Precision Measurement and Fundamental Constants II, B. N. Taylor and W. D. Phillips, Eds., Natl. Bur. Stand. (U.S.), Spec. Publ. 617 (1984).

Progress Toward a Stored Ion Frequency Standard at the National Bureau of Standards*

Wayne M. Itano, D. J. Wineland, J. C. Bergquist, and F. L. Walls

Frequency and Time Standards Group, Time and Frequency Division, National Bureau of Standards, Boulder, CO 80303

Two fundamental problems with the development of a primary frequency standard based on stored ions have long been apparent—the second-order Doppler shift and the low signal-to-noise ratio. Both problems have been addressed in experiments at the National Bureau of Standards (NBS)—the first by the development of the laser cooling technique and the second by the development of laser-optical-pumping techniques with high detection efficiency. Also, a hyperfine transition in $^{25}Mg^+$ has been observed by rf-optical double resonance with a linewidth of 0.012 Hz and a Q of 2.4×10^{10}. A possible microwave frequency and time standard based on a ground-state hyperfine transition in $^{201}Hg^+$ and a possible optical frequency standard based on the two-photon $5d^9\, 6s^2\, {}^2D_{5/2} \longleftrightarrow 5d^{10}\, 6s\, {}^2S_{1/2}$ transition in $^{199}Hg^+$ or $^{201}Hg^+$ are described.

Key words: atomic frequency standards; atomic hyperfine structure; double resonance; Hg^+; laser cooling; Mg^+; optical pumping; stored ions.

1. Introduction

It has long been realized that microwave or optical transitions of ions stored in electromagnetic traps might form the basis for new types of frequency standards. The basic advantage of such devices is that very long interrogation times (up to many seconds) and, therefore, high transition line Q's can be achieved, while the perturbations which usually accompany the confinement of atoms, such as collisions with buffer gas molecules or the cell walls, can be substantially avoided. Ground-state hyperfine transitions of $^3He^+$ [1], $^{199}Hg^+$ [2–4], and $^{137}Ba^+$ [5] ions stored in rf quadrupole traps have been observed with high resolution by direct or indirect optical pumping techniques. In fact, Q's greater than 10^{10} have been observed on the 40.5 GHz hyperfine transition of $^{199}Hg^+$. The accuracies of the measurements were limited largely by the uncertainty of the second-order Doppler (time dilation) shift. The signal-to-noise ratios were relatively low, because the maximum number of ions stored was about $10^5 - 10^6$ and the transitions were detected with an efficiency much less than one. Techniques developed at NBS in the last three years address both of these problems. Resonant light pressure has been used to cool stored ions to temperatures below 1 K, thus reducing the second-order Doppler shift. Laser-optical-pumping techniques have been developed which are, in principle, capable of detecting transitions with nearly unit efficiency, so that the signal-to-noise ratio is limited only by the statistical fluctuations in the number of ions that make the transition.

2. Laser Cooling and Double Resonance of Mg^+

Laser cooling of Mg^+ ions stored in a Penning trap has been investigated in a series of experiments at NBS [6–10]. Ground-state hyperfine transitions have been detected with extremely high resolution by rf-optical double resonance techniques [10]. Laser cooling of Ba^+ ions stored in a quadrupole rf trap has been demonstrated in a related series of experiments at Heidelberg [11].

2.1 Apparatus

In a Penning trap, ions are confined by a combination of a uniform magnetic field and a quadrupolar electrostatic potential [12, 13]. The trap used had dimensions $r_0 = 1.64\ z_0 = 0.63$ cm in the notation of Ref. [12]. Typical operating parameters were $V_0 \simeq 7$ V and $B_0 \simeq 1$ T, where V_0 is the potential across the electrodes and B_0 is the magnetic field. The storage time for Mg^+ ions in the ultrahigh vacuum environment ($P \lesssim 10^{-7}$ Pa) was about a day.

