paper discusses the prospects for developing molecular clocks in near future.

2 Previous measurement of molecular transition frequencies

Frequency stabilization of lasers, which are used to transform information via optical fiber, has been an important subject to increase the volume of transformable information. Lasers with wavelength of 1.4 – 1.6 μm have been used for this purpose because of the low loss in the fiber, but no atomic transition frequencies are used as the frequency standards in this region. Frequency standards using molecular vibrational-rotational transitions may open-up this possibility. The broadening of the spectrum observed with a room temperature cell is generally caused by the Doppler broadening. Narrower linewidth can be obtained by saturation spectroscopy using high Q-cavity. The C_2H_2 transition frequency has been measured with the uncertainty of 6.8×10^{-12} [12]. The shifts induced by the Stark, Zeeman, and relativistic effects are negligible within this stability.

Shelkovnikov *et al* have observed the vibrational transition spectrum of SF_6 molecule in a beam [13]. Here, the two-photon Ramsey spectroscopy has been used to reduce the spectrum linewidth. Correcting the Stark shift induced by the probe laser and the quadratic Doppler shift, they have reduced the uncertainty in the frequency measurement to 2.8×10^{-14}. To our knowledge, this is currently the highest accuracy achieved for a molecular transition. This seems to be close to the limit of the accuracy obtained with molecules at the room temperature.

3 Cold molecules

To achieve higher accuracies in the molecular transition frequencies, measurements should be carried out in the ultra-cold molecules. There are two ways to get cold molecules; one is the deceleration of trapped molecules [5, 14-18] and the other is production of cold molecules binding ultra-cold atoms [19-23]. In this section, current situation of the research for cold molecules is reviewed.

3.1 Molecular deceleration

Laser cooling has been considered to be difficult for molecules, because of complicated energy structure. The simplest cooling method is buffer gas cooling. The Doyle group in Harvard succeeded in magnetic trap of CaH molecules after precooling using He buffer gas (vapor of liquid He) [14]. The temperature of trapped molecules was attainted to be 400 mK. Evaporative cooling was considered to be the best method for further cooling, but it is realistic only with the molecular density higher than 10^{11} /cm^3.

It is also possible to decelerate polar molecules in a beam using time-varying inhomogeneous electric field. Bethlem *et al* and Crompvoets *et al* had succeeded to load decelerated ND_3 molecules into an electrostatic trap [15, 16].

Recently also molecular laser cooling has been studied for diatomic molecules, whose bonding-length and the vibrational frequencies are almost same at the electronically ground X and excited A states (diagonal coupling). For these molecules, the dipole coupling between the X and A states are strong only between the same vibrational quantum state v. The absorption and the spontaneous emission transitions between the X($v = 0$, $N = 1$) and A($v = 0$, $N = 0$) states repeat almost 100 cycles, where N is the rotational quantum state. After employing repump lasers, which are resonant with the X($v = 1$, $N = 1$) - A($v = 0$, $N = 0$) and X($v = 2$, $N = 1$) and A($v = 1$, $N = 0$) transitions, the cooling can continue for more than 10000 cycles. Therefore, the kinetic energy of molecules can be reduced from 1 K to lower than 1 mK by laser cooling. Norrgard *et al* succeeded with three-dimensional magnetic optical trapping (3D-MOT) of laser cooled SrF molecules with the temperature of 400 K [17].

Also the opt-electric cooling is useful for polar molecules. With this method, molecular beam passes the area with high and low electric field periodically. Molecules in the low-electric-field region are in a state with a strong positive Stark shift. Then molecules are decelerated upon entering a high-electric-field region. At the high-electric-field region, molecules are pumped to another state with weaker Stark shift, so that the acceleration at the entering to the low electric field region is smaller than the deceleration at the entering to the high electric field region. Prehn *et al* had cooled H_2CO molecules with this method down to temperature 400 K [18].

