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Trapped Ions, Laser Cooling, and Better Clocks

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Summary. Ions that are stored in electromagnetic "traps" provide the basis for extremely high resolution spectroscopy. By using lasers, the kinetic energy of the ions can be cooled to millikelvin temperatures, thereby suppressing Doppler frequency shifts. Potential accuracies of frequency standards and clocks based on such experiments are anticipated to be better than one part in 10^{15}.

In a recent experiment (*1*) at the National Bureau of Standards (NBS) in Boulder, Colorado, the frequency of a particular hyperfine transition in the ground state of beryllium atomic ions was measured with an inaccuracy of only about one part in 10^{13}. In this experiment, the ions were confined or "trapped" in a small region of space by using static electromagnetic fields and their kinetic temperature was lowered to less than 1 K by a process sometimes called "laser cooling." In all of physics, only a few measurements can boast a higher accuracy; those experiments measure similar transitions in neutral cesium atoms.

Experimental spectroscopy (the study of the interaction between radiation and matter) has traditionally provided a means of checking the theory of quantum mechanics which predicts the internal energy structure of atoms and molecules. In the case of hyperfine structure, which represents the magnetic coupling between the nucleus and atomic electrons, the theory quickly becomes very complicated. For alkali-like ions, the most sophisticated calculations (*2*) agree with experiment at a level of only a few tenths of a percent. On the experimental side, about 8 years ago a measurement (*3*) of beryllium ion hyperfine structure to an accuracy of 3 ppm (parts per million) was made. Since the accuracy of this previous measurement is presumably good enough to satisfy the theorists for quite some time in the future, one can logically ask why anyone would want to make a better measurement. Briefly, I will give three of the reasons.

1) The primary driver in several laboratories (including NBS) is to provide better clocks and frequency standards. The principal use of atomic clocks is in navigation and communications, where requirements have continued to press the state of the art. The way an atomic clock works is perhaps apparent in the internationally agreed on definition of the second: "The second is the duration of 9,192,631,770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the cesium-133 atom." A simplified model for the practical realization of the second involves making a device (an atomic beam apparatus) which allows one to induce and detect transitions between the two ground-state hyperfine energy levels. When the frequency of the radiation for maximum transition probability is attained, the cycles are electronically counted; when 9,192,631,770 cycles have occurred, 1 second has passed. Several laboratories are trying to apply this same idea to the internal energy levels of ions; there is reason to believe that the inaccuracy of a time standard based on stored ions can eventually be much smaller than that of the cesium clock, which can have an accuracy of about one part in 10^{13} or less (*4*).

2) With the extreme accuracy attained with stored ion techniques, it may be possible to measure various small effects which would otherwise be masked by measurement imprecision. As an example, it should be possible to measure nuclear magnetic susceptibility as a small perturbation to atomic hyperfine structure (*5*). Nuclear magnetic susceptibility, which has not been measured previously, could give a new kind of information about nuclear structure. Trapped ions may provide a way to make the required precise measurements.

3) The system itself, laser-cooled stored ions, is intrinsically interesting and may provide the basis for other experiments which are only peripherally related to spectroscopy. An example is the study of strongly coupled three-dimensional plasmas (*6*).

For brevity, this article will only touch on some aspects of stored ion spectroscopy where laser cooling is employed and how they are related to better clocks and frequency standards. A recent review article (*7*) includes many interesting trapped ion experiments which are not discussed here.

Trapped Ions

The principal attraction of the stored ion technique is that charged particles, including electrons and atomic ions, can be stored for long periods of time (days are not uncommon) without the usual perturbations associated with confinement [for example, the frequency shifts associated with the collisions of ions with buffer gases in a more traditional optical pumping experiment (*8*)].

Storage has principally been accomplished in four types of "traps": the RF (radio frequency) or Paul trap, the Pen-

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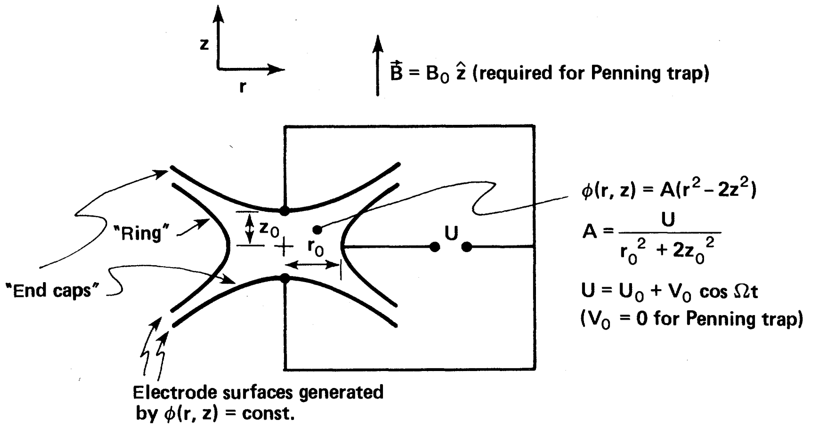

Fig. 1. Schematic representation of the electrode configuration for the "ideal" Paul (RF) or Penning trap. Electrode surfaces are figures of revolution about the z axis and are equipotentials of $\phi(r,z) = A(r^2 - 2z^2)$. (Cylindrical coordinates are used with the origin at the center of the trap.) Typical dimensions are $\sqrt{2}\, z_0 = r_0 \cong 1$ cm. Typical operating parameters are: for the Paul trap, $V_0 \cong 300$ V/cm, $\Omega/2\pi \cong 1$ MHz; for the Penning trap, $U_0 \cong 1$ V, $B \cong 1$ T.