Narrowband, tunable radiation resonant with the 3s $^2S_{1/2} \rightarrow$ 3p $^2P_{3/2}$ transition at 279.6 nm was required for the laser cooling and the double resonance experiments. This was produced by frequency doubling the output of a single-mode cw Rhodamine 110 dye laser in a 90° phase-matched AD*P crystal. Between 5 and 30 μW of UV power was generated in a bandwidth of about 1 MHz. The dye laser could be long-term stabilized at discrete frequencies to less than 1 MHz by locking it to saturated absorption features in I_2. Fine tuning could be accomplished by varying the trap magnetic field to Zeeman shift the Mg^+ levels.

The UV radiation was focused at the center of the trap, passing through holes in the ring electrode. Resonance fluorescence photons emitted by the ions in the backward direction were detected by a photomultiplier tube and counted. The net detection efficiency for a photon emitted from an ion, taking into account the collection solid angle, mirror reflectivity, transmission of the lenses and filters, and photomultiplier quantum efficiency, was about 2×10^{-5}.

*Supported in part by the Air Force Office of Scientific Research and the Office of Naval Research.

2.2 Laser Cooling

The basic principle of laser cooling of free or harmonically bound atoms [14, 15] can be explained as follows: Consider a monochromatic, directed beam of light whose frequency is slightly below that of a strong resonance line of the atoms. Atoms whose velocities are directed toward the light source see a frequency Doppler shifted closer to resonance; if their velocities are directed away from the source, the frequency shift is away from resonance. Therefore, the atoms tend to absorb photons when their velocity is directed toward the source. This slows them down, since the momentum of the absorbed photons reduces the atomic momentum. (The photons are reemitted in random directions.) All velocity components could be reduced with six laser beams directed along the $\pm x$, $\pm y$, and $\pm z$ directions. A single beam suffices to cool all oscillational modes of an atom bound in a three-dimensional harmonic potential, if the modes are nondegenerate and if the beam is not directed along one of the principal axes [11, 15, 16].

For an ion in a Penning trap, cooling of the axial and cyclotron modes takes place in the same way as for harmonically bound atoms, if the laser is tuned below resonance [16]. Cooling of the magnetron mode, which is an $\mathbf{E} \times \mathbf{B}$ drift of the center of the cyclotron orbit around the trap axis, can be accomplished by focusing the laser beam so that it is more intense on the side of the trap axis on which the magnetron motion recedes from the laser [6–9, 16].

It is easiest to achieve very low temperatures with small numbers of ions. This is because the radial electric field due to space charge increases the magnetron velocity. This problem does not exist for a single, isolated ion, and the lowest temperatures were observed for this case [9]. A recording of the fluorescence intensity from a small number of $^{24}Mg^+$ ions is shown in Fig. 1. After the ions were cooled and localized at the trap center, an oven containing ^{25}Mg was heated in order to induce the resonant charge exchange reaction ($^{24}Mg^+ + {}^{25}Mg \rightarrow {}^{24}Mg + {}^{25}Mg^+$). The resulting $^{25}Mg^+$ ions were ejected from the trap by resonant cyclotron-magnetron rf excitation. We attribute the step decreases in the fluorescence to individual charge exchange events and the last plateau above background to the fluorescence from a single ion.

