2. Primary Atomic-Frequency Standards: New Developments

R. E. Drullinger[1], *S. L. Rolston*[2], *and W. M. Itano*[1]
National Institute of Standards and Technology

[1]Time and Frequency Division
325 Broadway
Boulder, CO 80303 USA
Fax: (303) 497-6461

[2]Atomic Physics Division
National Institute of Standards and Technology
Gaithersburg, MD 20899-0001
Fax: (301) 975-3038

1. Abstract

Optical technologies, for manipulating the population distribution and motions of atoms and ions, developed over the last two decades, are being applied to new classes of atomic-frequency standards. Current results are already impressive, but the concepts promise to improve accuracy by many orders of magnitude. In this article, we describe a new generation of optically pumped primary standards, the emergence of cooled-atom frequency standards, and the amazing potential of standards based on stored ions.

2. Introduction

Since the beginning of atomic timekeeping, primary frequency standards have been based on thermal-atomic beams of cesium. The choice of the transition and approach were no doubt influenced primarily by the technology available at the time. See *Ramsey* [*1983*] and *Forman* [*1985*] for reviews of the early historical development of the technology. Most current primary standards are based on magnetic state selection in thermal atomic beams. The general technology has been well reviewed [*Audoin, 1992*; *Vanier and Audoin, 1989*], and current primary standards based on this technology are reviewed by *Mungall* [*1986*].

The recent development of tunable diode lasers has had a positive influence on primary standards. Optical methods for state preparation and detection can now replace the earlier magnetic methods, resulting in higher accuracy and improved short-term stability. These methods should carry the technology of thermal, atomic-beam frequency standards to practical limits. Radically new methods will be needed to achieve further advances. Fortunately, two such methods are under very active development.

Cooled-neutral-atom frequency standards are in a very early stage of development, compared, for example, to atomic-beam standards. While not promising as high an accuracy as the stored-ion standards described below, cooled-neutral-atom standards offer higher signal-to-noise ratio at potential accuracies that are still well beyond those of present cesium-beam standards. One approach, the atomic fountain, is being developed in several laboratories. An attractive feature of this approach is the use of neutral cesium. This allows continued use of the present definition of the second.

Stored-ion frequency standards are also in an early state of development. However, they have certain fundamental advantages. The ions whose resonances determine the frequency of the standard are surrounded by a vacuum (or, in some cases, a low-pressure buffer gas), and do not make contact with the material walls of the chamber. Thus, their frequencies are not significantly perturbed. The time during which an ion can be observed is much greater than for an atomic beam, or even a laser-cooled atomic fountain. The long observation times lead to dramatically higher resonance Q's. In the case of laser-cooled devices, Doppler shifts of all orders are very small. It is quite possible that an ion-based frequency standard might prove to be more reproducible than those based on cesium, so, with a suitable change in the definition of the second, it could become a primary-frequency standard.

3. Standards based on optical pumping of thermal beams

Conventional, thermal-atomic-beam frequency standards use magnetic state selection and detection: see *Audoin* [*1992*] for a review of the technology, and *Mungall* [*1986*] for a review of existing primary standards. The technical concept has remained essentially the same for 40 years, and has been developed almost as far as it can be. The limits to the accuracy and stability of these standards largely result from several side effects of the Stern-Gerlach magnets, used for state selection and detection. Still, the magnets provide initial-state preparation and final-state analysis, which are necessary in any thermal-atomic-beam standard. Long ago, *Kastler* [*1950*] pointed out that the interaction of atoms with resonant light could be used to modify the population distribution within an ensemble of atoms, as well as to detect the result of RF-excited transitions within the atoms. The process has come to be known as "optical pumping." It promised great benefits in stability and accuracy, if applied to the problem of state preparation and detection in atomic-beam frequency standards. However, it did not become practically useful until the development of long-lived, highly efficient diode lasers, which are used for optical communication and data storage. The general physics and applications to atomic physics have been reviewed by *Cohen-Tannoudji and Kastler* [*1966*] and *Happer* [*1972*], while the application to atomic-beam frequency standards is detailed by *Audoin* [*1992*].

3.1 Optical pumping: state preparation and detection

As an example of optical state preparation, refer to the partial energy-level diagram for cesium, shown in Figure 1. Many different combinations of resonance transition and light polarization will lead to optical pumping. We take a simple but relevant example. Light, resonant with the transition $F = 4$ $F' = 3$ is absorbed by atoms in the $F = 4$ state. The excited atoms in the $F' = 3$ state decay by spontaneous emission of a photon, in about 30 ns, falling with nearly equal probability to either of the two ground-state hyperfine levels. After just a few such interactions, all of the population originally in the $F = 4$ state is transferred to the $F = 3$ state. Optical-pumping rates and the resulting population distributions for many different pumping schemes have been studied [*Avila et al., 1987*].

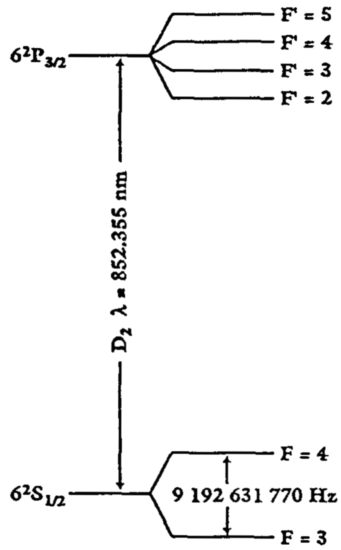

Figure 1. A partial energy-level diagram for cesium.

Preparing the optical state in this way has many advantages over magnetic-state selection. For the example just given, approximately 2/16 of the atoms are prepared in the initial "clock" state, as opposed to only 1/16 for magnetic-state selection. Other, more-complex pumping schemes can be used to pump all the atoms into the initial clock state [*Cutler, 1984*; *Avila et al., 1987*]. Furthermore, if the optical beam is orthogonal to the atomic beam, the process is not velocity selective. This produces a more intense and spatially homogenous atomic beam. The increase in atom use is more than an order of magnitude higher than that of some magnetically operated systems. The result is better clock stability, and the ability to evaluate the effects of cavity-phase shift with more precision [*De Marchi et al., 1988*]. An additional benefit is the elimination of Rabi pulling [*De Marchi et al., 1984*]. This is because, for most pumping schemes, the Zeeman substates have a symmetric population distribution about the clock state. More importantly, they all have the same velocity profile.

Just as important as the process of optical state preparation is the process of state detection after the clock transition is excited. If, as in the example above, the clock's initial state is the $F=3$ level, then the desired final state would be $F=4$. Again referring to Figure 1, and remembering the quantum-mechanical selection rules of $\Delta F = 0,\pm 1$, light resonant with the $F=4 \rightarrow F'=5$ transition results in excited $F'=5$ atoms, which can decay only to the $F=4$ level from which they came. This is called a cycling transition, and allows many photons to be "scattered" from each atom. This quantum multiplication (one microwave photon absorbed resulting in many visible photons being scattered) leads to the desired unit detection probability. Furthermore, unlike a conventional hot-wire detector, the detection region is not physically blocked, and is transparent to the passage of other beams. The atomic-beam reversal required for the evaluation of cavity phase shift therefore does not involve moving ovens and/or detectors. In fact, both atomic beams can be operated simultaneously, as shown in Figure 2. Limits to the attainable signal-to-noise ratio, for various pumping and detection schemes, have been determined [*Dimarcq et al., 1993*].

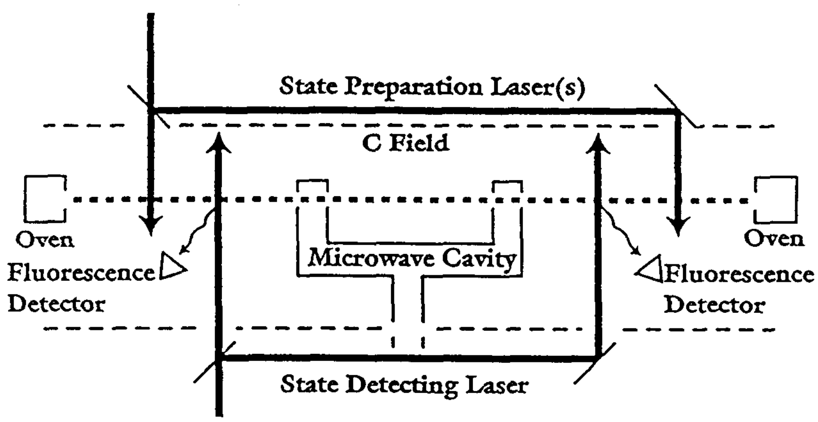

Figure 2. A schematic diagram of an optically pumped cesium-atomic-beam frequency standard.

The Stern-Gerlach magnets are eliminated when these optical methods are used. This allows much better magnetic-field homogeneity in the microwave-interrogation region, as well as eliminating Majorana transitions [*Schröder and Bauch, 1993*].

These advantages do not come without a price, however. A by-product of optical-state preparation and detection is fluorescence light, some of which travels down the beam tube to the microwave-excitation region. This has the potential to introduce a frequency bias, called the AC Stark shift. Calculations and measurements show that this is not a concern in properly designed standards [*Brillet, 1981*; *Shirley, 1985*; *Hisadome, 1991*; *Ohshima et al., 1991*]. Also, the velocity-nonselective-state preparation means that both the average velocity, and the velocity spread in the atomic beam, are larger than in magnetically-state-selected machines. The higher velocity decreases the transit time, and broadens the clock transition for a given machine length, thus putting a greater burden on the line-centering requirement for the frequency-control servo. Even more serious is the fact that the greater velocity spread increases the coupling between microwave power, and the velocity of the atoms that effectively contribute to the signal. This complicates, and ultimately limits, the evaluation and control of the second-order-Doppler shift.