ning trap, the Kingdon (electrostatic) trap, and the magnetostatic trap ("magnetic bottle"). Magnetic bottles have had limited use in high-resolution work because the trapping relies on spatially inhomogeneous magnetic fields, which can cause shifts and broadening of magnetic field–dependent lines. A notable exception is the electron g factor measurements at the University of Michigan by H. R. Crane, A. Rich, and their colleagues (*9*). The Kingdon trap (*10*) is perhaps the simplest, using only static electric fields for trapping. Since an electrostatic potential minimum cannot exist in a charge-free region, the Kingdon trap relies on a dynamical equilibrium for trapping (ions orbit around an attractive wire). Kingdon traps have been used in spectroscopic experiments by Prior and his colleagues (*11*), but so far neither Kingdon traps nor magnetic bottles have been used in laser cooling experiments, and therefore they will not be discussed further here.

The Paul (*12*) or RF trap uses inhomogeneous RF electric fields to provide confinement in a pseudopotential well (*7*, *13*). It is the three-dimensional analog of the Paul quadrupole mass filter. To see how it works, we first note that in a (homogeneous) sinusoidal RF electric field, ion motion is sinusoidal but is 180° out of phase with respect to the electric force. If the field is somewhat inhomogeneous, it is easy to show that the force on the ion averaged over one cycle of the driven motion is toward the region of weaker field. Since an electric field minimum can exist in a charge-free region, stable trapping can be accomplished. Such a trap is shown schematically in Fig. 1, where the three trap electrodes are shaped to provide an electric potential of the form $(r^2 - 2z^2)$ inside the trap. For this "ideal" trap shape, an ion is bound in a nearly harmonic well; detection of the ion well frequencies can then be used to perform mass analysis.

The "ideal" Penning (*14*) trap uses the same electrode configuration as in Fig. 1 but uses static electric and magnetic fields. A harmonic potential well is provided along the z axis by static electric fields. This, however, results in a radial electric field, which forces the ions toward the "ring" electrode. This effect can be overcome if a static magnetic field **B** is superimposed along the z axis. In this case the x-y motion of the ions is a composite of circular cyclotron orbits (primarily due to the **B** field) and a circular $\mathbf{E} \times \mathbf{B}$ drift magnetron motion about the trap axis.

Both the Paul and Penning traps can provide long-term confinement. Storage times of days are not uncommon; in the first single-electron (Penning trap) experiments (*15*) the same electron was used in experiments for several weeks! This long-term storage is important in spectroscopy because (i) "transit time" broadening (the broadening of transitions due to the time-energy uncertainty relation associated with the time the ion stays in the trap) can be made negligible and (ii) the average velocity $\langle \mathbf{v} \rangle$ of the ions approaches zero. The latter is important because it can make averaged first-order Doppler frequency shifts negligible. Suppression of such first-order Doppler shifts is perhaps the chief advantage over the atomic beam method; for example, residual first-order Doppler shifts (due to the net velocity of the atomic beam) are the main limitation to accuracy for the cesium beam frequency standard. (Actually, even though $\langle \mathbf{v} \rangle \rightarrow 0$ for the traps, the first-order Doppler effect is proportional to $\langle \mathbf{k} \cdot \mathbf{v} \rangle$, where **k** is the wave vector of the radiation. For spatially inhomogeneous radiation fields, shifts can occur. If the lifetime of the ion's internal transition is long compared to the periods of ion motion, these effects result in asymmetric sidebands at the ion motional frequencies; however, the "pulling" caused by these sidebands can be extremely small.)

The perturbation of the ions' internal structure due to trapping can be extremely small. Perhaps the most troublesome frequency shifts are caused by electric fields. Shifts which are linearly dependent on the electric field are absent because the average electric field $\langle \mathbf{E} \rangle = 0$. (We know that because if $\langle \mathbf{E} \rangle \neq 0$ the ions would leave the trap.) Second-order shifts can be quite small. As an example, the shift of the ground-state hyperfine frequency of Hg^+ ions, ν_0 (Hg^+), has been calculated (*16*) as $\delta\nu/\nu_0$ (Hg^+) $\cong -1.4 \times 10^{-18} E^2$, where E is in volts per centimeter. Radio-frequency electric fields in an RF trap may be as high as 300 V/cm; this could give a fractional shift of 10^{-13}. However, for small samples of laser-cooled ions electric fields can be smaller than 1 mV/cm (*17*), yielding negligible shifts. (The restoring electric forces become less as the ion's kinetic energy is reduced.) Of course, there are also shifts associated with electric fields due to ion-ion collisions, but these are expected to be smaller than the trapping fields (*17*).

In most cases the magnetic field (**B**) of the Penning trap (typically about 1 T or 10^4 gauss) causes large frequency shifts to the ions' internal structure. The energy separation of the beryllium hyperfine transition mentioned in the introduction goes to zero at zero magnetic field (*1*); therefore, in some sense, the energy separation is entirely due to the external magnetic field. This might be regarded as a severe disadvantage, except that this transition and some others become independent of magnetic field to first order at certain magnetic fields. Second-order field dependence can be small; for the beryllium example $\Delta\nu/\nu_0 = -0.017\,(\Delta B/B)^2$, so if the field is held to 10^{-8} of the nominal field (this can be done with a superconducting magnet), the fractional shifts are only 1.7×10^{-18}. Thus, magnetic fields can strongly perturb the internal structure but these perturbations may only be a philosophical disadvantage. For the clock application we do not care about their existence if they can be made reproducible and stable; more-