The "temperature" of a single ion was determined from the Doppler width by optical-optical double resonance (see Fig. 2). (We define the "temperature" of a single ion in terms of its average kinetic energy.) When the light is polarized perpendicular to the magnetic field and is close to resonance with the ($^2S_{1/2}$, $M_J = -1/2$) $\rightarrow$ ($^2P_{3/2}$, $M_J = -3/2$) Zeeman component, most of the $^2S_{1/2}$ population is pumped into the $M_J = -1/2$ sublevel by the following mechanism [8]: The electric dipole selection rules allow M_J to change by ± 1 in the $^2S_{1/2} \rightarrow {}^2P_{3/2}$ transition and by 0 or ± 1 in the subsequent $^2P_{3/2} \rightarrow {}^2S_{1/2}$ decay. Thus, the $-1/2 \rightarrow -3/2$ and $+1/2 \rightarrow +3/2$ transitions (we denote the $^2S_{1/2}$ and $^2P_{3/2}$ M_J-values by the first and second numbers respectively) do not optically pump the ground state, since the ion must decay back to the same sublevel. The other allowed transitions, $+1/2 \rightarrow -1/2$ and $-1/2 \rightarrow +1/2$, do cause optical pumping, because the ion can decay to either sublevel. These off-resonance transitions are driven in their Lorentzian wings (the Zeeman splitting is much greater than the Doppler broadening), at a rate $\gtrsim 1\ s^{-1}$, which is much faster than any other relaxation rate between ground-state sublevels. The detuning of the light from the $-1/2 \rightarrow +1/2$ transition is four times its detuning from the $+1/2 \rightarrow -1/2$ transition. Hence, the $M_J = +1/2$ ground-state sublevel is depopulated 16 times faster than the $M_J = -1/2$ sublevel. In the steady state, $16/17 \simeq 94\%$ of the population is in the $M_J = -1/2$ sublevel. Since the photon scattering rate is proportional to the number of ions in the $M_J = -1/2$ sublevel, any process that changes this number is detectable as a change in the fluorescence intensity. This is the basis of the double resonance technique. To obtain the data shown in Fig. 2, one laser was tuned slightly below the $-1/2 \rightarrow -3/2$ transition, in order to provide cooling and fluorescence detection, while a low power laser was swept across the $-1/2 \rightarrow -1/2$ transition in order to deplete the $M_J = -1/2$ sublevel. The resulting lineshape reflects both the natural and Doppler broadenings. Also shown in Fig. 2 are simulated curves for temperatures $T = 0$ K and 100 mK. We estimate from this data that $T = 50 \pm 30$ mK. Since the light beam was incident at an angle of 82° with respect to the magnetic field, this is primarily a measurement of the cyclotron-magnetron (x-y) temperature. The axial (z) motion was not cooled as efficiently as the cyclotron-magnetron motion because of the beam angle. The axial temperature was estimated to be about 600 mK by lowering the well depth and noting the decrease in the fluorescence due to the decreased fraction of time the ion spent in the laser beam. According to a theoretical model, it should be possible to obtain a cyclotron-magnetron temperature of about 1 mK and an

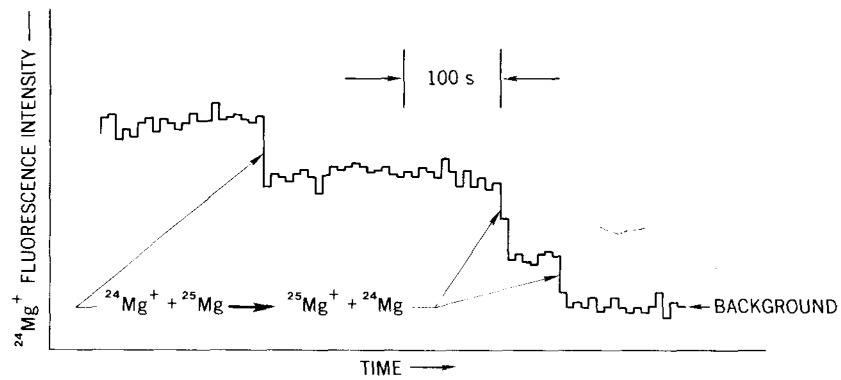

FIGURE 1. *$^{24}Mg^+$ fluorescence as a function of time. Each point represents a 10 s integration. The three large steps are due to single charge exchange events, which remove the $^{24}Mg^+$ ions, one at a time. The last plateau above background is due to a single ion. (From Ref. [9].)*