A final point about the optical-state preparation and detection is that the laser(s) must have adequate AM and FM control, to avoid degradation of the signal-to-noise ratio [*Dimarcq et al., 1993*; *Ohshima et al., 1989a*]. Monolithic, Fabry-Perot diode lasers have excessive FM noise, resulting from spontaneous events inside the gain medium [*Osinski and Buus, 1987*]. This noise couples with the optical-state preparation and detection in ways that degrade the overall signal-to-noise ratio and, hence, the stability of the standard. The existing primary standards, to be described below, all use external feedback to reduce the diode-laser FM noise. As of this writing, we know of no frequency-standard experiments, using monolithic-diode lasers, which employ some kind of internal linewidth reduction (for example, distributed-Bragg-reflection feedback).

3.2 Characteristics of existing primary standards based on optical pumping

There are currently three primary standards that are based on optical-state preparation and detection, for which evaluations have been published. All use similar optical-pumping schemes: single laser pumping into the $F = 3$ level, followed by detection on the $F = 4 \rightarrow F' = 5$ cycling transition. All are currently using some form of extended-cavity optical feedback for line narrowing on simple, monolithic Fabry-Perot laser diodes. In all three, the C-field region extends over the regions of optical-state preparation and detection. The most significant differences between the machines is in their microwave cavity designs.

3.2.1 National Research Laboratory of Metrology (Japan)

The first to come into operation and be evaluated was at the Japanese National Research Laboratory of Metrology (NRLM) [*Ohshima, 1988*; *Ohshima, 1989b*; *Koga et al., 1989*]. It is called NRLM-III, and its geometry is based on their previous standards, which used magnetic state selection [*Nakadan and Koga, 1985*]. The microwave cavity is 0.96 m long. The cavity uses the conventional E-plane bend (transverse C field), with shorted waveguide ends, and atomic-beam windows $\lambda/2$

from the short. The atomic-beam cross section is 3.2×3.2 mm. A single optical-interaction zone is placed 22 cm from each end of the Ramsey cavity. The frequency-control-servo system uses slow square-wave modulation and blanking during the resulting switching transients. The microwave power and C-field current run open-loop. The measured short-term stability (characterized by $\sigma_y(\tau) \propto \tau^{-1/2}$) is limited by their reference clock, but modeled stability, based on measured signal-to-noise ratio and line Q, indicate $\sigma_y(\tau) \approx 1.1 \times 10^{-12} \tau^{-1/2}$ The published evaluation [*Ohshima, 1989c*] is dominated by uncertainty in cavity-phase shift, and has a total uncertainty (rms average of errors) of 0.69×10^{-13}.

3.2.2 Laboratoire Primaire du Temps et des Fréquences (France)

A second machine has been developed by the Laboratoire Primaire du Temps et des Fréquences (LPTF) at the Paris Observatory [*de Clercq et al., 1993*]. It is similar to the NRLM machine, in that its microwave cavity uses the conventional *E*-plane bend with atomic-beam windows $\lambda/2$ from the shorted ends of the waveguide, and a drift region 1.01 m long. The atomic beam windows are 3 × 8 mm. Two zones of optical interaction are separated by 34 cm and 24 cm from each end of the cavity. Generally, the zone farther from the cavity is used for state preparation, while the zone closer to the cavity is used for detection. Two different frequency-control-servo systems have been employed, both of which use slow square-wave modulation and blanking during the switch transients. In one, both the *C* field and the microwave power can be operated under closed-loop control. The short-term stability is characterized by $\sigma_y(\tau) \approx 5.8 \times 10^{-13} \tau^{-1/2}$. The published evaluation [*Rovera et al., 1994*] is dominated by the uncertainty in the cavity-phase shift, and an "unexplained shift." The total (rms) uncertainty of the standard is 1.1×10^{-13}.

3.2.3 National Institute of Standards and Technology (United States)

The US National Institute of Standards and Technology (NIST) has also developed an optically pumped primary standard [*Drullinger et al., 1991*]. It is called NIST-7. Its microwave cavity differs from the other two devices just described, in that it uses an H-plane cavity (longitudinal *C*-field), with ends terminated in a ring structure designed to minimize distributed-cavity-phase shift [*De Marchi et al., 1988*]. The drift region is 1.55 m long. The atomic-beam windows are 3 mm in diameter. Two zones of optical interaction are located at each end of the microwave cavity. The optical-state-preparation zone is 29 cm from the cavity, while the optical-detection zone is 14 cm away from the cavity. Several different frequency-control-servo systems have been employed to search for different forms of systematic errors [*Lowe et al., 1994*]. During normal operation, a fully digital system, employing slow square-wave modulation and blanking of transients, is used. In this system, the *C* field and the microwave power are under closed-loop control. The short-term stability is characterized by $\sigma_y(\tau) \approx 7 \times 10^{-13} \tau^{-1/2}$. New evaluation techniques, which allow several of the very small systematic effects to be evaluated with simple low-precision measurements, have been developed [*Shirley et al., 1995*]. The published evaluation [*Lee et al., 1995*] is dominated by uncertainty in the cavity-phase shift, and correction for second-order-Doppler shift. The total (linear sum) uncertainty of the standard is 1×10^{-14}.

3.3 Performance limits of optically pumped standards

Two aspects of performance are important to primary standards: short-term stability and accuracy. Long-term stability follows from accuracy. Good short-term stability is necessary only to the degree that measurements to evaluate the accuracy can be carried out in a time span where the various systematic effects are stable. The high efficiency of use of the atomic flux in optical pumping leads to adequate short-term stability, as indicated by the presently operating standards: Frequency measurements with a statistical uncertainty of the order of 1×10^{-14} can be made in a few hours.

Accuracy is more correctly described in terms of the uncertainties in magnitude of the various systematic frequency biases. Many of the potential systematic frequency biases scale as the reciprocal of the Q of the atomic line, and we may be tempted to try to design a standard with higher Q. However, none of the presently operating standards is limited by this type of error. All three of the machines have a substantial uncertainty in the evaluation of the cavity-phase shift, but for very different reasons. The NRLM and LPTF machines are limited to about one part in 10^{13} by the uncertainty in the contribution of the distributed-cavity-phase shift, resulting from their cavity design. The NIST machine has been limited, in the evaluation of end-to-end-phase shift, at several parts in 10^{15}, simply by the duration of the frequency measurements made.

The ultimate limit to optically pumped, thermal-beam technology seems to be the second-order-Doppler shift, and its dependence on microwave power. The shift is $\sim 3 \times 10^{-13}$ at optimum power, and its control to 1% requires control of the microwave power to about 0.1 dB, about the limit of present technology. This implies a limit to uncertainty of the order of several parts in 10^{15}. Very careful engineering of a power servo, or some clever, new servo technique, may allow this limit to be reduced. However, at that point, we would be faced with errors that scale with the reciprocal of the atomic line Q, and very difficult engineering challenges would have to be overcome. There seems to be no reason to address these problems, because of the rapid emergence of the new technologies outlined below. These promise enhancements of the observed Q of the atomic line by orders of magnitude over thermal-atomic-beam technology.

4. Standards based on cooling of neutral atoms

In this section, we discuss advanced primary frequency standards, primarily microwave standards, that will use recent advances in laser cooling and trapping of neutral atoms.

4.1 Concepts of laser cooling

4.1.1 Introduction

Laser cooling of neutral atoms has developed rapidly since the first deceleration of an atomic beam [*Phillips and Metcalf, 1982*]. Numerous advances in trapping and cooling have produced temperatures in cesium, in three dimensions, as low as 700 nK [*Kastberg et al., 1995*] and, in one dimension, as low as 23 nK [*Reichel et al., 1994*]. Much of the development of laser cooling has been performed with alkali atoms, due to the advantageous level structure and convenient transition wavelengths. It is especially fortuitous that cesium is an ideal candidate for laser cooling. This allows rapid incorporation of advances associated with atom cooling in next-generation cesium-frequency standards.

4.1.2 Deceleration techniques

Laser-cooling techniques have relatively low capture velocities ($v_{capture} \approx 10-20$ m/s), well below the typical velocities (200-1000 m/s) of a thermal atomic beam. It is therefore necessary to decelerate the atoms from these typical beam velocities, until they are slow enough that they can be captured, stored, and cooled to very low velocities with laser cooling.

Deceleration is performed by using a counter-propagating laser, resonant with a strong cycling transition. On average, an atom is decelerated by one photon-recoil momentum for every absorption/emission cycle, reducing its velocity by $v_{rec} = \hbar k/m$ (3.5 mm/s for Cs). To decelerate an atomic beam to low velocities requires scattering on the order of 10^5 photons. If the deceleration laser is tuned to be resonant with an atom exiting the oven, it will be far off resonance by the time the atom is near zero velocity, since the Doppler shift during deceleration changes by many (~10^2) linewidths. This would prevent an atom from scattering enough photons to decelerate significantly. Two primary techniques have been developed to circumvent this difficulty, and to maintain resonance over the entire deceleration.

4.1.2.1 Zeeman deceleration

In Zeeman deceleration [*Phillips and Metcalf, 1982*; *Walhout et al., 1993*], a spatially varying magnetic field is used to compensate for the varying Doppler shift.

Typical Zeeman decelerators are ~1 m in length, and have maximum magnetic fields in the 50-150 mT range. To avoid optical pumping to a hyperfine state uncoupled from the laser, the decelerating laser is circularly polarized. In addition, a bias magnetic field is often applied, to make use of high-field-selection rules to further suppress transitions to the wrong hyperfine state. While this has been applied successfully to Na, the hyperfine splitting in Cs is too large for convenient bias fields, and thus Cs has never been decelerated with the Zeeman technique. Due to the different magnetic-field dependence of the repumping transition, compared to the primary slowing transition, it is not possible to apply a second laser frequency that will act as a repumper over the entire deceleration region.