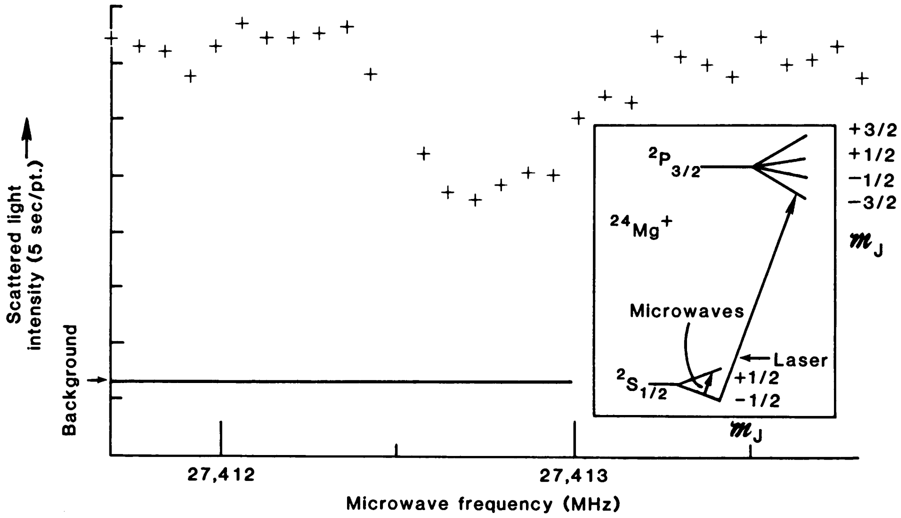

Fig. 2. Microwave/optical double resonance spectrum of $^{24}Mg^+$. Inset shows relevant energy levels of $^{24}Mg^+$ in a magnetic field. With the laser tuned to the transition shown, the ions are pumped into the $^2S_{1/2}$ ($M_J = -1/2$) ground state and a two-level system is formed with this ground state and the excited $^2P_{3/2}$ ($M_J = -3/2$) state. When incident microwaves are tuned to the ($M_J = -1/2$) ↔ ($M_J = +1/2$) ground-sate Zeeman transition, these levels are nearly equally populated, which causes a decrease in fluorescence scattering from the ions. Transitions in other ions are detected in a similar way to this example. [From (*27*)]

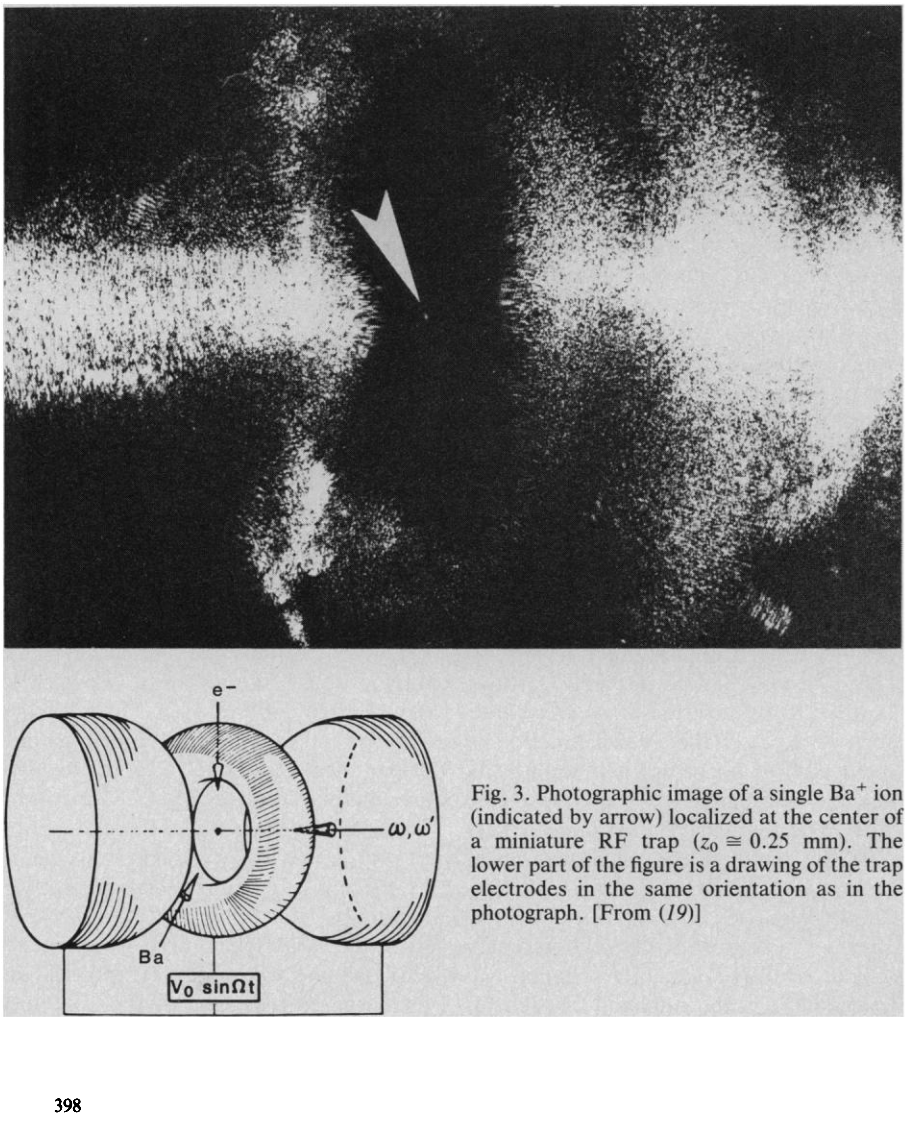

Fig. 3. Photographic image of a single Ba^+ ion (indicated by arrow) localized at the center of a miniature RF trap ($z_0 \cong 0.25$ mm). The lower part of the figure is a drawing of the trap electrodes in the same orientation as in the photograph. [From (*19*)]