Molecular ions can be trapped by rf-electric field. When some other ion is trapped and laser cooled, a molecular ion can reduce its kinetic energy (sympathetic cooling). Sympathetic cooling has been used to cool $^{27}Al^+$ ion [5]. Note that the vibrational-rotational energy is not reduced with this method, and the localization to a selected quantum state can be attained in this method of treating a molecular ion.

3.2 Production of cold molecules binding clod atoms

The simplest method to get molecules with low kinetic energy is binding ultra-cold atoms. In this method the first step is photo-association. A laser light is irradiated with a frequency lower than the transition frequency to an excited state, which gives a negative energy shift at the collision with another atom. If the negative energy shift at the excited state is larger than that at the ground state, atoms are excited to the binding state. Molecules in the excited states are produced in this procedure and they are transformed to the ground state via spontaneous emission. This method was used to produce homo-nuclear diatomic molecules at first [19], but also hetero-nuclear molecules have been produced afterwards [20].

Another method is transform of atoms in the Bose-Einstein-condensation (BEC) to the molecular state by controlling the condition (electric or magnetic field). When the atomic density is high and there is a significant interatomic interaction, there are two different states possible: being separated atoms or molecules. There is energy gap between both the states, which depend on the circumstances. At a certain electric or magnetic field, the energy gap could be zero and coupling between both the states is significant (known as Feshbach resonance) [21]. By controlling the circumstance passing through the Feshbach resonance, separated atoms are transformed to the molecular state adiabatically. Molecules with the kinetic energy lower than 1 mK have been produced by this method.

With both the methods, the produced molecules are initially in the higher internal states. They can be eventually transformed to the vibrational-rotational ground state by the stimulated Raman transition [22, 23].

4 Possible precise measurement of vibrational transitions of cold molecules

In this section, we discuss the possibilities to measure the transition frequencies of cold molecules with the uncertainty lower than 10^{-16}. The molecular vibrational-rotational transition frequencies are given by the nuclear motion, while the atomic transition frequencies in the optical region are mostly given by the electron motion (reduced mass between the electron and nucleus is given by the electron mass with the accuracy of 0.01 %). Therefore, the precise measurement of the molecular vibrational-rotational transition is useful to test the variation in the proton-to-electron mass ratio. To reduce the ratio of Stark and Zeeman shifts to the transition frequency, the vibrational transitions in the infrared region are much more advantageous than the rotational transitions in the microwave region. The vibrational transition frequencies with $\Delta N = 0$ is particularly advantageous to suppress the Stark and Zeeman shifts, because the shifts of the upper and the lower states are mostly cancelled out. Therefore, we discuss here only on the vibrational transitions.

4.1 Molecular ion

The reduction of kinetic energy seems to be much simpler for molecular ions than the neutral molecules. The Duesseldorf group have measured the vibrational transition frequency of HD^+ molecular ion with the uncertainty of 2×10^{-9} [24]. The molecular ions in a linear trap are sympathetically cooled with laser cooled $^9Be^+$ ion. The problem of HD^+ molecular ion is that there is a complicated hyperfine structure and measurements in many molecular ions in a Coulomb crystal (broadened in radial directions) are required. Therefore, the Stark shift induced by the trap electric field (proportional to the displacement from the node) is significant. Also the quadratic Doppler shift is not negligible in this case because of small mass of this molecule (1×10^{-16} with 1 mK). Therefore, measurement with the uncertainty lower than 10^{-15} seems to be difficult.