4.1.2.2 Chirped deceleration

Another common technique used to decelerate a beam of atoms is to "chirp" the laser frequency, to remain resonant with a group of atoms during the entire deceleration time [*Prodan and Phillips, 1983*; *Ertmer et al., 1985*]. This technique is inherently pulsed. For a thermal beam of Cs atoms, the laser must be chirped 0.25 GHz to decelerate atoms with an initial velocity of 250 m/s. This requires a minimum stopping distance of 0.5 m, although a somewhat longer region is typically used. The length of the slowing region is dictated by the maximum velocity to be decelerated ($L = v_0^2\, \tau / v_{rec}$, where L is the minimum length required to slow an atom with velocity v_0, and τ is the lifetime of the excited state). A shorter slowing region may not result in much loss of flux, due to the increased solid angle available. For chirped slowing, a repumping laser is also chirped, to optically pump any atoms that fall into the wrong hyperfine level back into the cycling transition.

4.1.3 Capture from thermal vapor

The increased solid angle for a shorter slowing region can be extrapolated to the limit where there is no slowing region at all, and we simply capture atoms out of the low-velocity tail of the thermal distribution in a vapor cell [*Cable et al., 1990*; *Monroe et al., 1990*]. This has been successfully applied, especially for capture into a magneto-optical trap (MOT, see below). The number of atoms trapped is proportional to v_c^4, where v_c is the capture velocity (typically 10-20 m/s), which depends on trap parameters: laser-beam size, intensity, detuning, and magnetic-field gradients. These techniques have been refined such that 3.6×10^{10} Cs atoms were captured from a thermal vapor [*Gibble et al., 1992*], using large laser beams and relatively high laser power.

4.1.4 Doppler cooling

For a simple two-level atom, the lowest temperature achievable is known as the Doppler-cooling limit. It is found by equating the damping rate, due to the Doppler effect, to the heating rate, due to the stochastic nature of photon scattering [*Lett et al., 1989*]. The Doppler limit is $k_B T_{Doppler} = \hbar\gamma/2$, where γ is the width of the excited state. For Cs, this corresponds to 125 μK, and the root-mean-square thermal velocity $v_{rms} = 9$ cm/s.

4.1.5 Polarization-gradient cooling

In 1988, it was discovered [*Lett et al., 1988*] that the temperature of a sample of laser-cooled Na was ~10 times lower than the Doppler limit of 240 μK. This was subsequently explained [*Dalibard and Cohen-Tannoudji, 1989*] as being due to the interplay between the multi-level nature of the atoms, and the effects of optical pumping and spatially varying optical potentials (light shifts). This new type of cooling, known as polarization-gradient cooling, produces a very strong damping force over a velocity range substantially less than Doppler cooling. Nonetheless, a significant fraction of the atoms can be cooled by this effect, and three-dimensional temperatures in Cs were sometimes as low as 2 μK [*Salomon et al., 1990*]. Experimentally and theoretically, the limit to polarization-gradient cooling is found to be about $10T_{Recoil}$, where $T_{Recoil} = \hbar^2 k^2 / m k_B$ is the temperature associated with the recoil of a single photon. For Cs, the minimum temperature for polarization-gradient cooling yields $v_{rms} = 1.1$ cm/s. These low polarization-gradient-cooling temperatures will substantially improve the performance of a laser-cooled frequency standard over one operated at the Doppler limit.

4.1.6 Other cooling mechanisms

Temperatures well below the single-photon-recoil limit have been achieved in one and two dimensions, using an effect known as velocity-selective coherent-population trapping (VSCPT). This cooling mechanism relies on the creation of a "dark state:" a velocity-dependent coherent superposition of ground Zeeman sublevels that is uncoupled from the excited state due to quantum interference. For long interaction times, the momentum width of such a state can be very small (sub-recoil). The state has nonzero-momentum components (the state is a superposition of $\pm\hbar k$ momenta), but with a small spread around them. Recent results, in metastable He [*Bardou et al., 1994*], have found one-dimensional temperatures of $0.06T_{Recoil}$. Such techniques require a $J \rightarrow J$ transition, and will be degraded by nearby hyperfine structure, as is the case in Cs.

A similar technique that also relies on velocity-space optical pumping is Raman cooling, developed at Stanford [*Davidson et al., 1994*]. In this technique, atoms are subjected to a carefully tailored set of Raman and optical-pumping pulses that induce transitions between the ground-hyperfine levels. The pulse-excitation spectrum is designed so that atoms that find themselves very near zero velocity after a spontaneous emission have no probability of re-excitation. Repeated cycles of pulses accumulate atoms around $v = 0$. Raman cooling is most effective in one dimension (due to additional phase space in higher dimensions) [*Davidson et al., 1994*]. Recent application of Raman cooling in Cs [*Reichel et al., 1994*] has produced a one-dimensional temperature of only 23 nK, 9 times below T_{Recoil}.

4.2 Molasses and MOTs

The minimum laser-cooling temperatures quoted above were achieved in what is known as optical molasses. Optical molasses involves a configuration of laser beams tuned slightly below (~5 MHz) the resonance. This provides viscous confinement and cooling of atoms, due to both Doppler cooling and polarization-gradient cooling. A typical configuration consists of three orthogonal pairs of retroreflected-laser beams, with intensities near saturation. The capture velocity of optical molasses is dominated by Doppler-cooling effects, and is typically about 10 m/s. Molasses temperatures are very sensitive to magnetic field, and the achievement of the lowest temperatures requires residual fields of less than 1 μT. In fact, this necessity of small magnetic fields is conveniently compatible with the stringent stray-field requirements of frequency standards.

Recent results of laser cooling, in a four-beam configuration known as an optical lattice (where atoms are trapped in optical-potential wells), have found temperatures in Cs down to about 1 μK [*Kastburg et al., 1995*]. Application of adiabatic cooling (where the intensity of the lasers is reduced adiabatically over ~200 μs) have produced three-dimensional temperatures of 700 nK [*Kastberg et al., 1995*]. Such techniques should be compatible and applicable to advanced frequency standards.

The magneto-optical trap (MOT) has provided a robust way to increase the capture velocity and, hence, the number of confined atoms. It is essentially a molasses geometry, with an added quadrupole-magnetic field. The spatially varying field produces a spatially varying restoring force, creating a true trap. The increased capture velocity allows MOTs to capture enough atoms from the low-velocity tail of a thermal distribution, making possible a much more compact apparatus [*Monroe et al., 1990*]. The most critical drawbacks of MOTs, for primary frequency standards, are their requirement of ~1 mT/cm gradient fields, and the impact on a frequency standard from the associated fringing fields. Since the lowest temperatures are achieved in zero field, it is necessary to switch off the MOT field, which may have an adverse impact on the magnetic shielding of a frequency standard.

4.3 The atomic fountain

4.3.1 Techniques

Laser-cooled neutral-atom frequency standards are based on the concept of an atomic fountain, first attempted, albeit unsuccessfully, by *Zacharias* [*1954*]. Atoms are launched upward and pass twice through the same interaction region, once on the way up, and once on the way down. This forms the two interactions, separated in time, to produce Ramsey fringes, with the resolution determined by the time between interactions. This time, $T=(2h/g)^{1/2}$, can be very long: $T=0.5\,\text{s}$, for a fountain height of $h=30\,\text{cm}$. The correspondingly narrow linewidth allows for substantial improvements in clock performance. One other important feature of the atomic fountain is that there is only a single microwave cavity, so that effects present in traditional standards, due to cavity differences (for example, end-to-end phase shifts), are eliminated.

The original Zacharias experiment failed because the thermal-beam source did not have a sufficient flux of slow atoms. Laser-cooled sources can provide the necessary flux. Low temperatures are important, so that the spread of the sample during the long flight time is small enough that there is a usable number of atoms in the interaction region during the second interaction. A sample of Cs atoms, at 2 μK, will spread only 1.1 cm in 1 s, so 40% of the atoms fall within a 1 cm interaction region. By contrast, if the Cs atoms were at the Doppler limit of 125 μK, they would spread to 9 cm, and only ~0.7% of the atoms would be usable.

Laser-cooled atoms need to be launched in a way that does not introduce excess heating of the atoms. This is accomplished with "moving molasses:" the laser beams with upward components are shifted up in frequency by an increment Δf, and vice versa for downward components. The atoms therefore see a moving optical field, with a velocity of $v=\lambda\Delta f$. The atoms laser-cool into equilibrium with this moving field, and when the light is suddenly switched off, the atom cloud is left moving upward uniformly, with only the relative velocity spread due to the laser-cooling limits, not the launch velocity (typically 1-4 m/s).

4.3.2 Prototype standards

The atomic fountain was first successfully demonstrated on the 1.77 GHz microwave transition in Na [*Kasevich et al., 1989*], although in this case, the atoms never left the cavity, which was pulsed to produce the two Ramsey zones. Nonetheless, the 2 Hz linewidth was a powerful demonstration of the potential of the atomic fountain. An atomic fountain in Cs was first demonstrated in Paris [*Clairon et al., 1991*]. A Cs fountain was constructed at Stanford, and used to measure the important effects of collisions between the cold atoms and the associated line shifts [*Gibble and Chu, 1993*].

Atomic-fountain Cs standards are under development in several laboratories around the world. The group at LPTF in Paris has recently reported preliminary results of an operational fountain [*Santarelli et al., 1994*]. The fountain uses optical molasses, loaded from a vapor cell. It is launched using one-dimensional moving molasses, followed by horizontal cooling after the atoms are at the final velocity. The flight time can be adjusted to be between 0 and 700 ms, yielding a narrowest achievable linewidth of 700 mHz. The stability of the fountain has been measured to be $\sigma_y(\tau) = 6 \times 10^{-13} \tau^{-1/2}$, which is a factor of five higher than expected for the 10^5 atoms detected per cycle. The LPTF group believes that this is due to a limitation from local-oscillator-frequency noise. The accuracy has not yet been evaluated.