that was used for cooling was the $6s^2S_{1/2} - 6p^2P_{1/2}$ transition ($\lambda = 493$ nm). A second laser ($\lambda = 650$ nm) was required to empty the metastable $^2D_{3/2}$ state to which atoms could decay from the $^2P_{1/2}$ state. More recently, laser cooling experiments on trapped ions have been carried out at Seattle (*20*) and Orsay (*29*). In addition, laser cooling on neutral atomic beams has also been observed (*30*).

In both kinds of traps, it has become customary to describe the resulting ion kinetic energy in terms of temperature; however, this must be interpreted with caution. For a cloud of ions in a Penning trap it is theoretically possible (*31*) to cool the cyclotron and axial energy to approximately $h\Delta\nu_a/2$. Equating this energy to k_BT where k_B is Boltzmann's constant, we get $T \cong 1$ mK for $\Delta\nu_a = 43$ MHz (Mg^+). However, the kinetic energy in the magnetron motion depends on the space charge density and size of the cloud (*6*) and can be much larger than this for more than a few ions in the trap. In a similar vein, for a cloud of ions in an RF trap, the energy of motion in the pseudopotential well can be cooled to the same limit as the cyclotron or axial motion in a Penning trap (*28*). However space charge repulsion tends to push the ions toward the edge of the cloud where the energy in the driven motion can be much larger than this. These problems (*17*) which can cause undesirable second-order Doppler shifts can be suppressed in both traps by going to very small numbers of ions—down to one.

Single Ions

In subsequent Heidelberg experiments (*19*) single ions were observed in an RF trap by laser fluorescence scattering. Figure 3 is a photograph of a single Ba^+ ion. The size of the image determined the extent of the ion motion; therefore the temperature in the pseudopotential well was measured to be between 10 and 36 mK. [The driven motion "temperature" will be equal to or larger than this (*13*, *17*).] Laser cooling of single Mg^+ ions in Penning (*32*) and RF (*20*) traps has also been accomplished. The lowest temperatures attained are those of the Seattle group (*20*), where the temperature in at least two directions of the pseudopotential motion was determined to be less than 20 mK. [Cooling in all directions will be straightforward (*19*).] In both of the magnesium experiments, the temperature was determined from the Doppler broadening on the optical cooling over, these perturbations are physically interesting since they can sometimes be calculated with high precision.

A third feature of the traps may be regarded as either a disadvantage or advantage. Typically, the number of ions that can be trapped is rather small. Densities in the range of 10^5 to 10^7 cm^{-3} are typical; therefore the total number of ions may be quite small. Fortunately, atomic ions can be sensitively detected; this is apparent in the single-ion experiments discussed below. In many spectroscopic experiments it is anticipated that the signal-to-noise ratio can approach the theoretical limit (*18*)—that is, that it can be limited only by the statistical fluctuations in the number of ions that make the transition. We note that if we could obtain much higher densities by using larger confining fields then we would lose one of the advantages of the technique because electric field frequency shifts would become troublesome in very high resolution work.

The small sample sizes can actually be regarded as an advantage in a couple of ways. First, the small numbers imply that the ions can be confined to a small region of space—down to dimensions on the order of 1 μm or less for single ions (*19, 20*). This means that field imperfections—deviations from the quadratic electric potential or deviation from uniformity of the magnetic field in Penning traps—can be quite small over the ion sample. Therefore accuracy in magnetic field–dependent studies (mass spectroscopy, *g* factor measurements) can be extremely high. Second, in single-photon absorption spectra it is desirable to satisfy the Lamb-Dicke criterion (*21*)—that is, confinement to dimensions $\lesssim \lambda/2\pi$, where λ is the wavelength of the radiation. When the Lamb-Dicke criterion is satisfied, first-order Doppler effects (broadening or sideband generation) are suppressed. For optical wavelengths this condition can be met only for single confined ions.

For high-resolution spectroscopy, Paul and Penning traps have many desirable features in common, but they differ in some important respects. The magnetic field of the Penning trap may be a disadvantage in some experiments but it may also be the clear choice for magnetic field–dependent studies. The RF trap is able to provide tighter spatial confinement and may be the best choice for optical frequency standards (where it is desirable to satisfy the Lamb-Dicke criterion), although the Penning trap can nearly satisfy the Lamb-Dicke criterion on optical transitions in certain cases. Heating mechanisms in the Paul trap (due to the large RF fields) are typically more severe than in the Penning trap. This can be an important problem for large numbers of stored ions.

Laser Cooling

The experiments of Dehmelt and collaborators (*13*) in the 1960's showed the ability of the stored ion technique to obtain very high resolution in atomic spectra. Prior to 1970, the ground-state hyperfine transition in the $^3\text{He}^+$ ($\nu_0 \cong 8.7$ GHz) ion was measured in an RF trap with a line width of only 10 Hz (*22*), but the accuracy was limited by the second-order Doppler shift ($\Delta\nu/\nu_0 = -1/2\langle v^2\rangle/c^2$) to 10 Hz ($c$ = speed of light). The second-order Doppler effect is due to relativistic time dilation. Because the atoms are moving, their time proceeds slower than a laboratory observer; this effect must be accounted for. The relatively large second-order Doppler frequency shifts imposed by the high velocities of the stored ions and the difficulty of measuring their velocity distribution have historically been the main limitation to achieving high accuracy in stored ion spectra.