We have proposed the precise measurement of the $X_1 \Sigma$ $(v,N,M) = (0,0 \pm 1/2)$ - $(1,0 \pm 1/2)$ transition frequencies of XH^+ molecular ions, where X is the even isotope of group II atoms [25,26]. M is the component of the total angular momentum parallel to the magnetic field. XH^+ molecular ions are produced by the chemical reaction between the trapped and optically excited X^+ ions and H_2 molecules. The nuclear spin of X and H atoms are 0 and 1/2, respectively. Irradiating two lasers, which are resonant to the $(v, N) = (0, 2)$-$(1, 1)$ and (0,1)-(2, 0) transitions, molecular ions are pumped to the $(v, N) = (0, 0)$ state, where there is no hyperfine splitting [27]. The estimated Zeeman and DC Stark shifts in these ions are given in Table 1. Since the Zeeman shift induced by the earth magnetic field is less than 10^{-17}, the selection between $M = \pm 1/2$ is not required. The electric quadrupole shift is zero with this transition. To keep the Stark shift induced by the trap electric field lower than 10^{-17}, the trap electric field should be smaller than 0.05 V/cm. Therefore, measurement should be performed with molecular ion in a string crystal localized at the node of linear trap. The vibrational transition should be monitored by the quantum logical detection [28]. The $N = 0 - 0$ transition is one-photon forbidden, and it should be observed with two-photon transition. The Stark shift induced by the probe laser is generally significant, which can be eliminated by observing the Hyper-Ramsey spectrum [29, 30]. It is also useful to observe Raman transition using two lasers with proper frequencies, where the Stark shifts induced by both the lasers cancel each other [31]. In this way it seems possible to reduce the frequency uncertainty to lower than 10^{-16}. The main problem is that the measurement cycle can be perturbed by the unfavorable transitions induced by the blackbody radiation. Cryogenic chamber is required for the stable operation. Using cryogenic chamber, the Stark shift induced by the blackbody radiation is less than 10^{-19}. Khanyile *et al* had observed the $^{40}CaH^+$ overtone-vibrational transition spectrums, however, those transitions cannot not be resolved to each rotational components [32].

We had also proposed the measurement of the N_2^+ ($I = 0$, where I is nuclear spin) $X_2\Sigma$ $(v, N, M) =$ $(0,0, \pm 1/2)$ - $(1,0, \pm 1/2)$ transition frequencies [33]. In the $^{14}N_2^+$ ($^{15}N_2^+$) molecular ion, only even rotational states can exist with $I = 0$ and 2 ($I = 0$) and only odd rotational states can exist with $I = 1$ ($I = 1$). There is no electric dipole transition possible between different vibrational-rotational states in the $X^2\Sigma$ state. Therefore, no unhopeful transition is induced by the blackbody radiation and the cryogenic chamber is not required. The optical pump to a selective state is not possible, but initial preparation of N_2^+ molecular ion in a selective vibrational-rotational state is possible by the resonance-enhanced-multiphoton-ionization (REMPI) [34]. The DC Stark coefficient is much smaller than that of XH^+ molecular ions (see Table 1). Therefore, it can be measured with molecular ions in a Coulomb crystal, broadened by 1-3 μm in the radial directions. As can be seen the Zeeman and electric quadrupole shifts are zero. The transition should be induced by two-photon transition, and the Stark shift induced by the probe lasers can be eliminated by observing the Hyper-Ramsey spectrum or the Raman transition using two lasers with proper frequencies [29, 30, 33]. The Stark shift induced by the blackbody radiation with the surrounding temperature of 300 K is less than 10^{-17}. Measurement with the uncertainty lower than 10^{-17} is expected to be possible. With I = 1 and 2, there is complicated hyperfine structure, so elimination of the Zeeman and electric quadrupole shifts are difficult. For the selective production of $^{14}N_2^+$ molecular ion with $I = 0$, REMPI with high resolution is required. Measurement with $^{15}N_2^+$ is useful, because even rotational states are possible only with $I = 0$. Germann *et al* had observed the $^{14}N_2^+$ $X^2\Sigma$ (v, N) = (0,0)- (1,2) transition [35], where the attainable accuracy with this transition is expected to be of the order of 10^{-14}. This is because of negligibly small electric quadrupole shift [36]. The quadratic Doppler shift is less than 10^{-17} with the kinetic energy of 1 mK for the XH^+ and N_2^+ molecular ions.

