# TRAPPED-ION FREQUENCY STANDARDS*

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## *Abstract*

***Frequency standards based on stored atomic ions are briefly reviewed. Specific examples are chosen to illustrate what is currently possible. Both rf/microwave and optical devices are discussed. The present limitations to existing experiments and possibilities for future improvement are outlined.***

## INTRODUCTION

The interest in stored ion frequency standards is reflected by the large number of laboratories using the stored-ion technique for high resolution atomic spectroscopy with application to frequency standards. The authors are aware of related work currently being pursued at (in alphabetical order) Communications Research Laboratory (CRL), Tokyo; Hamburg University; Hewlett Packard, San Jose; IBM, San Jose; Imperial College, London; Jet Propulsion Laboratory (JPL), Pasadena; Korea Standards Research Institute, Taejon, Korea; Laboratoire de l'Horloge (LHA), Orsay; Mainz University; Max Planck Institute, Garching; National Institute of Standards and Technology (NIST), Boulder; National Physical Laboratory (NPL), Teddington; National Research Council (NRC), Ottawa; National Research Laboratory of Metrology (NRLM), Tsukuba; Physikalisch-Technische Bundesanstalt (PTB), Braunschweig; and the University of Washington, Seattle. With apologies to many of these laboratories, this paper gives only a brief review of progress toward realizing frequency standards based on stored ions. It is not intended to be comprehensive. The reader is referred to recent proceedings of this conference and those of the Symposium on Frequency Control, the proceedings of the Fourth Symposium on Frequency Standards and Metrology[1], a forthcoming review[2], or the specific laboratories for further information.

Although there is overlap of the work between various groups, historically there has been a natural division in experiments performed in the rf/microwave spectral region versus those in the optical spectrum. One reason for this division has been that the required stable local oscillators have been difficult to provide in the optical domain and relatively easier in the rf/microwave region. This distinction is disappearing because better sources are now required in the rf/microwave region. Another reason for the division is that the ability to generate time (measure the phase of the clock radiation) in the rf/microwave region is straightforward, while it remains a difficult problem for optical frequencies.

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# RF/MICROWAVE EXPERIMENTS

The particular ion for an rf/microwave frequency standard should have a high frequency to increase stability (other things being equal). However, a primary consideration seems to be availability of a convenient optical source for use in optical pumping and double resonance detection of the clock transition. In addition, some experiments require a narrow band optical source for laser cooling. Some representative examples of rf/microwave clocks are given below:

## A. $^{199}$Hg$^+$ Paul trap frequency standards

In 1973, Major and Werth observed the 40.5 GHz ground-state hyperfine transition of $^{199}$Hg$^+$ with a linewidth of a few hertz[3]. $^{199}$Hg$^+$ has some advantages over other ions as a frequency standard. Its hyperfine transition has a relatively high frequency. Because of its large mass, it has a low second-order Doppler shift at a given temperature.

The detection of the resonance is based on optical pumping. The lowest electronic levels are shown in Fig. 1. An rf-excited lamp containing the $^{202}$Hg isotope will emit 194 nm radiation that will drive $^{199}$Hg$^+$ ions in the F=1 hyperfine level of the ground state to the 5d$^{10}$6p $^2$P$_{1/2}$ state. The ions can then decay to either the F=0 or F=1 hyperfine levels. The lamp eventually pumps most of the ions to the F=0 ground state. If microwave radiation near the 40.5 GHz resonance is applied, some ions are driven to the $m_F = 0$ sublevel of the F=1 state. They then can be re-excited to the 5d$^{10}$6p $^2$P$_{1/2}$ state by light from the lamp. When they decay, the 194 nm photons are detected with a photomultiplier tube. Jardino *et al*[4] made the first frequency standard based on this system. They measured $\sigma_y(\tau) = 3.6 \times 10^{-11}\tau^{-1/2}$, for $10 < \tau < 3500$, where $\tau$ is the measurement time interval in seconds. This stability was comparable to that of some commercial cesium atomic clocks.

This basic system was developed further by Cutler *et al* [5, 6, 7, 8]. They introduced helium buffer gas to reduce the temperature of the ions to near room temperature. The lamp was turned off when the microwave radiation was applied, in order to avoid light shifts of the microwave resonance frequency. The number of ions was about $2 \times 10^6$. The resonance linewidth was 0.85 Hz. Fractional frequency fluctuations of $7.6 \times 10^{-15}$ for integration times of one day have been reported[6].