In 1975 proposals were made (*23, 24*) to get around this general problem of the second-order Doppler shift by a process commonly called laser (or sideband) cooling. The idea is outlined for the case of an atom with internal (optical) transition frequency ν_a having natural (radiative) line width $\Delta\nu_a$. Assume that the atom is constrained to move in a harmonic well along the z axis (one-dimensional model of the ion trap). Therefore its velocity is given by $v_z = v_0 \cos 2\pi\nu_v t$, where ν_v is its oscillation frequency in the well and we assume $\nu_v >> \Delta\nu_a$. When observed along the direction of the motion, the spectrum in the laboratory contains the central resonance line (at frequency ν_a) with sidebands generated by the first-order Doppler effect at frequencies $\nu_a + n\nu_v$ having intensity $J_n^2(v_0\nu_a/c\nu_v)$ (with n a positive or negative integer); here, J_n is the Bessel function of order n. This spectrum is a simple frequency modulation (FM) spectrum where the frequency modulation is supplied by the first-order Doppler effect (*21*). If we irradiate the atom with photons of frequency $\nu_L = \nu_a + n\nu_v$, the frequencies of the resonantly scattered photons occur at ν_a and nearly symmetrically around ν_a at the sideband frequencies $\nu_a \pm \nu_v$, $\nu_a \pm 2\nu_v$, ... Therefore, although photons of energy $h(\nu_a + n\nu_v)$ are absorbed, on the average photons of energy $h\nu_a$ are reemitted; when n is negative, this energy difference causes the kinetic energy of the atom to decrease by $nh\nu_v$ per scattering event.

This explanation in terms of sidebands (*24*) is easily visualized for $\nu_v >> \Delta\nu_a$. For all experiments done so far $\Delta\nu_a >> \nu_v$; however, the above conclusion is still valid. An alternative explanation (*23*) for this limit (note that when $\nu_v \rightarrow 0$ the atoms are free) is that when $\nu_L < \nu_a$, the atom predominantly interacts with the incident radiation when it moves toward the source of radiation and Doppler shifts the frequency into resonance—that is, when $\nu_L(1 + v_z/c) = \nu_a$. In the absorption process, the photon momentum is first transferred to the atom, causing its momentum to change by h/λ, where h is Planck's constant. Since the remission occurs nearly symmetrically in the $\pm z$ directions, the net effect is to change the velocity of the atom by $\Delta v_z = h/M\lambda$ (M = mass of the atom). If $\Delta v_z << v_z$, then the kinetic energy of the absorber decreases by an amount $Mv_z\Delta v_z = nh\nu_v$. The cooling process is weak in that it takes about 10^4 scattering events to do substantial cooling below room temperature; it is strong in that, for allowed transitions, the resonant scattering rate can approach 10^8 sec^{-1}. Clearly, however, we require a situation where a two-level system is approached in order to have 10^4 scattering cycles; hence we usually think in terms of simple atomic systems.

Laser cooling was first observed in 1978 in experiments at both NBS (Boulder) and Heidelberg University. In the NBS experiments (*25*), the temperature of Mg^+ ions was monitored by observing the induced currents (*26*) in the trap electrodes of a Penning trap. At magnetic fields of about 1 T a two-level system is formed in $^{24}\text{Mg}^+$ (the most abundant isotope) by driving the $3s^2S_{1/2}$ ($M_J = -1/2$) $\leftrightarrow$ $3p^2P_{3/2}$ ($M_J = -3/2$) transition with linearly polarized light (see inset in Fig. 2). From the selection rule $\Delta M_J = 0, \pm 1$, the ion must fall back to the original ground state. In addition, because other allowed transitions are driven weakly, about 16/17 of the ions are pumped into the $M_J = -1/2$ ground state (*27*). In these experiments, cooling to $\cong$40 K was observed and was limited by the noise in the induced current detection.

In the first Heidelberg experiments (*28*), cooling was observed through the increased storage time of Ba^+ ions in a miniature Paul trap. (Separation between the end caps $2z_0 \cong 0.5$ mm.) The line transition. For temperatures below about 0.1 K this Doppler broadening contributes only a small part of the total line width, which is now primarily due to radiative decay. Therefore, very low temperature becomes difficult to measure. In the future this problem may be circumvented by probing narrow optical transitions as described below. In any case, the amount of cooling that has already been achieved gives a significant reduction in the second-order Doppler shift correction. If we can assume, for example, that magnesium ions have been cooled to 10 mK, then the second-order Doppler shift correction is about one part in 10^{16}.