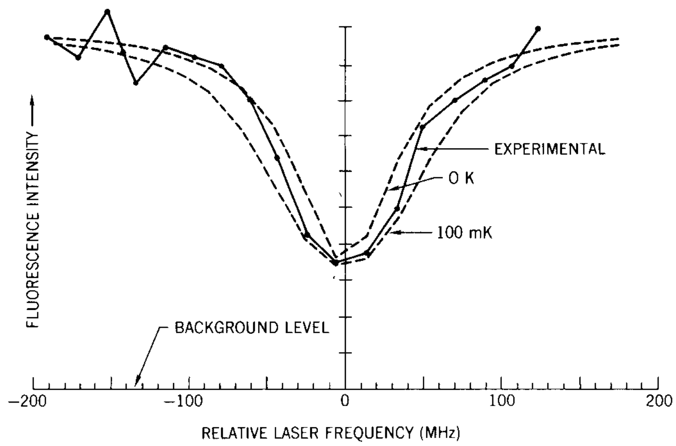

FIGURE 2. *Optical-optical double resonance of a single $^{24}Mg^+$ ion. The fluorescence due to a strong laser tuned to the ($^2 2S_{1/2}$, $M_J = -1/2$) → ($^2P_{3/2}$, $M_J = -3/2$) transition is plotted as a function of the frequency of a weak laser, which is tuned continuously across the ($^2S_{1/2}$, $M_J = -1/2$) → ($^2P_{3/2}$, $M_J = -1/2$) transition. Each dot represents a 10 s integration. The dashed curves are simulated data for ion "temperatures" 0 K and 100 mK. (From Ref. [9].)*

axial temperature of about 11 mK for these conditions [16]. At present, the discrepancy is not understood, but may be due to the presence of impurity ions in the trap.

2.3 RF-Optical Double Resonance

The microwave Zeeman transition in the ground state ($^2S_{1/2}$, $M_J = -1/2 \rightarrow +1/2$) also can be detected by a decrease in the fluorescence intensity [8]. This "flop-out" detection method can be very efficient. In effect, a transition due to a single microwave "photon" interrupts the stream of scattered optical photons until the ion is pumped back to the $M_J = -1/2$ sublevel by weak, off-resonance scattering. Since the decrease in the number of scattered photons can be very large, it is possible to make up for poor light collection and detector quantum efficiencies, so that the transition can be detected with nearly unit efficiency. "Flop-in" detection where a large increase in the number of photons scattered is caused by absorption of a single microwave photon, is also possible [17]. Similar detection methods have been proposed previously [18].

Various ground-state rf and microwave transitions in $^{25}Mg^+$ were detected by double resonance. $^{25}Mg^+$ has nuclear spin $I = 5/2$; in a high magnetic field, the ground-state sublevels can be denoted by (M_I, M_J). If the laser is tuned to the ($^2S_{1/2}$, $M_I = -5/2$, $M_J = -1/2$) → ($^2P_{3/2}$, $M_I = -5/2$, $M_J = -3/2$) transition, pumping into the $M_J = -1/2$ ground-state manifold takes place in the same way as for $^{24}Mg^+$, which has $I = 0$. The pumping of nearly all of the population into the $M_I = -5/2$ sublevels occurs because of hyperfine coupling in the excited state [7, 8]. The excited-state sublevels which are labeled (M_I, $M_J = -3/2$) all contain small admixtures of states with lower M_I, except for ($M_I = -5/2$, $M_J = -3/2$), which is pure. Hence, if an ion in the (M_I, −1/2) ground-state sublevel is excited to the (M_I, −3/2) excited-state sublevel, it has a small probability of decaying to a ground-state sublevel with lower M_I, unless $M_I = -5/2$. Eventually, the ions are trapped in the $M_I = -5/2$ sublevels. After this pumping takes place, the (−5/2, −1/2) → (−5/2, +1/2) electronic spin flip transition and the (−5/2, −1/2) → (−3/2, −1/2) nuclear spin flip can be detected by a decrease in the fluorescence intensity when resonant rf is applied. When the laser is tuned to the ($^2S_{1/2}$, $M_I = +5/2$, $M_J = +1/2$) → ($^2P_{3/2}$, $M_I = +5/2$, $M_J = +3/2$) transition, most of the population is pumped into the (+5/2, +1/2) sublevel, and the (+5/2, +1/2) → (+5/2, −1/2) and (+5/2, +1/2) → (+3/2, +1/2) transitions can be observed.