4.3.3 Optical atomic-fountain standards

The concept of the atomic-fountain frequency standard can also be applied to optical transitions: the most promising is a Doppler-free two-photon transition. There are a number of candidates for a standard with a Q of greater than 10^{14}, including a UV transition in Ag [*Hall et al., 1989*], and an IR transition in metastable Xe [*Rolston and Phillips, 1991*]. This high Q, coupled with the large numbers of atoms available, produce an extraordinary potential stability (better than 10^{-17} at 100 s). The two most challenging issues affecting the stability will be the AC Stark shift (comparable to the linewidth, for a $\pi/2$ pulse [*Rolston and Phillips, 1991*]), and the effect of collisional shifts, which are currently completely unknown.

4.3.4 Performance limits

To estimate the stability of a microwave Cs atomic fountain, we assume the following set of parameters: a launch of 10^6 atoms every second, with a Ramsey time of 0.5 s (to allow for reloading). We will assume that the atoms are all optically pumped into the $F = 3$, $m_F = 0$ Zeeman sublevel before entering the interaction region, and that 40% of the atoms will be within the useful interaction region on the downward traverse of the cavity. Since the number of atoms from shot to shot will invariably fluctuate, it will be necessary to measure both the number of atoms that have made the transition, and those that did not, with a precision of 10^{-3} or better. We then find an Allan variance of 1×10^{-14} at 10 s. This will clearly place significant demands on the flywheel oscillator, a challenge that we will not address here. (The LPTF fountain is using a hydrogen maser for this application.)

This good stability will allow rapid evaluation of effects that are important in determining the accuracy of the standard. Second-order-Doppler shifts and gravitational-red shifts are reduced to 10^{-16}, with uncertainties below 10^{-19}, due to the use of slow atoms. The use of a single high-Q cavity, and the narrow lines afforded by the long interaction time of the fountain, should reduce the effects of distributed cavity-phase shifts and cavity pulling to levels substantially below conventional standards, to 10^{-16} or less. The compact size of the fountain will allow good magnetic shielding, and the narrower linewidth will permit operation at low C fields (~0.1-1 μT), which will reduce uncertainties due to magnetic fields to 10^{-16} or less, as well.

By far the most challenging issue affecting the accuracy of the Cs atomic fountain will be the shift due to collisions between the cold atoms. This pressure shift is large, measured by *Gibble and Chu* [*1993*] to be 5 mHz, at a density of 3.5×10^8 cm^{-3} for Cs atoms in the $m_F = 0$ state. If we assume that extrapolation to zero density at a precision of 5% of the shift is possible, this will require operating at a density of 10^6 cm^{-3}, to achieve a 10^{-16} accuracy. It is clear that we do not want any atoms that can contribute to the shift, but not the signal. Thus, it will be important to optically pump the sample: the colder the transverse temperature, the more atoms that make it back through the cavity for the second interaction. This limit on density is four to five orders of magnitude below typical MOT densities and will prevent MOTs from being used directly as the source of atoms. Optical molasses alone is attractive, since it offers more than sufficient density (typical density $\sim 10^8$ cm^{-3}) and has no magnetic fields. It is nonetheless clear that understanding and characterizing the collisional shift will be of primary importance in the evaluation of a laser-cooled Cs standard.

5. Standards based on stored ions

Great progress has been made in recent years in applying trapped atomic ions to frequency standards. Devices containing many ions have demonstrated extremely high stabilities at microwave frequencies. Optical transitions of single ions have been observed with very high resolution, and there is much interest in using single-ion devices as frequency standards. The following section will describe the types of ion traps, the methods of cooling ions in traps, and the current status and future prospects of ion-trap frequency standards. Some general reviews on ion traps and their applications to spectroscopy are given in [*Wineland et al.*, *1983*; *Paul*, *1990*; *Blatt et al.*, *1992*; *Thompson*, *1993*; *Werth*, *1993*]. *Itano* [*1991*] and *Werth* [*1994*] deal specifically with the applications of trapped ions to frequency standards.

5.1 Ion traps

An ion trap is a device which uses electric fields, or a combination of electric and magnetic fields, to suspend ions in space. The two main types are called Penning traps and Paul (or RF) traps.

5.1.1 Penning traps

The Penning trap uses static electric and magnetic fields. The electrostatic potential is

$$\phi(x,y,z) = \frac{U_0\left(x^2 + y^2 - 2z^2\right)}{r_0^2 + 2z_0^2}. \tag{1}$$

A typical electrode configuration used to create such a potential is shown in Figure 3. A uniform magnetic field, B, is applied along the symmetry (z) axis of the trap. The two endcap electrodes are held at the same potential, U_0, relative to the ring electrode. Here, r_0 and z_0 are lengths that depend on the electrode geometry. The sign of U_0 is chosen to generate an electric field that forces the ion back toward the center, if it is displaced in either direction along the z axis. However, if the ion is displaced radially (that is, in the $x-y$ plane), it is subjected to an electric force that forces it away from the center. The magnetic field is required to provide radial confinement. A single ion undergoes simple harmonic motion along the z axis, and a superposition of two circular motions in the $x-y$ plane.

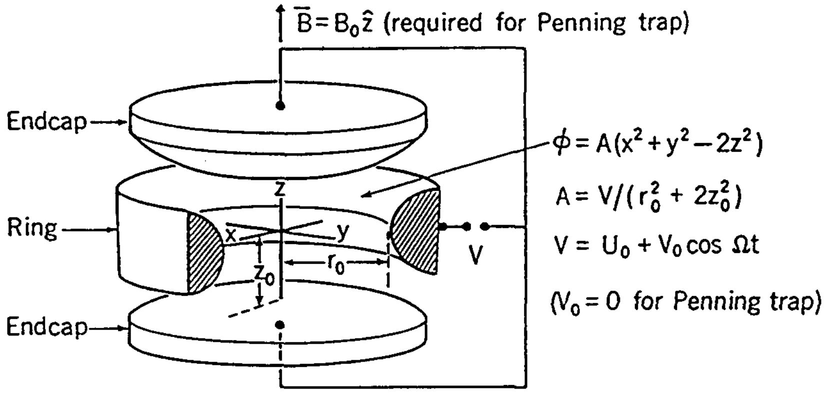

Figure 3. Penning or spherical Paul trap electrodes.

Motion along the z axis is stable, because work has to be done to increase z^2. On the other hand, if the orbit of an ion is displaced radially outward, its potential energy decreases. Hence, energy conservation does not prevent the ions from being lost from the trap. However, conservation of the z component, L_z, of the canonical angular momentum of the ions leads to radial confinement. In a real trap, L_z is only approximately conserved, because of collisions with neutral molecules, and because of deviations of the trap electric and magnetic fields from cylindrical symmetry.

5.1.2 Spherical Paul traps

In a Paul or RF trap, an oscillating electric field provides confinement, and a magnetic field is not required. The most commonly used form of Paul trap–which we call the spherical Paul trap, to distinguish it from the linear Paul trap–uses an electrode configuration like the Penning trap (Figure 3). To be more precise, the electric potential has the form

$$\phi(x,y,z,t) = \frac{U_0 + V_0\cos(\Omega t)}{r_0^2 + 2z_0^2}\left(x^2 + y^2 - 2z^2\right). \tag{2}$$

Here, U_0 and V_0 are the static and RF potentials. Dynamic trapping is possible for some range of values of U_0, V_0, and Ω. With such values, the time-averaged force (the force averaged over a period of the oscillation) confines an ion in all dimensions. The static part of the electric potential can be adjusted to vary the ratio of the radial and axial restoring forces. The trajectory of an ion is a superposition of a driven motion, at frequency Ω, and a low-frequency motion, due to the time-averaged force. The driven motion is called the micromotion, and the low-frequency motion is called the secular motion.

5.1.3 Linear Paul traps

A schematic drawing of a linear Paul trap is shown in Figure 4. An RF potential is applied between the rods. The phase of the potential at each rod differs by 180° from that of the two that are nearest to it. In the region between the rods, the RF electric potential is approximately

$$\phi(x,y,t) = \frac{V_0\left(x^2 - y^2\right)}{2R^2}\cos(\Omega t). \tag{3}$$

Here, R is the distance from the central axis to the surface of one of the rods. This creates a time-averaged force that attracts an ion to the central axis. An electrostatic potential, applied to the electrodes at the ends, prevents the ions from escaping along

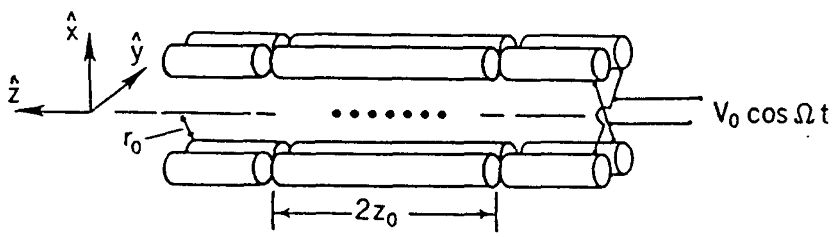

Figure 4. Linear Paul trap electrodes.

the axis. In such a trap, the RF fields approach 0 along a line, rather than at only a point. In this trap, the kinetic energy of the micromotion is less than in a spherical Paul trap with the same number of ions and the same radial restoring force. Traps of this type have been constructed by several groups for frequency-standard applications [*Prestage et al., 1991*; *Raizen et al., 1992*; *Fisk et al., 1993*].

5.1.4 Other types of traps

Other forms of traps may prove useful for frequency standards. A "racetrack" trap can be made by connecting the ends of the rods into rings. Mg ions have been laser-cooled in a racetrack trap [*Waki et al., 1992*]. The electric potentials described by Equations (1-3) are all of quadrupole form. The use of an octupole potential in an RF trap has been demonstrated [*Walz et al., 1994*]. Such a trap may have advantages for the storage of large numbers of ions at relatively low kinetic energies.

5.2 Ion-cooling methods

Trapped ions can easily gain several electron volts of kinetic energy, equivalent to temperatures of thousands of K, from electric fields in the trap. Since the ions are well isolated thermally from their environment, they do not quickly cool to room temperature. On the other hand, this thermal isolation makes it possible to cool the ions, using a weak process like laser cooling, to less than 1 K, in a room-temperature apparatus.