Prestage *et al*[9] have demonstrated a $^{199}$Hg$^+$ frequency standard based on a linear rf trap. Ramsey's separated oscillatory field method was employed to drive the resonance. In this method, two short rf pulses are applied. This yields a linewidth in hertz of about 1/(2T), where T is the time between the two pulses in seconds. The frequency standard was operated with a linewidth of 0.16 Hz and a Q of $2.5 \times 10^{11}$. The short-term stability of the device was $\sigma_y(\tau) = 1.6 \times 10^{-13}\tau^{-1/2}$ for $50 < \tau < 800$.

## B. $^9$Be$^+$ Penning trap frequency standard

Bollinger *et al* [10, 11] demonstrated the first frequency standard based on laser-cooled ions where the second-order Doppler shift can be significantly reduced. This standard was based on a 303 MHz hyperfine transition in the ground electronic state of $^9Be^+$. The hyperfine sublevels of the ground state are shown in Fig. 2. The first derivative of the frequency of the transition between the $(m_I = -3/2,\ m_J = 1/2)$ sublevel and the $(m_I = -1/2,\ m_J = 1/2)$ sublevel approaches zero at a value of the magnetic field near 0.8194 T. A frequency-doubled cw dye laser was used to generate 313 nm radiation to laser-cool and optically detect the ions.

In the most recent version of the $^9Be^+$ frequency standard, sympathetic laser cooling was used[12]. Magnesium ions were trapped at the same time and were continuously laser cooled. The Coulomb interaction between the ions kept the $^9Be^+$ ions cold continuously. The number of $^9Be^+$ ions was about 5000 to 10,000. The 313 nm radiation source was tuned so that most of the ions would be pumped to the ($m_I = 3/2$, $m_J = 1/2$) ground-state sublevel in a few seconds. The 313 nm radiation was then turned off. Ions in the ($m_I = 3/2$, $m_J = 1/2$) sublevel were transferred to the ($m_I = 1/2$, $m_J = 1/2$) sublevel and then to the ($m_I = -1/2$, $m_J = 1/2$) sublevel by two successive rf pulses. The Ramsey method was then used to drive some of the ions to the ($m_I = -3/2$, $m_J = 1/2$) sublevel. Then rf pulses were applied in the reverse order, to bring ions which had remained in the ($m_I = -1/2$, $m_J = 1/2$) sublevel back to the ($m_I = 3/2$, $m_J = 1/2$) sublevel. The 313 nm source was then turned back on and the fluorescence intensity was measured. The intensity was proportional to the ($m_I = 3/2$, $m_J = 1/2$) population. If ions were left in the ($m_I = -3/2$, $m_J = 1/2$) sublevel, there was a decrease in the intensity. The time between the two rf pulses was as long as 550 s, although 100 s was more typical. With T=550 s, the width of the resonance was 900 $\mu$Hz. The stability was better than $3 \times 10^{-12}\tau^{-1/2}$. However, a frequency shift with changes in pressure was observed[12]. This limited the long-term stability of the standard to about $3 \times 10^{-14}$. The uncertainty of the second-order Doppler shift was only $5 \times 10^{-15}$.

### C. Other work

Other ions have been investigated for use in microwave frequency standards. Lasers have been used for optical pumping and detection of hyperfine transitions in several other ions, including $^{25}Mg^+$ [13], $^{137}Ba^+$ [14], $^{135}Ba^+$ [15], and $^{171}Yb^+$ [16]. Frequency standards based on $^{137}Ba^+$ [17] and $^{171}Yb^+$ have been reported[18].

## OPTICAL FREQUENCY STANDARDS

An optical standard has the chief advantage that, if the transition linewidth and signal-to-noise ratio can be maintained, the stability of the standard improves linearly with the increase in frequency of the atomic transition used for the reference. This factor of improvement can be as much as $10^4$. Conversely, by going to higher frequency, we can sacrifice some signal-to-noise ratio by using smaller numbers of ions and still maintain good stability. This is important because in general, the second-order Doppler shift is reduced as the number of ions is reduced. The penalty for using optical frequencies is that the required local oscillators (lasers) are more difficult to produce and the measurement of frequencies and the phase of the oscillation is difficult. Nevertheless, it seems that this approach will ultimately yield fundamental improvements in performance and several labs are pursuing these experiments.