The observed resonances were broadened by magnetic field fluctuations. However, the magnetic field derivative of the (−3/2, +1/2) ⟷ (−1/2, +1/2) transition frequency goes to zero at $B_0 \simeq 1.2398$ T. The transition was observed near this field with linewidths as narrow as 12 mHz [10]. The following method was used to detect the transition: The ions were optically pumped into the (−5/2, −1/2) sublevel. Some population was transferred to the (−3/2, 1/2) sublevel by saturating the (−5/2, −1/2) ⟷ (−5/2, +1/2) and (−5/2, +1/2) ⟷ (−3/2, +1/2) transitions with rf. The (−3/2, +1/2) → (−1/2, +1/2) transition was driven with the light blocked and the saturating rf off. The laser and saturating rf were turned on again, and the number of transitions made to the (−1/2, +1/2) sublevel was indicated by a decrease in the fluorescence level. The Ramsey interference method [19] was implemented by pulsing the rf, resulting in an oscillatory lineshape (see Figs. 3a, 3b). Several transition frequencies were measured in order to determine the hyperfine constant $A = -596.254\ 376(54)$ MHz and the nuclear-to-electronic g factor ratio $g_I/g_J = 9.299\ 484(75) \times 10^{-5}$ [10]. (Estimated standard deviations in parentheses.) The uncertainties of A and g_I/g_J are dominated by the uncertainties of the field-sensitive transitions, which are due to fluctuations of about 1 ppm in B_0. Further experimental efforts are directed toward developing a trap with greatly improved light collection efficiency in order to continue studies of Mg^+ and to initiate similar studies of Be^+.

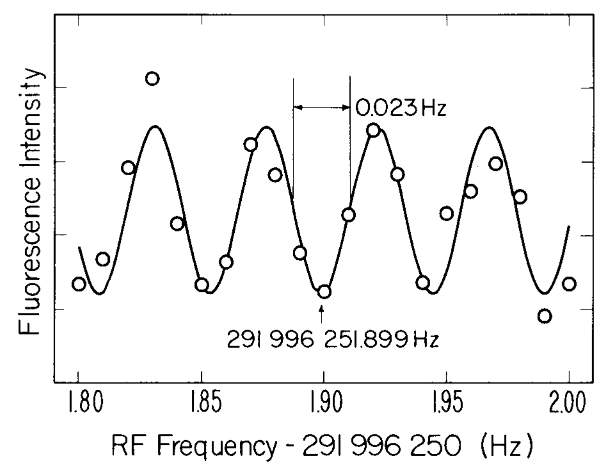

FIGURE 3a. *(M_I, M_J) = (−3/2, +1/2) ⟷ (−1/2, +1/2) $^{25}Mg^+$ ground-state hyperfine resonance. Each circle represents the average of four measurements (total fluorescence detection integration time of 8 s). The oscillatory lineshape results from the use of the Ramsey method. Two coherent rf pulses of duration τ = 1.02 s separated by T = 20.72 s were applied. The solid curve is a theoretical fit. The vertical arrow marks the central minimum, which corresponds to the resonance frequency. The magnetic field B_0 was set so that the (−5/2, −1/2) ⟷ (−5/2, +1/2) electronic spin flip resonance was in the range of 36 248.374 ± 0.750 MHz, which corresponds to $B_0 \simeq 1.2398$ T.*

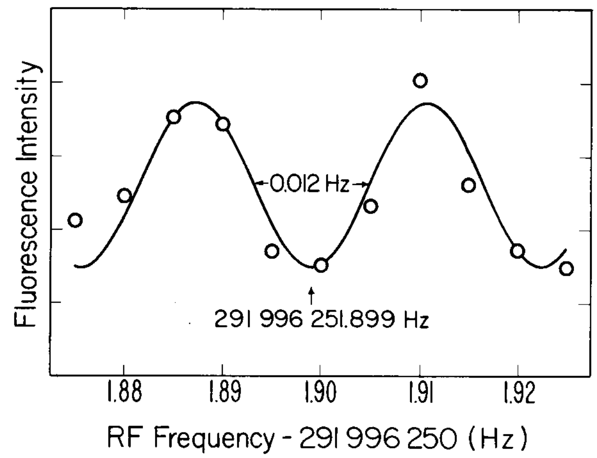

FIGURE 3b. *(−3/2, +1/2) ⟷ (−1/2, +1/2) $^{25}Mg^+$ hyperfine resonance. The total fluorescence detection integration time was 16 s per point and T was 41.40 s. The experimental conditions were otherwise the same as for Fig. 3a. The vertical arrow marks the central minimum. (From Ref. [10].)*

3. Proposals for Hg^+ Frequency Standards

Here we outline proposals for a microwave frequency and time standard based on a hyperfine transition in $^{201}Hg^+$ and for an optical frequency standard based on a two-photon transition in $^{199}Hg^+$ or $^{201}Hg^+$. These proposals incorporate the laser cooling and laser-optical-pumping techniques demonstrated with Mg^+. They use the Penning trap instead of the rf trap because cooling (of more than one ion) appears to be easier. Preliminary experimental work on these devices has begun at NBS. Further details are published elsewhere [17].