5.2.1 Buffer gas

Collisional cooling with neutral gas molecules is a simple way of cooling ions in a Paul trap. *Cutler et al.* [*1985*] have collisionally cooled $^{199}Hg^+$ ions in a Paul-trap frequency standard with helium gas. The secular motion was cooled to near room temperature, but the micromotion was hotter. Other frequency standards, using buffer-gas cooling, have been reported by *Prestage et al.* [*1991*] (Hg^+), by *Schnier et al.* [*1992*] (Yb^+), by *Tamm et al.* [*1995*] (Yb^+), and by *Fisk et al.* [*1995*] (Yb^+).

Collisional cooling with neutral atoms, without the application of additional forces, is not feasible for ions in a Penning trap. This is so because there is no restoring force in the radial direction. Collisions would quickly drive the ions out of the trap. However, it is possible to use a combination of collisional cooling and RF-sideband excitation [*Savard et al., 1991*]. Collisions with buffer-gas molecules will cool the axial and cyclotron motions, but heat the magnetron motion. RF excitation can be used to couple the magnetron and cyclotron motions, so that their excitation is exchanged. Thus, collisional cooling of the cyclotron motion is transferred to the magnetron motion.

5.2.2 Doppler laser cooling

Doppler laser cooling is a very effective method for cooling certain kinds of ions to very low temperatures [*Stenholm, 1986*; *Wineland and Itano, 1987*]. The basic idea is to irradiate the ions with light having a frequency slightly lower than that of a strong resonance line of the ion. Ions moving toward the source of the light absorb and re-radiate photons at a high rate, because the Doppler shift brings the light closer to resonance. The ions lose energy, since they absorb the momentum of the photons. When the ions move away from the source of light, the Doppler shift is away from resonance, and photons are scattered at a low rate. The velocity is damped, on the average. The minimum temperature, $T_{Doppler}$, that can be obtained in this manner is given by $k_B T_{Doppler} \approx \hbar\gamma/2$, where k_B is Boltzmann's constant, $\hbar$ is Planck's constant divided by 2π, and γ is the radiative-decay rate of the upper state. For typical cases, $T_{Doppler}$ is about 1 mK. This kind of laser cooling is called Doppler cooling, to distinguish it from other kinds of laser cooling [*Cohen-Tannoudji and Phillips, 1990*].

5.2.3 Sympathetic laser cooling

Unfortunately, the nearly resonant light field perturbs the transition frequencies of the ion. One way of dealing with this problem is to turn off the light used for cooling for short periods. Another way is to simultaneously trap two species of ions. One species is continuously laser cooled. It cools the other species by long-range Coulomb collisions. The cooling radiation for one species does not perturb the resonance frequencies of the other species very much. This cooling method, called sympathetic laser cooling, was demonstrated by *Larson et al.* [*1986*].

5.2.4 Other laser-cooling methods

Other kinds of laser cooling have been demonstrated with trapped ions. Resolved-optical-sideband cooling has been used to cool a single ion to the zero-point energy [*Diedrich et al., 1989*]. Polarization-gradient cooling has been demonstrated in a "racetrack" trap [*Birkl et al., 1994*]. This type of cooling is based on optical pumping between Zeeman sublevels, which are light-shifted differently by a nearly resonant standing-wave field [*Cohen-Tannoudji and Phillips, 1990*].

5.3 Ion-frequency standards

5.3.1 Buffer-gas-cooled standards

Research on optically pumped microwave-frequency standards, based on large numbers of ions stored in Paul traps, has advanced greatly in recent years. To date, these standards have used buffer-gas cooling, rather than laser cooling. Thus, the second-order-Doppler shifts are relatively high, (approximately a part in 10^{12}), but the stability can be very good, because of the combination of high Q and high signal-to-noise ratio. Most of the recent research has focused on Hg^+ and Yb^+, although some other ions have been considered.

5.3.1.2 Hg^+

Major and Werth [*1973*] were the first to observe the 40.5 GHz ground-state hyperfine transition of $^{199}Hg^+$. The Q of the resonance was approximately 10^{10}. The detection of the resonance was based on optical pumping. The ground electronic state of Hg^+ has the electronic configuration $5d^{10}6s\,^2S_{1/2}$. An RF-excited lamp, containing the ^{202}Hg isotope, emits 194 nm radiation that drives $^{199}Hg^+$ ions in the $F = 1$ hyperfine level of the ground state to the $5d^{10}6p\,^2P_{1/2}$ 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 $F = 0$ 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. Then they can be excited to the $5d^{10}6p\,^2P_{1/2}$ state by light from the lamp. When they decay, the 194 nm photons are detected.

Jardino et al. [*1981*] made the first frequency standard based on this system. They measured $\sigma_y(\tau) = 3.6 \times 10^{-11}\tau^{-1/2}$, for $10\text{ s} < \tau < 3500\text{ s}$, where τ is the time interval in seconds. This stability was comparable to that of some commercial Cs atomic clocks. Buffer gas for cooling was not deliberately introduced, although the background Hg vapor probably provided some cooling.

This basic system was developed further by *Cutler et al.* [*1981*, *1987*]. They introduced He buffer gas to reduce the temperature of the ions. The number of ions was about 2×10^6. The resonance linewidth was 0.85 Hz, so the Q was approximately 5×10^{10}. The results of a 115 day test showed fractional frequency fluctuations of 7.6×10^{-15} for integration times of 1 day [*Cutler et al.*, *1987*]. The frequency difference between two standards was between 1 and 2 parts in 10^{13}, which is some indication of their accuracy.

The group at the NASA Jet Propulsion Laboratory [*Prestage et al.*, *1991*; *Tjoelker et al.*, *1993*] has demonstrated a $^{199}Hg^+$ frequency standard based on a linear RF trap. The frequency standard was operated with a Q of 2×10^{12}. The short-term stability of the device was better than $\sigma_y(\tau) = 7 \times 10^{-14}\tau^{-1/2}$. Measurements of stability have been made out to 10 days. *Tjoelker et al.* [*1993*] anticipate that a stability floor of 10^{-16}, and an accuracy of 10^{-14} may be achievable.

5.3.1.2 Yb^+

There has also been much experimental progress with microwave-frequency standards based on Yb^+. Unlike Hg^+, lasers rather than lamps must be used for optical pumping. *Schnier et al.* [*1992*] and *Bauch et al.* [*1995*] have observed a linewidth of 16 mHz on the 12.6 GHz ground-state hyperfine transition of $^{171}Yb^+$. They reported $\sigma_y(\tau = 100\ \mathrm{s}) \approx 5 \times 10^{-13}$. Their apparatus used a spherical Paul trap and a He buffer gas. *Casdorff et al.* [*1991*] have reported $\sigma_y(\tau) = 2 \times 10^{-11} \tau^{-1/2}$ for a $^{171}Yb^+$-based frequency standard, which used a spherical Paul trap.

Fisk et al. [*1993; 1995*] have demonstrated a $^{171}Yb^+$ frequency standard, based on buffer-gas-cooled ions in a linear Paul trap. They have reported a linewidth of 800 μHz on the 12.6 GHz transition. This corresponds to a *Q* of 1.5×10^{13}, currently the highest reported for microwave spectroscopy. The high phase stability required for this measurement was derived from a sapphire-loaded superconducting-cryogenic-resonator oscillator. The stability of the Yb^+ frequency standard was measured to be $\sigma_y(\tau) = 3.7 \times 10^{-13} \tau^{-1/2}$ for $\tau < 3000$ s.

5.3.2 Microwave transitions using laser-cooled ions

One of the largest sources of systematic uncertainty in buffer-gas-cooled ion-trap frequency standards is the second-order-Doppler shift. Lower temperatures and, hence, lower second-order-Doppler shifts, can be achieved by laser cooling. However, the number of ions which can be laser cooled in a spherical Paul trap is relatively small, and the potential signal-to-noise ratio is correspondingly low. Two traps, which are better suited to laser-cooling clouds of many ions, are the Penning trap and linear or racetrack Paul traps.

5.3.2.1 $^9Be^+$ in a Penning trap

Bollinger et al. [*1985*] demonstrated the first frequency standard based on laser-cooled ions. This standard was based on a 303 MHz hyperfine transition in the ground electronic state of $^9Be^+$. 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 0 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 [*Bollinger et al.*, *1991*]. Magnesium ions were trapped at the same time, and were continuously laser cooled. The number of $^9Be^+$ ions was 5000 to 10 000. A sequence of optical and RF pulses was used to transfer the ions to the

$(m_I = -1/2,\ m_J = 1/2)$ sublevel. The Ramsey two-pulse-resonance 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 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 Ramsey pulses was sometimes as long as 550 s, although 100 s was more typical. With $T = 550$ s, the width of the resonance was 900 μHz. The stability was better than $3\times10^{-12}\tau^{-1/2}$ for $10^3\ \mathrm{s} < \tau < 10^4\ \mathrm{s}$. However, there was a frequency shift with change in pressure. This limited the long-term stability of the standard to about 3×10^{-14}. The uncertainty of the second-order-Doppler shift, though, was only 5×10^{-15}. The longest time that the standard was operated continuously was about 10 hours.

5.3.2.2 $^{199}Hg^+$ in a linear Paul trap

Frequency standards based on Paul traps suffer from high second-order-Doppler shifts, due to the micromotion. *Wineland et al.* [*1990*] proposed to use a linear RF trap to confine a single string of ions, such as $^{199}Hg^+$, along the central axis. The ions could be laser cooled, and would have negligible micromotion. Such a standard might combine high accuracy and high stability.

To test these ideas, linear Paul traps have been built for $^{199}Hg^+$ ions [*Raizen et al., 1992*; *Poitzsch et al., 1994*]. "Crystallized" strings of laser-cooled ions have been observed. The 40.5 GHz hyperfine transition has been observed in a string of ions with a linewidth of 0.25 Hz. In the latest version, the trap and surrounding chamber are at a temperature of 4 K [*Poitzsch et al., 1994*]. This eliminates problems due to collisions with neutral molecules, and reduces frequency shifts due to blackbody radiation.