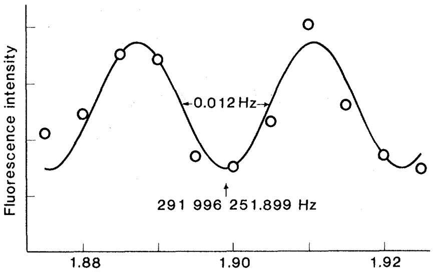

Fig. 4. Graph of a hyperfine resonance of trapped $^{25}Mg^+$ ions. The oscillatory line shape results from the use of the Ramsey resonance method, implemented by applying two coherent RF pulses 1.02 seconds long, separated by 41.4 seconds. The solid curve is a theoretical line shape [From (*32*)]

Spectra

Strongly allowed transitions, which are desirable for the laser cooling, are perhaps not so interesting for high-resolution spectroscopy since the resolutions are limited by the radiative line width (as in the case of Mg^+ above). For high-resolution spectroscopy we usually think in terms of optical pumping/double-resonance detection schemes. A simple example which is characteristic of the method is shown in Fig. 2. In this case, the object was to detect the $(M_J = -1/2) \leftrightarrow (M_J = +1/2)$ ground-state Zeeman transition. The ions are both laser-cooled and pumped into the $^2S_{1/2}$ $(M_J = -1/2)$ ground state as discussed above. The fluorescence (scattered) light intensity is monitored while a microwave generator whose output is directed at the ions is frequency swept through the Zeeman transition. When the resonance condition is satisfied the ground-state populations are nearly equalized; this causes a decrease in the scattered light, which is then the signature of the microwave resonance. This example is illustrative of the various detection schemes used but it is not so interesting for high-resolution spectroscopy since here the line width of the transition was limited by magnetic field fluctuations.

A more interesting example is given by the ground state $(M_I = -3/2, M_J = +1/2) \leftrightarrow (M_I = -1/2, M_J = +1/2)$ nuclear spin flip hyperfine transition of $^{25}Mg^+$. At a field of about 1.24 T, the first derivative of this transition frequency with respect to magnetic field goes to zero; therefore the transition frequency becomes highly insensitive to magnetic field fluctuations. At this field, the resonance shown in Fig. 4 was measured (*33*) with a line width of only 0.012 Hz. The oscillatory line shape results from the use of the Ramsey method (*34*) in the time domain: two phase coherent RF pulses 1.02 seconds long separated in time by 41.4 seconds were used to drive the transition. In order to avoid light shifts, the laser was shut off while the RF transition was driven.

A similar transition was used for the beryllium "clock" mentioned in the introduction. For the beryllium case, the most important limitation to accuracy was caused by a second-order Doppler shift. This resulted because when the laser was off during the RF transition period (about 20 seconds), the ions were heated slightly due to background gas collisions. This problem can be suppressed in the future by using cryogenic pumping.

Frequency Standards and Clocks

In a frequency standard or clock, measurement imprecision $(\delta\nu_{error}/\nu_0)$ is approximately equal to $(Q\ S/N)^{-1}$, where $Q \equiv \nu_0/\Delta\nu_0$ and S/N is the signal-to-noise ratio for detecting the number of ions that have made the transition. If the radiative line width is small enough, then the experimentally observed line width $(\Delta\nu_0)$ need only be limited by the length of time taken to induce the transition. Because of this, $\Delta\nu_0$ is probably independent of the species of trapped ion used. Therefore, we would like to use as high a frequency (ν_0) as possible in order to increase Q and reduce measurement imprecision. This is the single disadvantage of either Mg^+ or Be^+ ions, since the interesting "clock" transitions are only around 300 MHz $(Q \gtrsim 10^{10})$. A better ion for a laser-cooled microwave clock is perhaps Hg^+ (*18*) $(\nu_0 \cong 40$ GHz for $^{199}Hg^+)$. Very important frequency standard work has already been accomplished with this ion (*35*), but laser cooling is much harder to achieve than for Be^+ or Mg^+ (partly because the 194-nm cooling radiation is difficult to produce), and has not been done yet.

A logical extension of this idea is to go to much higher frequency—for example, to use a narrow optical transition. The anticipated Q in this case can be extremely high, 10^{15} or more. A number of transitions in various ions have been proposed (*7*); Dehmelt (*36*) was the first to suggest that such extremely high resolution spectroscopy could be carried out by using single-photon transitions in, for example, single group IIIA ions. For instance (*36*), the $^1S_0 \leftrightarrow {}^3P_0$ transition in Tl^+ $(\lambda = 202$ nm) has a $Q \cong 5 \times 10^{14}$. For such single-photon optical transitions, it is desirable to approximately satisfy the Lamb-Dicke criterion; this is most easily accomplished with single trapped ions. Others (*37*) have proposed using two-photon Doppler-free transitions, for example the $^2S_{1/2} \rightarrow {}^2D_{5/2}$ transitions in Hg^+ $(\lambda = 563$ nm, $Q = 7 \times 10^{14})$. Two-photon optical transitions with equal frequency photons have the advantage of eliminating the first-order Doppler effect for a cloud of many ions, where it is impossible to satisfy the Lamb-Dicke criterion. They ultimately have the disadvantage that the rather large optical fields necessary to drive the transition cause undesirable a-c Stark shifts.

Already, in experiments at Heidelberg and Washington (*38*), the two-photon $^2S_{1/2} \rightarrow {}^2P_{1/2} \rightarrow {}^2D_{3/2}$ stimulated Raman transition in Ba^+ has been observed. In these transitions, the first-order Doppler effect is present; its magnitude (for copropagating beams) is the same as that of a single laser beam at the difference frequency. Present results (*38*) are limited by laser line width broadening, but such transitions should also be extremely narrow; the lifetime of the $^2D_{3/2}$ state in Ba^+ is 17.5 seconds (*39*), which would give an intrinsic Q of 1.6×10^{16}.