Also, the energy structure of H_2^+ molecular ion has same energy structure as the $^{15}N_2^+$ molecular ion, but the quadratic Doppler shift is 15 times larger (inversely proportional to the mass) than for $^{15}N_2^+$ molecular ion with the same kinetic energy. Considering the mass ratio between the H_2^+ and $^9Be^+$ ions (lighter ion can be laser cooled faster), the sympathetic cooling efficiency of H_2^+ molecular ion cannot be particularly high.

Table 1. Transition frequencies, Zeeman and DC Stark coefficients in the (v, N) = (0,0) – (1,0) transitions of few molecules that are suitable for molecular clocks.

	Transition frequency (THz)	Zeeman coefficient (/G)	DC Stark coefficient (/(V/cm)^2
$^{40}CaH^+$	43.2	1×10^{-18}	-3×10^{-15}
$^{88}SrH^+$	40.3	9×10^{-19}	-5×10^{-15}
$^{174}YbH^+$	43.0	5×10^{-18}	-3×10^{-15}
$^{14}N_2$	65.2	0	8×10^{-20}

4.2 Neutral molecules

As precise measurements have been performed with neutral atoms in optical lattices [7,8], the same method seems to be useful also for the neutral molecules. Zelevinski *et al* and Kotochigova *et al* have suggested measuring the vibrational transition frequency of the Sr_2 molecules trapped in an optical lattice [37, 38]. They demonstrated the existence of the magic frequency, where the Stark shift in the transition frequency is eliminated. However, the proposed magic frequencies are in the region quasi-resonant to the electric transitions and the Stark shift becomes significant with a slight fluctuation of the lattice laser frequency.

The vibrational transition frequencies of the diatomic molecules including a light atom seem to be advantageous for the precise measurement because of their large transition frequencies. Seeing that ^6Li (nuclear spin 1) is the lightest atom, which can be laser cooled in the ground state, we have proposed for the precise measurement of the $X\,^2S$ (v, N, M) = (0, 0, ±3/2)- (1, 0, ±3/2) transition frequencies of the X^6Li molecules [39, 40]. The transition frequencies of the $^{40}Ca^6Li$, $^{88}Sr^6Li$, and $^{174}Yb^6Li$ molecules are 5.77 THz, 5.06 THz, and 4.17 THz, respectively. Ivanova *et al* and Krois *et al* had observed the CaLi molecular spectra in the optical region [41, 42]. The simultaneous quantum degenerate states of the ^{174}Yb and ^6Li atoms have already been observed [43]. X^6Li molecules with ultra-low temperature are expected to be produced via the photo-association or Feshbach resonance technique and can be transformed to the vibrational-rotational ground state [22, 23]. Cold molecules are generally trapped in an optical lattice with the magic frequency. Table 2 lists the magic frequencies ($f_M s$), the power density giving the potential depth 10 mK, and the gradient of the Stark shifts (Ss) by the lattice laser frequencies (f_L) with this power density for different molecules. Figure 1 shows the Stark shift in the ^{174}Yb^{6}Li transition frequency induced by the lattice laser with power density of 23 kW/cm^2 as a function of the lattice laser frequency f_L. The magic frequency f_M listed in Table 2 is highlighted.

The Zeeman shift induced by the earth magnetic field is less than 10^{-17} in all the X^{6}Li molecules. The quadratic Doppler shift is estimated to be less than 10^{-18}. The Stark shift induced by the blackbody radiation with the surrounding temperature of 300 K is less than 10^{-14} and its uncertainty is less than 10^{-17} when the temperature is stabilized within 1 K. This transition can be observed with two-photon transition, as it is one-photon forbidden. The Stark shift induced by the probe laser can be eliminated by Raman transition using two lasers at the frequencies where the shifts induced by two lasers will cancel each other.