5.3.3 Optical transitions using laser-cooled ions

An optical-frequency standard might be based on a transition with a narrow natural linewidth. The Q could then be so high that the signal from even a single ion could yield good stability, as well as good accuracy. The upper state of the transition must be metastable. Direct detection of the photons emitted by such a transition would be very difficult.

Sensitive detection of a single ion can be carried out by a double-resonance method called electron shelving [*Dehmelt, 1982*]. An example of an atomic level structure that is suitable for this method is shown in Figure 5. First, a pulse of resonant radiation is applied at wavelength λ_2, to try to drive the transition to the metastable state. Then, in a time less than the lifetime of the metastable state, another pulse of radiation is applied at wavelength λ_1. This radiation is resonant with a transition from the same lower state to a short-lived upper state. If the atom is shelved in the metastable state, no λ_1 photons are emitted from the short-lived state. If the atom is in the lower state after the λ_2 pulse, it can absorb and emit λ_1 photons at a high rate. Thus, the absorption of a single λ_2 photon, which drives the atom to the metastable state, results in the absence of many λ_1 photons. Individual λ_2 transitions can be detected, even if not all of the λ_1 photons are detected.

5.3.3.1 Hg^+ Single-ion optical spectroscopy

Hg^+ has a level structure which is suitable for an optical-frequency standard. The $5d^9 6s^2\ ^2D_{5/2}$ state is metastable, with a lifetime of about 90 ms. The 194 nm transition from the ground $5d^{10}6s^2\ S_{1/2}$ to the $5d^{10}6p\ ^2P_{1/2}$ state can be used for laser cooling, and for detection by electron shelving. Some hyperfine components of the 281.5 nm transition in $^{199}Hg^+$ are nearly independent of magnetic field, near zero 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.* [*1994*] 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 optical transition. The laser frequency was servoed to the single-ion resonance for periods of several minutes [*Bergquist et al., 1994*]. Further work on this system might yield a frequency standard with $\sigma_y(\tau) \approx 10^{-15}\tau^{-1/2}$ and an accuracy of one part in 10^{18} [*Wineland et al., 1990*].

5.3.3.2 Ba^+ Single-ion fine-structure transition

Whitford et al. [*1994*] have investigated the use of the 12.5 µm, $5d\ ^2D_{3/2}$ – $5d\ ^2D_{5/2}$ fine-structure transition in Ba^+ as an optical-frequency standard. This line can be driven with an optically pumped ammonia laser. The natural linewidth of the transition is less than 0.02 Hz. The transition was observed in a single trapped ion, with a linewidth of 30 kHz. The transition frequency was measured to an accuracy of 1 kHz, by comparison to a phase-locked-laser chain.

5.3.3.3 Other single-ion optical transitions

Experimental work has been done with other ions which can be laser cooled, and which have narrow optical transitions. In some cases, the transitions have been observed with relatively high resolution. In Ba^+, for example, *Nagourney et al.* [*1990*] have observed the 1.76 µm $6s\ ^2S_{1/2} - 5d\ ^2D_{5/2}$ transition with a linewidth of about 40 kHz. Similar observations have been made by *Siemers et al.* [*1994*]. Among the other ions that have been studied experimentally for use in a single-ion optical frequency standard are Sr^+ [*Barwood et al., 1994*], Yb^+ [*Bell et al., 1992*; *Lehmitz et* *al., 1989*], Ca^+ [*Urabe et al., 1994; Arbes et al., 1994; Knoop et al., 1994*], and In^+ [*Peik et al., 1994*].

5.4 Performance limits of ion standards

For trapped-ion frequency standards, there is usually a trade-off between short-term stability and accuracy. The high-stability limit is currently represented by the $^{199}Hg^+$ buffer-gas-cooled microwave standard [*Tjoelker et al., 1993*]. The high stability is largely a result of the high Q and the large number of ions. However, there are systematic uncertainties which limit the accuracy: the largest (at present) is the second-order-Doppler shift. The magnitude of the shift is on the order of 10^{-12}. Control of this shift, by control of the number of ions, may be feasible to about 10^{-14}.

A laser-cooled standard, like the $^{199}Hg^+$ linear Paul trap, has the potential of higher accuracy, mainly because the Doppler shifts are very small (on the order of 10^{-18}) [*Wineland et al., 1990; Wineland et al., 1987*]. Other shifts, such as those due to collisions or external electric and magnetic fields, also appear to be controllable to about this level. However, the short-term stability is likely to be less than for buffer-gas-cooled standards, because of the small number of ions.

The ultimate accuracy might be achieved by a single-ion optical-frequency standard [*Wineland et al., 1990; Wineland et al., 1987*]. Because of the extremely high line Qs that might be achieved (greater than 10^{15}), good stability could also be achieved. As already stated, the second-order-Doppler shifts should be extremely low for a laser-cooled standard. Other shifts, such as those due to blackbody radiation or electric-field gradients, may be controllable to the 10^{-18} level.

6. References

F. Arbes, M. Benzing, T. Gudjons, F. Kurth, and G. Werth [1994], "Improved Lifetime Measurements of the $3D_{3/2}$ and $3D_{5/2}$ States of Ca II," *Z. Phys. D*, **29**, pp. 159-161.

C. Audoin [1992], "Caesium Beam Frequency Standards: Classical and Optically Pumped," *Metrologia*, **29**, pp. 113-134.

G. Avila, V. Giordano, V. Candelier, E. de Clercq, G. Théobald, and P. Cérez [1987], "State Selection in a Cesium Beam by Laser-Diode Optical Pumping," *Phys. Rev. A*, 36, pp. 3719-3728.

F. Bardou, B. Saubamea, J. Lawall, K. Shimizu, O. Emole, C. Westbrook, A. Aspect, and C. Cohen-Tannoudji [1994], "Sub-Recoil Laser Cooling with Precooled Atoms," *C. R. Acad. Sci. Ser. 2*, **318**, pp. 877-886.

G. P. Barwood, C. S. Edwards, P. Gill, G. Huang, H. A. Klein, and W. R. C. Rowley [1994], "Precision Interferometric Frequency Measurement of the 674 nm $^2S_{1/2}$ – $^2D_{5/2}$ Transition in a Single Cold Sr^+ Ion," *IEEE Trans. Instrum. Meas.*, **IM-44**, pp. 117-119.

A. S. Bell, P. Gill, H. A. Klein, A. P. Levick, and W. R. C. Rowley [1992], "Precision Measurement of the $^2F_{7/2} - {}^2D_{5/2}$ 3.43 μm Interval in Trapped $^{172}Yb^+$," *J. Mod. Opt.*, **39**, pp. 381-387.

J. C. Bergquist, W. M. Itano, and D. J. Wineland [1994], "Laser Stabilization to a Single Ion," in T. W. Hänsch (ed.) *Frontiers in Laser Spectroscopy, Proceedings of the International School of Physics "Enrico Fermi,"* Course 120, Amsterdam, North-Holland, pp. 359-376.

G. Birkl, J. A. Yeazell, R. Rückerl, and H. Walther [1994], "Polarization Gradient Cooling of Trapped Ions," *Europhys. Lett.*, 27, pp. 197-202.

R. Blatt, P. Gill, and R. C. Thompson [1992], "Current Perspectives on the Physics of Trapped Ions," *J. Mod. Opt.*, **39**, pp. 193-220.

J. J. Bollinger, J. D. Prestage, W. M. Itano, and D. J. Wineland [1985], "Laser-Cooled-Atomic Frequency Standard," *Phys. Rev. Lett.*, 54, pp. 1000-1003.

J. J. Bollinger, D. J. Heinzen, W. M. Itano, S. L. Gilbert, and D. J. Wineland [1991], "A 303-MHz Frequency Standard Based on Trapped Be^+ Ions," *IEEE Trans. Instrum. Meas.*, **IM-40**, pp. 126-128.

A. Brillet [1981]. "Evaluation of the Light Shifts in an Optically Pumped Cesium Beam Frequency Standard," *Metrologia*, 17, pp. 147-150.

A. Cable, M. Prentiss, and N. Bigelow [1990], "Observation of Sodium Atoms in a Magnetic Molasses Trap Loaded by a Continuous Uncooled Source," *Opt. Lett.*, **15**, pp. 507-509.

R. Casdorff, V. Enders, R. Blatt, W. Neuhauser, and P. E. Toschek [1991], "A 12-GHz Standard Clock on Trapped Ytterbium Ions," *Ann. Phys. (Leipzig)*, **48**, pp. 41-55.

A. Clairon, C. Salomon, S. Guelatti, and W. Phillips[1991], "Ramsey Resonance in a Zacharias Fountain," *Europhys. Lett.*, **16**, pp. 165-170.

C. Cohen-Tannoudji and A. Kastler [1986], "Optical Pumping," in E. Wolf (ed.), *Progress in Optics, Vol. 5*, Amsterdam, North-Holland Publishing, pp. 3-81.

C. N. Cohen-Tannoudji and W. D. Phillips [1990], "New Mechanisms for Laser Cooling," *Phys. Today*, **43**, 10, pp. 33-40.

L. S. Cutler, R. P. Giffard, and M. D. McGuire [1981], "A Trapped Mercury 199 Ion Frequency Standard," in *Proceedings of the 13th Annual Precise Time and Time Interval (PTTI) Applications and Planning Meeting*, December 1-3, 1981, Washington, DC, USA, NASA Conference Publication 2220 (available from U. S. Naval Observatory, Timer Service, 3450 Massachusetts Ave., N. W., Washington, DC 20392-5420, USA), pp. 563-573.

L. S. Cutler [1984], "Atomic Beam Device Using Optical Pumping,", US Patent 4,425,653.

L. S. Cutler, R. P. Giffard, and M. D. McGuire [1985], "Thermalization of ^{199}Hg Ion Macromotion by a Light Background Gas in an RF Quadrupole Trap," *Appl. Phys. B*, 36, pp. 137-142.