High resolution experiments have been reported in $Ba^+$ [19, 20, 21], $Yb^+$ [18, 22], and $Sr^+$ [23] and $Hg^+$. As an example, we briefly discuss the experiment on $Hg^+$ at NIST.

### A. $Hg^+$ single-ion optical spectroscopy

$Hg^+$ has a level structure which seems to be suitable for an optical frequency standard. The $5d^96s^2$ $^2D_{5/2}$ state is metastable, with a lifetime of about 90 ms. The 194 nm transition from the ground $5d^{10}6s$ $^2S_{1/2}$ to the $5d^{10}6p$ $^2P_{1/2}$ state can be used for laser cooling and for electron shelving detection[24]. Near zero field, some hyperfine components of the 281.5 nm transition in $^{199}\mathrm{Hg}^+$ are nearly independent of magnetic field. One of these is the transition from $F = 0$ in the ground state to $(F = 2,\ m_F = 0)$ in the upper state. Recently, Bergquist *et al*[25] observed this transition with a linewidth of under 80 Hz. The resonance line Q is over $10^{13}$ and is the highest ever observed in an atomic or molecular transition. The laser frequency was servoed to the single-ion resonance for periods of several minutes[25].

## FUTURE

In general, the second-order Doppler shift increases as the number of ions is increased. This effect can be reduced by using a linear trap geometry[26] as has recently been demonstrated by Prestage, *et al*[9]. For more than one ion in a linear rf or Penning trap the second-order Doppler shift can be reduced to its minimum value by stacking a line of individual ions along the trap axis of symmetry[27, 28, 29]. This may provide a microwave or optical frequency standard with an extremely small second-order Doppler shift[28].

Throughout the history of high resolution trapped-ion spectroscopy, the most difficult systematic perturbation to eliminate has been the second-order Doppler shift. If this shift is reduced, other systematic effects may become more important. A surprising result (to us) was the large pressure shift measured on the $^9\mathrm{Be}^+$ hyperfine transition[12, 28]. This may be caused by sticking of molecular background gas ions to the $^9\mathrm{Be}^+$ ions. These kinds of shifts should also be investigated in other ions.

As the systematic shifts of the ion clock transitions are reduced, the demands on local oscillator spectral purity become more stringent. This is apparent in the experiments on $\mathrm{Hg}^+$ and $\mathrm{Be}^+$ microwave/rf transitions and is the most important limitation in the $\mathrm{Hg}^+$ optical experiments.

Although the light sources for optical pumping, detection, and laser cooling can be difficult to produce, we anticipate that simple, cheap, solid state optical sources in the ultraviolet will eventually become available. This development will probably be driven by the optoelectronic industry rather than developers of clocks, but there is such a large effort to develop shorter wavelength solid state sources that there is reason to be optimistic.

Certainly, the new laser-cooling schemes will result in significant advances for neutral atom clocks[30]. It appears that the main advantage of the new cooling schemes is not the further reduction in the second-order Doppler shift, but the dramatically increased control over the positions and velocities of the atoms. Neutral atom clocks can work with much larger numbers of atoms and can therefore have high signal-to-noise ratio and stability. These experiments have the added advantage that diode lasers for optical pumping and laser cooling are available now. Therefore the ion trappers will have competition from these neutral atom experiments. Although there is no clear overall advantage to either approach, we expect to see dramatically improved frequency standards for both neutral atom and trapped ion experiments.

## ACKNOWLEDGMENTS

The work at NIST has been supported by the Air Force Office of Scientific Research and the Office of Naval Research.