For single ions, optical spectra should give precise temperature information through the intensity of the motional sidebands generated by the Doppler effect (*35, 40*). In the near future, the resolution of the sideband structure in the transitions noted above will probably be limited by the laser line widths. This problem might be alleviated by driving a stimulated Raman transition between two nearly degenerate levels in the electronic ground state of the ion. In $^{24}Mg^+$, for example, the $^2S_{1/2}$ $(M_J = -1/2) \rightarrow {}^2P_{1/2}$ $(M_J = -1/2) \rightarrow {}^2S_{1/2}$ $(M_J = +1/2)$ transition could be driven by using two laser beams separated in frequency by the $M_J = -1/2$, and $M_J = +1/2$ ground-state frequency difference. The effects of the laser line width would be suppressed by generating the two laser lines with a phase modulator (*41*); the line width of the overall transition would be limited by the ground-state lifetime. The intensity of the motional sidebands would depend on $\mathbf{v} \cdot (\mathbf{k}_1 - \mathbf{k}_2)$, where $\mathbf{k}_1$ and $\mathbf{k}_2$ are the wave vectors of the two laser beams and $\mathbf{v}$ is the ion velocity. Thus the angle between the beams could be chosen to optimize the temperature information.

Conclusions

The projected accuracy for optical frequency standards is extremely high. As an example, in In$^+$, the line width of the $^1S_0 \rightarrow {}^3P_1$ "cooling" transition is about 1.3 MHz; this implies a second-order Doppler shift of 10^{-19} or lower. Other systematic shifts can occur (*1, 7, 13, 16, 18, 33, 35–38, 42*) but it is not unreasonable to think they will be controllable to this level. These extreme accuracies make important the problem of measurement imprecision, since the signal-to-noise ratio on a single ion will be about one for each measurement cycle. Practically speaking, this means that a long averaging time will be required to reach a measurement precision equal to these accuracies. In fact, for a while, the accuracy and resolution may be limited by laser line width characteristics (line width and line width symmetry); however, the potential for extremely narrow lasers also exists (*43*).

With the great potential for the optical frequency standards, one can logically ask why we bother thinking about RF or microwave frequency standards, where the desired large numbers of ions (to increase signal-to-noise and measurement precision) causes unwanted second-order Doppler effects (*17*). At present, the answer concerns the utility of optical frequency standards within current technological limitations. To use such devices as clocks as in communications and navigation, one must count cycles of the radiation. At microwave frequencies this is straightforward. At optical frequencies it is technically feasible but very hard (*44*); it has not been done yet. To illustrate further, one might also have asked why we do not push the frequency even higher, that is, make a clock based on narrow Mössbauer transitions in bound nuclei. Here, however, the technological problems become even more apparent. In spite of the technical problems of making an optical "clock," optical frequency standards will, of course, find many immediate uses. An obvious class of experiments are cosmological in nature; for example, more precise measurements of the gravitational red shift will arise. In any case, the potential accuracy for stored ion spectroscopy in all spectral regions seems extremely high. Frequency standards and clocks with inaccuracy of one part in 10^{15} appear very reasonable; eventually they could be orders of magnitude better than this.