L. S. Cutler, R. P. Giffard, P. J. Wheeler, and G. M. R. Winkler [1987], "Initial Operational Experience with a Mercury Ion Storage Frequency Standard," in *Proceedings of the 41st Annual Frequency Control Symposium*, May 27-29, 1987, Philadelphia, PA, USA, AD-A216858 (available from National Technical Information Service, Springfield, VA 22161, USA), pp. 12-17.

J. Dalibard and C. Cohen-Tannoudji [1989], "Laser Cooling below the Doppler Limit by Polarization Gradients: Simple Theoretical Models", *J. Opt. Soc. Am. B*, 6, pp. 2023-2045.

N. Davidson, H. Lee, M. Kasevich, and S. Chu [1994], "Raman Cooling of Atoms in Two and Three Dimensions," *Phys. Rev. Lett.*, 72, pp. 3158-3161.

E. de Clercq, G. D. Rovera, S. Bouzid, and A. Clairon [1993], "The LPTF Optically Pumped Primary Frequency Standard," *IEEE Trans. Instrum. Meas.*, **IM-42**, pp. 457-461.

H. G. Dehmelt [1982], "Mono-Ion Oscillator as Potential Ultimate Laser Frequency Standard," *IEEE Trans. Instrum. Meas.*, **IM-31**, pp. 83-87.

A. De Marchi, G. D. Rovera, and A. Premoli [1984], "Pulling by Neighbouring Transitions and its Effects on the Performance of Caesium-Beam Frequency Standards," *Metrologia* **21**, pp. 37-47.

A. De Marchi, J. Shirley, D. J. Glaze, and R. E. Drullinger [1988], "A New Cavity Configuration for Cesium Beam Primary Frequency Standards," *IEEE Trans. Instrum. Meas.*, IM-37, pp. 185-190.

F. Diedrich, J. C. Bergquist, W. M. Itano, and D. J. Wineland [1989], "Laser Cooling to the Zero-Point Energy of Motion," *Phys. Rev. Lett.*, 62, pp. 403-406.

N. Dimarcq, V. Giordano, P. Cérez, and G. Théobald [1993], "Analysis of the Noise Sources in an Optically Pumped Cesium Beam Resonator," *IEEE Trans. Instrum. Meas.*, **IM-42**, pp. 115-120.

R. E. Drullinger, D. J. Glaze, J. P. Lowe, and J. H. Shirley [1991], "The NIST Optically Pumped Cesium Frequency Standard," *IEEE Trans. Instrum. Meas.*, **IM-40**, pp. 162-164.

W. Ertmer, R. Blatt, J. L. Hall, and M. Zhu [1985], "Laser Manipulation of Atomic Beam Velocities: Demonstration of Stopped Atoms and Beam Reversal", *Phys. Rev. Lett.*, **54**, pp. 966-969.

P. T. H. Fisk, M. A. Lawn, and C. Coles [1993], "Laser Cooling of $^{171}Yb^{+}$ Ions in a Linear Paul Trap," *Appl. Phys. B*, **57**, pp. 287-291.

P. T. H. Fisk, M. J. Sellars, M. A. Lawn, C. Coles, A. G. Mann, and D. G. Blair [1995], "Very-High Q Microwave Spectroscopy on Trapped $^{171}Yb^{+}$ Ions: Application as a Frequency Standard," in *IEEE Trans. Instrum. Meas.*, **IM-44**, pp. 113-116.

P. Forman [1985], "Atomichron: The Atomic Clock from Concept to Commercial Product," *Proc. IEEE*, **73**, pp. 1181-1204.

K. Gibble, S. Kasapi, and S. Chu [1992], "Improved Magneto-Optic Trapping in a Vapor Cell," *Opt. Lett.*, **17**, pp. 526-528.

K. Gibble and S. Chu [1993], "Laser-Cooled Frequency Standard and a Measurement of the Frequency Shift Due to Ultracold Collisions," *Phys. Rev. Lett.*, **70**, pp. 1771-1774.

V. Giordano, V. Candelier, A. Hamel, C. Audoin, G. Théobald, and P. Cérez [1988], "Noise in the Optical Detection of Atoms in a Beam," *Opt. Commun.*, **67**, pp. 287-292.

J. Hall, M. Zhu, and P. Buch [1989], "Prospects for Using Laser-Prepared Atomic Fountains for Optical Frequency Standards Applications," *J. Opt. Soc. Am. B*, **6**, pp. 2194-2205.

W. Happer [1972], "Optical Pumping," *Rev. Mod. Phys.*, **44**, pp. 169-249.

K. Hisadome [1991], "Theoretical Analysis of Fluorescence Light Shifts in Optically Pumped Cesium Beam Frequency Standards," *IEEE Trans. Ultrason., Ferroelec., Freq. Contr.*, **UFFC-38**, pp. 407-412.

W. M. Itano [1991], "Atomic Ion Frequency Standards," *Proc. IEEE*, **79**, pp. 936-942.

M. Jardino, M. Desaintfuscien, R. Barillet, J. Viennet, P. Petit, and C. Audoin [1981], "Frequency Stability of a Mercury Ion Frequency Standard," *Appl. Phys.*, **24**, pp. 107-112.

M. Kasevich, E. Riis, S. Chu, and R. DeVoe [1989], "RF Spectroscopy in an Atomic Fountain," *Phys. Rev. Lett.*, **63**, pp. 612-615.

A. Kastberg, W. D. Phillips, S. L. Rolston, R. Spreeuw, and P. S. Jessen [1995], "Adiabatic Cooling of Cesium to 700 nK in an Optical Lattice," *Phys. Rev. Lett.*, **74**, pp. 1542-1545.

A. Kastler [1950], "Some Suggestions Concerning the Optical Production and Optical Detection of Inequalities of Population of the Spatially Quantized Levels of Atoms. Application to Stern-Gerlach Experiment and to Magnetic Resonance," *J. Phys. Radium*, **11**, pp. 255-265.

M. Knoop, M. Vedel, and F. Vedel [1994], "Investigations of a RF Stored Ca^+ Ion Cloud and Observations of the *S-D* Forbidden Transitions," *J. Physique II*, **4**, pp. 1639-1650.

Y. Koga, S. Ohshima, Y. Nakadan, and T. Ikegami [1989], "Performance of an Optically Pumped Cesium Frequency Standard," *Proceedings of the International Symposium on Electromagnetic Metrology*, August 19-22, 1989, Beijing, China, International Academic Publishers, pp. 267-273.

D. J. Larson, J. C. Bergquist, J. J. Bollinger, W. M. Itano, and D. J. Wineland [1986], "Sympathetic Cooling of Trapped Ions: A Laser-Cooled Two-Species Nonneutral Ion Plasma," *Phys. Rev. Lett.*, 57, pp. 70-73.

W. D. Lee, J. H. Shirley, J. P. Lowe, and R. E. Drullinger [1995], "The Accuracy Evaluation of NIST-7," *IEEE Trans. Instrum. Meas.*, **IM-44**, pp. 120-123.

H. Lehmitz, J. Hattendorf-Ledwoch, R. Blatt, and H. Harde [1989], "Population Trapping in Excited Yb Ions," *Phys. Rev. Lett.*, **62**, pp. 2108-2111.

P. Lett, R. Watts, C. Westbrook, W. Phillips, P. Gould, and H. Metcalf [1988], "Observation of Atoms Laser Cooled below the Doppler Limit," *Phys. Rev. Lett.*, **61**, pp. 169-172.

P. Lett, W. Phillips, S. Rolston, C. Tanner, R. Watts, and C. Westbrook [1989], "Optical Molasses," *J. Opt. Soc. Am. B*, **6**, pp. 2084-2107.

J. P. Lowe, W. D. Lee, F. L. Walls, and R. E. Drullinger [1994], "A Hybrid Digital/Analog Servo for the NIST-7 Frequency Standard," *Proceedings of the 1994 IEEE International Frequency Control Symposium*, June 1-3, 1994, Boston, MA, USA, IEEE Catalogue No. 94CH3446-2 (available from IEEE, 445 Hoes Lane, Piscataway, NJ 08854, USA), pp. 662-665.

F. G. Major and G. Werth [1973], "High-Resolution Magnetic Hyperfine Resonance in Harmonically Bound Ground-State ^{199}Hg Ions," *Phys. Rev. Lett.*, 30, pp. 1155-1158.

C. Monroe, W. Swann, H. Robinson, and C. Wieman [1990], "Very Cold Trapped Atoms in a Vapor Cell," *Phys. Rev. Lett.*, **65**, pp. 1571-1574.

A. G. Mungall [1986], "Frequency and Time: National Standards," *Proc. IEEE*, **74**, pp. 132-136.

Nagourney, N. Yu, and H. Dehmelt [1990], "High Resolution Ba^+ Monoion Spectroscopy with Frequency Stabilized Color-Center Laser," *Opt. Commun.*, **79**, pp. 176-180.

Y. Nakadan and Y. Koga [1985], "Recent progress in Cs beam frequency standards at the NRLM," *IEEE Trans. Instrum. Meas.*, **IM-34**, pp. 133-135.

S. Ohshima, Y. Nakadan, and Y. Koga [1988], "Development of an Optically Pumped Cs Frequency Standard at the NRLM," *IEEE Trans. Instrum. Meas.*, **IM-37**, pp. 409-413.

S. Ohshima, Y. Nakadan, T. Ikegami, Y. Koga, R. E. Drullinger, and L. Hollberg [1989a], "Characteristics of an Optically Pumped Cs Frequency Standard at the NRLM," *IEEE Trans. Instrum. Meas.*, **IM-38**, pp. 533-536.

S. Ohshima, Y. Nakadan, T. Ikegami, and Y. Koga [1989b], "A Beam Reversal Experiment for the Estimation of Microwave Power Shifts in an Optically Pumped Cs Beam Frequency Standard, *IEEE Trans. Instrum. Meas.*, **IM-38**, pp. 1100-1103.