3.1 Microwave Frequency Standard

The basic advantages of Hg^+ for a microwave frequency standard are the large hyperfine structure (hence high Q for a given linewidth) and high mass (hence low second-order Doppler shift for a given temperature). Other groups [2–4, 20] have worked with the $^{199}Hg^+$ $(F, M_F) = (1,0) \longleftrightarrow (0,0)$ transition using a $^{202}Hg^+$ lamp for optical pumping and an rf trap near zero magnetic field. For a Penning trap, the best transition appears to be the $^{201}Hg^+$ $(F, M_F) = (1,1) \longleftrightarrow (2,1)$ transition, which is field-independent to first order at $B_0 \simeq 0.534$ T, with frequency ≃25.9 GHz. If B_0 can be controlled to slightly better than 0.1 ppm over the volume of the ion cloud, the fractional second-order field shift can be kept below 10^{-15}. A laser tuned just below a particular hyperfine-Zeeman component of the 6s $^2S_{1/2} \rightarrow$ 6p $^2P_{1/2}$ 194.2 nm line could be used to cool the ions. All of the ground-state sublevels would have to be rf-mixed, in order to permit cyclic interaction with the laser. Essentially all of the ions could then be pumped into the $(F, M_F) = (1,1)$ sublevel by leaving it unmixed by the rf. The laser and mixing rf could then be shut off, and the $(1,1) \rightarrow (2,1)$ transition driven. The number of ions that made the transition could be determined by turning the laser on, rf-mixing all but the (1,1) sublevel, and counting the scattered photons. In order to keep the second-order Doppler shift below 10^{-15}, the "temperature" must be kept below 1.45 K. This should be easy for the cyclotron and axial modes, but the space-charge-induced magnetron velocity is a problem for a large cloud of ions. If the shift is to be kept below 10^{-15}, and the ions are to be contained within a 1 cm diameter spherical volume, the maximum number of ions is about 8.2×10^4. All other systematic shifts, such as those due to collisions, the trap fields, or thermal radiation, appear to be much less than 10^{-15}. For an interrogation time of 50 s, a Q of 2.6×10^{12} would be obtained using the Ramsey method. With 8.2×10^4 ions and a signal-to-noise ratio limited only by statistical fluctuations in the number of ions that make the transition, the fractional frequency uncertainty for measurement time, τ, is calculated to be $\sigma_y(\tau) \simeq 2 \times 10^{-15} \tau^{-1/2}$ for $\tau > 100$ s. Actual short-term stability may be limited by available local oscillators.

Various possibilities exist for the required 194.2 nm source. One is a narrowband, high repetition rate ArF* excimer laser. Another, which is being pursued at NBS, is sum-frequency mixing in a KB5 crystal of the output of a single-mode 790 nm cw ring dye laser and the second harmonic, generated in an ADP crystal, of the output of a 514 nm stabilized, single-mode cw Ar^+ laser. The basic method has been demonstrated previously with pulsed lasers [21].