This proposal is applicable only for the $N = 0 - 0$ transitions. With other rotational states, the Stark shift depends on the polarization of the trap laser. To suppress the collision shift, three-dimensional lattice is required, and the polarization cannot be uniform for all trapped molecules. The elimination of the Stark shift induced by the lattice laser is not possible with this situation. This can also be applicable for the X^{23}Na molecules, but it is less advantageous for the precise measurement than the X^{6}Li molecules because in this case the Zeeman shift is one order larger [44]. There is no useful magic frequency available for the ^{88}Sr^{87}Rb molecule.

Table 2. List of magic trap frequency f_M, power density where the potential depth is 10 mK I$_L$, and dS/df_L when the lattice laser frequency f_L is f_M (S is the Stark shift with the power density of I_L) of some cold molecules that are suitable for molecular clocks.

	f_M (THz)	I_L (kW/cm^2)	dS/df_L(/MHz)
^{40}Ca^{6}Li	268.9	11	1×10^{-16}
^{88}Sr^{6}Li	313.5	11	1×10^{-15}
^{174}Yb^{6}Li	361.4	17	6×10^{-17}

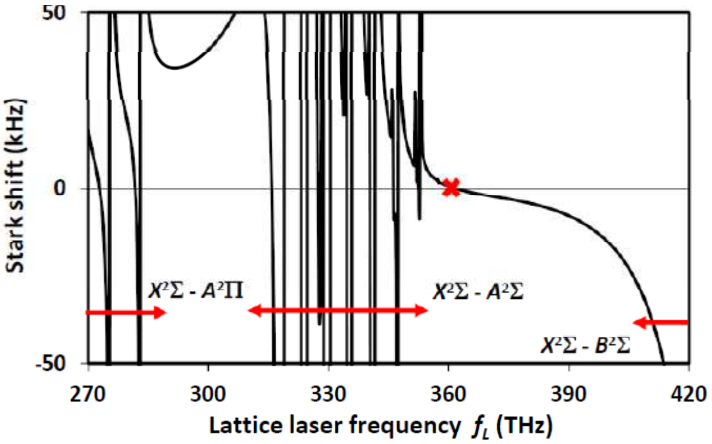

Fig 1. The Stark shift in the ^{174}Yb^{6}Li (v,N) = (0,0)-(1,0) transition frequency induced by the trap laser frequency with the power density of 23 kW/cm^2 as a function of trap laser frequency f_L. The magic trap frequency, listed in Table 2, is highlighted [(red) crosses]. The (red) arrows denote the frequency region that is quasi-resonant with the $X^2\Sigma$ $A^2\Pi$, $A2\Sigma$, and $B^2\Sigma$ transitions.

5 Conclusion

Precise measurement of molecular vibrational transition frequencies are useful to give information on the proton-to-electron mass ratio m_p / m_e. H_2^+ and HD^+ molecular ions, whose Schroedinger equation can be solved analytically, are useful to give the accurate value of m_p / m_e with the accuracy of 10^{-11} [45]. To test the variation in m_p / m_e, the molecular vibrational transition frequency need to be measured with the uncertainty lower than 10^{-16}. Therefore, molecular transitions should be selected suitably where the measurements can be carried out with the above attainable accuracy. A number of plausible molecular candidates have been discussed in this paper where it is possible to measure the transition frequencies very accurately. While some atomic transition frequencies have been measured with the uncertainty lower than 10^{-17}, molecular transition frequencies have never been measured with the uncertainty lower than 10^{-14}. However, there is a possibility that they can be measured with uncertainties lower than 10^{-16} in the proposed $(v, N) = (0,0) – (1,0)$ transitions of the XH^+ and N_2^+ molecular ions and X^6Li molecules for X being an even isotope of group II atoms in the periodic table. Among these candidates, N_2^+ molecular transition frequency seems to be the most interesting for achieving such unprecedented precise measurement, because of recent successful demonstration of its realization in an experiment [35].

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