References and Notes

1. J. J. Bollinger, W. M. Itano, D. J. Wineland, *Proc. 37th Annu. Symp. Freq. Control* (1983), p. 37 (copies available from Systematics General Corporation, Brinley Plaza, Route 38, Wall Township, N.J. 07719).
2. S. Garpman, I. Lindgren, J. Lindgren, J. Morrison, *Z. Phys. A* **276**, 167 (1976); S. Ahmad *et al.*, *Phys. Rev. A* **27**, 2790 (1983).
3. J. Vetter, H. Ackermann, G. ZuPutlitz, E. W. Weber, *Z. Phys. A* **276**, 161 (1976).
4. A. G. Mungall and C. C. Costain, *IEEE Trans. Instrum. Meas.* **IM-32**, 224 (1983); G. Becker, *Proc. 10th Int. Congr. Chronometry* **2**, 33 (1979); D. J. Wineland, D. W. Allan, D. J. Glaze, H. Hellwig, S. Jarvis, Jr., *IEEE Trans. Instrum. Meas.* **IM-25**, 453 (1976).
5. D. J. Larson, *Bull. Am. Phys. Soc.* **19**, 1193 (1974).
6. J. J. Bollinger and D. J. Wineland, *Phys. Rev. Lett.* **53**, 348 (1984).
7. D. J. Wineland, W. M. Itano, R. S. Van Dyck, Jr., *Adv. At. Mol. Phys.* **19**, 135 (1983).
8. E. W. Weber, *Phys. Rep.* **32**, 123 (1977).
9. A. Rich and J. C. Wesley, *Rev. Mod. Phys.* **44**, 250 (1972).
10. K. H. Kingdon, *Phys. Rev.* **21**, 408 (1923).
11. M. H. Prior and E. C. Wang, *Phys. Rev. A* **16**, 6 (1977).
12. E. Fisher, *Z. Phys.* **156**, 1 (1959); R. F. Wuerker, H. Shelton, R. V. Langmuir, *J. Appl. Phys.* **30**, 342 (1959).
13. H. G. Dehmelt, *Adv. At. Mol. Phys.* **3**, 53 (1967); *ibid.* **5**, 109 (1969).
14. F. M. Penning, *Physica* **3**, 873 (1936).
15. P. Ekstrom and D. Wineland, *Sci. Am.* **243** (No. 2), 104 (1980); D. J. Wineland, P. Ekstrom, H. Dehmelt, *Phys. Rev. Lett.* **31**, 1279 (1973).
16. W. M. Itano, L. L. Lewis, D. J. Wineland, *Phys. Rev. A* **25**, 1233 (1982).
17. D. J. Wineland, *Natl. Bur. Stand. (U.S.) Publ. 617*, in press.
18. D. J. Wineland, W. M. Itano, J. C. Bergquist, F. L. Walls, *Proc. 35th Annu. Symp. Freq. Control* (1981), p. 602 (copies available from Electronic Industries Association, 2001 Eye Street, NW, Washington, D.C. 20006).
19. W. Neuhauser, M. Hohenstatt, P. Toschek, H. Dehmelt, *Phys. Rev. A* **22**, 1137 (1980).
20. W. Nagourney, G. Janik, H. Dehmelt, *Proc. Natl. Acad. Sci. U.S.A.* **80**, 643 (1983).
21. R. H. Dicke, *Phys. Rev.* **89**, 472 (1953).
22. H. A. Schuessler, E. N. Fortson, H. G. Dehmelt, *ibid.* **187**, 5 (1969).
23. T. W. Hänsch and A. L. Schawlow, *Opt. Commun.* **13**, 68 (1975).
24. D. J. Wineland and H. G. Dehmelt, *Bull. Am. Phys. Soc.* **20**, 637 (1975).
25. D. J. Wineland, R. E. Drullinger, F. L. Walls, *Phys. Rev. Lett.* **40**, 1639 (1978).
26. H. G. Dehmelt and F. L. Walls, *ibid.* **21**, 127 (1968); D. A. Church and H. G. Dehmelt, *J. Appl. Phys.* **40**, 3421 (1969).
27. D. J. Wineland, J. C. Bergquist, W. M. Itano, R. E. Drullinger, *Opt. Lett.* **5**, 245 (1980).
28. W. Neuhauser, M. Hohenstatt, P. Toschek, H. Dehmelt, *Phys. Rev. Lett.* **41**, 233 (1978).
29. F. Plumelle, Abstracts for the 15th European Group on Atomic Spectroscopy Conference, Madrid, 5 to 8 July 1983.
30. S. V. Andreev, V. I. Balykin, V. S. Letokhov, V. G. Minogin, *JETP Lett.* **34**, 442 (1981); J. V. Prodan, W. D. Phillips, H. J. Metcalf, *Phys. Rev. Lett.* **49**, 1149 (1982); J. L. Hall, W. Ertmer, R. Blatt, in preparation; W. D. Phillips, Ed., "Laser-cooled and trapped atoms," *Natl. Bur. Stand. (U.S.) Spec. Publ. 653* (1983).
31. W. M. Itano and D. J. Wineland, *Phys. Rev. A* **25**, 35 (1982).
32. D. J. Wineland and W. M. Itano, *Phys. Lett. A* **82**, 75 (1981).
33. W. M. Itano and D. J. Wineland, *Phys. Rev. A* **24**, 1364 (1981).
34. N. F. Ramsey, *Molecular Beams* (Oxford Univ. Press, London, 1956).
35. F. G. Major and G. Werth, *Phys. Rev. Lett.* **30**, 1155 (1973); M. D. McGuire, R. Petsch, G. Werth, *Phys. Rev. A* **17**, 1999 (1978); M. Jardino *et al.*, *Appl. Phys.* **24**, 107 (1981); L. S. Cutler, R. P. Giffard, M. D. McGuire, *Proc. 37th Annu. Symp. Freq. Control* (1983), p. 32 (copies available from Systematics General Corporation, Brinley Plaza, Route 38, Wall Township, N.J. 07719); M. Jardino, F. Plumelle, M. Desaintfuscien, J. L. Duchêne, *Proc. 38th Annu. Symp. Freq. Control* (Philadelphia, 1984), in press.
36. H. Dehmelt, *IEEE Trans. Instrum. Meas.* **IM-31**, 83 (1982).
37. P. L. Bender *et al.*, *Bull. Am. Phys. Soc.* **21**, 599 (1976).
38. W. Neuhauser, M. Hohenstatt, P. E. Toschek, H. Dehmelt, in *Spectral Line Shapes*, B. Wende, Ed. (deGruyter, Berlin, 1981); W. Nagourney, *Bull. Am. Phys. Soc.* **29**, 815 (1984).
39. R. Schneider and G. Werth, *Z. Phys. A* **293**, 103 (1979).
40. H. A. Schuessler, *Appl. Phys. Lett.* **18**, 117 (1971); F. G. Major and J. L. Duchêne, *J. Phys. (Orsay)* **36**, 953 (1975); H. S. Lakkaraju and H. A. Schuessler, *J. Appl. Phys.* **53**, 3967 (1982); M. Jardino, F. Plumelle, M. Desaintfuscien, in *Laser Spectroscopy VI*, H. P. Weber and W. Lüthy, Eds. (Springer-Verlag, New York, 1983), p. 173.
41. J. E. Thomas *et al.*, *Phys. Rev. Lett.* **48**, 867 (1982).
42. D. J. Wineland and W. M. Itano, *Bull. Am. Phys. Soc.* **27**, 864 (1982).
43. J. L. Hall, L. Hollberg, Ma Long-Shen, T. Baer, H. G. Robinson, *J. Phys. (Orsay)* **42**, C8-59 (1981); A. Yariv and K. Vahala, *IEEE J. Quant. Electron.* **QE-19**, 889 (1983); R. W. P. Drever *et al.*, *Appl. Phys. B* **31**, 97 (1983); J. Hough *et al.*, *ibid.* **33**, 179 (1984).
44. See Proceedings of the Third Symposium on Frequency Standards and Metrology, *J. Phys.* **42**, Colloque C-8, December 1981; V. P. Chebotayev *et al.*, *Appl. Phys. B* **29**, 63 (1982); D. A. Jennings *et al.*, *Opt. Lett.* **8**, 136 (1983); K. M. Baird, *Phys. Today* **36** (No. 1), 52 (1983).
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