3.2 Optical Frequency Standard

It has previously been pointed out that the two-photon-allowed $5d^{10}$ 6s $^2S_{1/2} \rightarrow 5d^9$ $6s^2$ $^2D_{5/2}$ Hg^+ transition, which has a Q of 7.4×10^{14}, could be used in an optical frequency standard [22]. The first-order Doppler effect can be eliminated by driving the transition with counter-propagating 563.2 nm laser beams. Hyperfine-Zeeman components whose magnetic field derivatives vanish at particular values of B_0 exist in $^{199}Hg^+$ and $^{201}Hg^+$. The fractional frequency shifts are much smaller than for the microwave frequency standard for the same fractional change in B_0. The second-order Doppler shift can be reduced to the same degree as for the microwave standard by cooling with a 194.2 nm laser. The two-photon transition can be detected with high efficiency by a change in the 194.2 nm fluorescence intensity. Taking full advantage of the high Q transition would require a laser with a linewidth of less than 1 Hz, which does not exist at present. However, linewidths ≃100 Hz appear feasible and could be used for initial experiments. The largest systematic shift appears to be the ac Stark shift due to the 563.2 nm laser beams. If the laser linewidth is less than the natural linewidth, and the transition is near saturation, this shift is about 2×10^{-15}. Assuming ideal lasers are available, the stability of this standard is calculated to be $\sigma_y(\tau) \simeq 2 \times 10^{-18} \tau^{-1/2}$ for 8.2×10^4 ions and $\sigma_y(\tau) \simeq 6 \times 10^{-16} \tau^{-1/2}$ ($\tau \gtrsim 1$ s) for a single ion.

References

[1] H. A. Schuessler, E. N. Fortson, and H. G. Dehmelt, Phys. Rev. **187**, 5 (1969).
[2] F. G. Major and G. Werth, Phys. Rev. Lett. **30**, 1155 (1973); Appl. Phys. **15**, 201 (1978).
[3] M. D. McGuire, R. Petsch, and G. Werth, Phys. Rev. A **17**, 1999 (1978).
[4] M. Jardino and M. Desaintfuscien, IEEE Trans. Instrum. Meas. **IM-29**, 163 (1980); M. Jardino, M. Desaintfuscien, R. Barillet, J. Viennet, P. Petit, and C. Audoin, Appl. Phys. **24**, 107 (1981).
[5] R. Blatt and G. Werth, Z. Phys. **299**, 24 (1981); these Proceedings.
[6] D. J. Wineland, R. E. Drullinger, and F. L. Walls, Phys. Rev. Lett. **40**, 1639 (1978).
[7] R. E. Drullinger, D. J. Wineland, and J. C. Bergquist, Appl. Phys. **22**, 365 (1980).
[8] D. J. Wineland, J. C. Bergquist, W. M. Itano, and R. E. Drullinger, Opt. Lett. **5**, 245 (1980).
[9] D. J. Wineland and W. M. Itano, Phys. Lett. **82A**, 75 (1981).

[10] W. M. Itano and D. J. Wineland, Phys. Rev. A, **24**, 1364 (1981).
[11] W. Neuhauser, M. Hohenstatt, P. E. Toschek, and H. Dehmelt, Phys. Rev. Lett. **41**, 233 (1978); Appl. Phys. **17**, 123 (1978); Phys. Rev. A **22**, 1137 (1980).
[12] H. Dehmelt, in *Advances in Atomic and Molecular Physics*, Ed. by D. R. Bates and I. Estermann (Academic Press, New York, 1967), Vol. **3**, p. 53; Vol. **5**, p. 109 (1969).
[13] D. J. Wineland, these Proceedings.
[14] T. W. Hänsch and A. L. Schawlow, Opt. Commun. **13**, 68 (1975).
[15] D. J. Wineland and W. M. Itano, Phys. Rev. A **20**, 1521 (1979).
[16] W. M. Itano and D. J. Wineland, Phys. Rev. A **25**, 35 (1982).
[17] D. J. Wineland, W. M. Itano, J. C. Bergquist, and F. L. Walls, Proc. 35th Ann. Symp. on Freq. Control (U.S. Army Electronics Command, Fort Monmouth, NJ, 1981).
[18] H. Dehmelt, Bull. Am. Phys. Soc. **20**, 60 (1975).
[19] N. F. Ramsey, *Molecular Beams*, (Oxford University Press, London, 1956).
[20] M. D. McGuire, Bull. Am. Phys. Soc. **26**, 615 (1981).
[21] R. E. Stickel and F. B. Dunning, Appl. Opt. **17**, 981 (1978).
[22] P. L. Bender, J. L. Hall, R. H. Garstang, F. M. J. Pichanick, W. W. Smith, R. L. Barger, and J. B. West, Bull. Am. Phys. Soc. **21**, 599 (1976).