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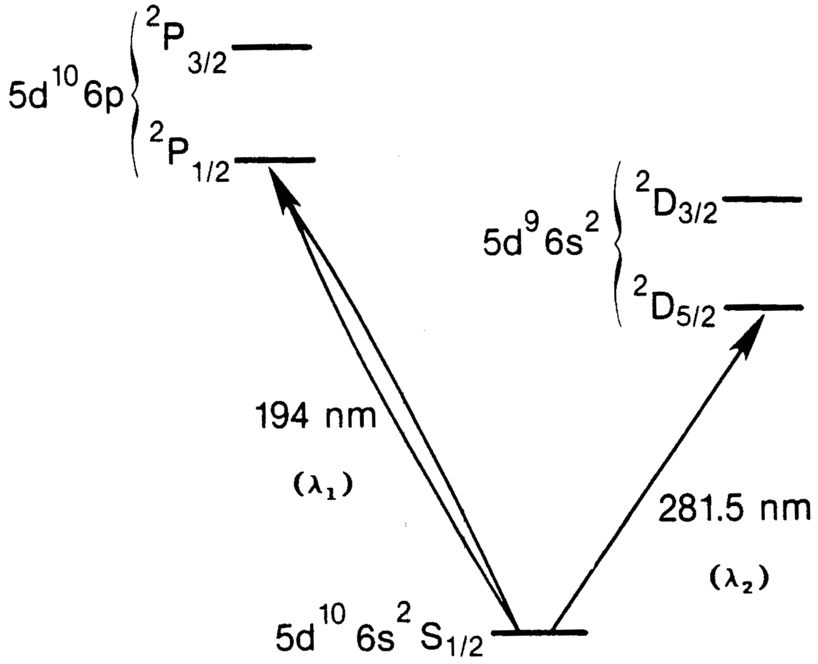

Fig. 1. Electronic energy levels of $Hg^+$. The ground electronic state of the $^{199}Hg^+$ isotope is made up of two hyperfine levels, separated by 40.5 GHz. Some microwave frequency standards are based on this transition. An optical frequency standard might be based on the 281.5 nm transition.

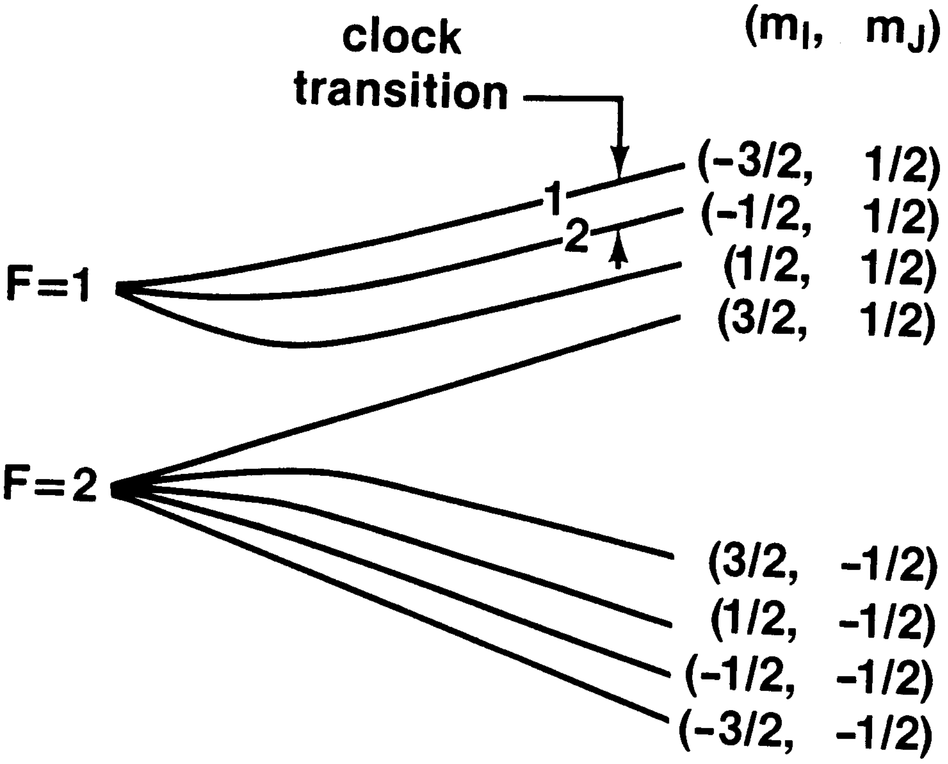

Fig. 2. $^9Be^+$ energy levels in a magnetic field. The frequency standard is based on the 303 MHz "clock transition" between the levels labeled "1" and "2."