S. Ohshima, Y. Nakadan, T. Ikegami, and Y. Koga [1991], "Light Shifts in an Optically Pumped Cs Beam Frequency Standard," *IEEE Trans. Instrum. Meas.*, **IM-40**, pp. 1003-1007.

M. Osinski and J. Buus [1987], "Linewidth Broadening Factor in Semiconductor Lasers–An Overview," *IEEE J. Quantum Electron.*, **QE-23**, pp. 9-29.

W. Paul [1990], "Electromagnetic Traps for Charged and Neutral Particles," *Rev. Mod. Phys.*, **62**, pp. 531-540.

E. Peik, G. Hollemann, and H. Walther [1994], "Laser Cooling and Quantum Jumps of a Single Indium Ion," *Phys. Rev. A*, 49, pp. 402-408.

W. D. Phillips and H. Metcalf [1982], "Laser Deceleration of an Atomic Beam," *Phys. Rev. Lett.* **48**, pp. 596-599.

M. E. Poitzsch, J. C. Bergquist, W. M. Itano, and D. J. Wineland [1994], " Progress on Cryogenic Linear Trap for $^{199}Hg^{+}$ Ions," *Proceedings of the 1994 IEEE International Frequency Control Symposium*, June 1-3, 1994, Boston, MA, USA, IEEE Catalogue No. 94CH3446-2 (available from IEEE, 445 Hoes Lane, Piscataway, NJ 08854, USA), pp. 744-746.

J. D. Prestage, G. J. Dick, and L. Maleki [1991], "Linear Ion Trap Based Atomic Frequency Standard," *IEEE Trans. Instrum. Meas.*, **IM-40**, pp. 132-136.

J. Prodan and W. Phillips [1983], "Chirp the Light Fantastic?" in W. Phillips (ed.), *Cooled and Trapped Atoms*, National Bureau of Standards (US) Special Publication 653, (available from Superintendent of Documents, US Government Printing Office, Washington, DC 20402-9325, USA), pp. 137-141.

M. G. Raizen, J. M. Gilligan, J. C. Bergquist, W. M. Itano, and D. J. Wineland [1992], "Ionic Crystals in a Linear Paul Trap," *Phys. Rev. A*, **45**, pp. 6493-6501.

N. F. Ramsey [1983], "History of Atomic Clocks," *J. Res. Natl. Bur. Stand.*, **88**, pp. 301-320.

J. Reichel, O. Morice, G. Tino, and C. Salomon [1994], "Subrecoil Raman Cooling of Cesium Atoms," *Europhys. Lett.* **28**, pp. 477-482.

S. Rolston and W. Phillips [1991], "Laser-Cooled Neutral Atom Frequency Standards," *Proc. IEEE*, **79**, pp. 943-951.

G. D. Rovera, E. de Clercq, and A. Clairon [1993], "An Analysis of Major Frequency Shifts in the LPTF Optically Pumped Primary Frequency Standard," *IEEE Trans. Ultrason., Ferroelec., Freq. Contr.*, **UFFC-41**, pp. 245-249.

C. Salomon, J. Dalibard, W. Phillips, A. Clairon, and S. Guelatti [1990], "Laser Cooling of Cesium atoms below 3 μK," *Europhys. Lett.*, **12**, pp. 683-687.

G. Santarelli, P. Laurent, S. Lea, A. Nadir, and A. Clairon [1994], "Preliminary Results in a Cesium Atomic Fountain Frequency Standard," in *Proceedings of the 8th European Frequency and Time Forum*, March 9-11, 1994, Weihenstephan, Germany (available from EFTF Secretariat, FSRM, Rue de l'Orangerie 8, CH-2000, Neuchâtel, Switzerland), pp. 46-57.

G. Savard, St. Becker, G. Bollen, H.-J. Kluge, R. B. Moore, Th. Otto, L. Schweikhard, H. Stolzenberg, and U. Wiess [1991], "A New Cooling Technique for Heavy Ions in a Penning Trap," *Phys. Lett. A*, **158**, pp. 247-252.

D. Schnier, A. Bauch, R. Schröder, and C. Tamm [1992], "Ion Trap Frequency Standard Research at PTB," in *Proceedings of the 6th European Frequency and Time Forum*, March 17-19, 1992, Noordwijk, Netherlands (available from EFTF Secretariat, FSRM, Rue de l'Orangerie 8, CH-2000, Neuchâtel, Switzerland), pp. 415-420.

R. Schröder and A. Bauch [1993], "The Effect of Majorana Transitions on the Frequency of a Cesium Atomic Clock," *Proceedings of the 7th European Frequency and Time Forum*, March 16-18, 1993, Neuchâtel, Switzerland (available from EFTF Secretariat, FSRM, Rue de l'Orangerie 8, CH-2000, Neuchâtel, Switzerland), pp. 483-488.

J. H. Shirley [1985], "Fluorescent Light Shift in Optically Pumped Cesium Standards," *Proceedings of the. 39th Annual Symposium on Frequency Control*, May 29-31, 1985, Philadelphia, PA, USA, IEEE Catalogue No. 85CH2186-5 (available from IEEE, 445 Hoes Lane, Piscataway, NJ 08854, USA), pp. 22-23.

J. H. Shirley, W. D. Lee, G. D. Rovera and R. E. Drullinger [1995], "Rabi Pedestal Shifts as a Diagnostic Tool in Primary Frequency Standards," *IEEE Trans. Instrum. Meas.*, IM-44, pp. 136-139.

I. Siemers, B. Appasamy, Y. Stalgies, V. Enders, Ph. Courteille, R. Huesmann, L. S. Ma, W. Neuhauser, R. Blatt, and P. E. Toschek [1994], "Optical Double-Resonance on Single Cold Ions," in E. DeWeese, G. Bennett, (eds.) *1994 Conference on Precision Electromagnetic Measurements Digest*, IEEE Catalogue No. 94CH3449-6 (available from IEEE, 445 Hoes Lane, Piscataway, NJ 08854, USA), pp. 33-34.

S. Stenholm [1986], "The Semiclassical Theory of Laser Cooling," *Rev. Mod. Phys.*, 58, pp. 699-739.

C. Tamm, D. Schnier, and A. Bauch [1995], "Radio-Frequency Laser Double-Resonance Spectroscopy of ^{171}Yb Ions and Determination of Line Shifts of the Ground-State Hyperfine Resonance," *Apply. Phys. B*, 60, pp. 19-29.

R. C. Thompson [1993], "Spectroscopy of Trapped Ions," in D. Bates and B. Bederson (eds.), *Advances in Atomic and Molecular Physics, vol. 31*, New York, Academic Press, pp. 63-136.

R. L. Tjoelker, J. D. Prestage, G. J. Dick, and L. Maleki [1993], "Long Term Stability of Hg^+ Trapped Ion Frequency Standards," in *Proceedings of the 1993 IEEE International Frequency Control Symposium* June 2-4, 1993, Salt Lake City, UT, USA, IEEE Catalogue No. 93CH3244-1 (available from IEEE, 445 Hoes Lane, Piscataway, NJ 08854, USA), pp. 132-138.

S. Urabe, K. Hayasaka, M. Watanabe, H. Imajo, and R. Ohmukai [1994], "Laser Cooling of Ca^+ Ions and Observation of Collision Effects," *Jpn. J. Appl. Phys.*, **33**, pp. 1590-1594.

J. Vanier and C. Audoin [1989], *The Quantum Physics of Atomic Frequency Standards, Vols. 1 and 2*, Bristol, Adam Hilger.

I. Waki, S. Kassner, G. Birkl, and H. Walther [1992], "Observation of Ordered Structures of Laser-Cooled Ions in a Quadrupole Storage Ring," *Phys. Rev. Lett.*, 68, pp. 2007-2010.

M. Walhout, H. Megens, A. Witte, and S. L. Rolston [1993], "Magneto-Optical Trapping of Metastable Xenon: Isotope Shift Measurements", *Phys. Rev. A*, **48**, pp. R879-R882.

J. Walz, I. Siemers, M. Schubert, W. Neuhauser, R. Blatt, and E. Teloy [1994], "Ion Storage in the rf Octupole Trap," *Phys. Rev. A*, **50**, pp. 4122-4132.

G. Werth [1993], "Microwave and Radiofrequency Spectroscopy in Ion Traps," *Comments on Atomic and Molecular Physics*, **28**, pp. 229-243.

G. Werth [1994], "Present Status and Prospects of Ion Trap Frequency Standards," *Jpn. J. Appl. Phys.*, **33**, pp. 1585-1589.

B. G. Whitford, K. J. Siemsen, A. A. Madej, and J. D. Sankey [1994], "Absolute-Frequency Measurement of the Narrow-Linewidth 24-THz *D-D* Transition of a Single Laser-Cooled Barium Ion," *Opt. Lett.*, **19**, pp. 356-358.

D. J. Wineland, W. M. Itano, and R. S. Van Dyck, Jr. [1983], "High-Resolution Spectroscopy of Stored Ions," in D. Bates and B. Bederson (eds.), *Advances in Atomic and Molecular Physics, vol. 19*, New York, Academic Press, pp. 135-186.

D. J. Wineland and W. M. Itano [1987], "Laser cooling," *Phys. Today*, **40**, 6, pp. 34-40.

D. J. Wineland, W. M. Itano, J. C. Bergquist, and R. G. Hulet [1987], "Laser-Cooling Limits and Single-Ion Spectroscopy," *Phys. Rev. A*, **36**, pp. 2220-2232.

D. J. Wineland, J. C. Bergquist, J. J. Bollinger, W. M. Itano, D. J. Heinzen, S. L. Gilbert, C. H. Manney, and M. G. Raizen [1990], "Progress at NIST towards Absolute Frequency Standards Using Stored Ions," *IEEE Trans. Ultrason., Ferroelec., Freq. Contr.*, **UFFC-37**, pp. 515-523.

J. Zacharias [1954], "Precision Measurements with Molecular Beams," *Phys. Rev.*, 94, pp. 715.