# SPECTROSCOPY OF STORED ATOMIC IONS

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## I. INTRODUCTION

In this paper, we briefly review measurements of atomic ion spectra made with the stored ion technique in the last few years. By design, its scope is limited; for example, in these proceedings G. Werth will review experiments specifically relating to high resolution microwave spectra of stored ions and R. S. Van Dyck Jr. and D. A. Church will discuss applications of the stored ion technique to g-2 measurements and collision studies respectively. We will also omit the interesting excited state lifetime measurements made using traps[1-3] and measurements of molecular spectra[3]. More comprehensive reviews are given elsewhere[3-16]; we also refer the reader to the abstracts for this conference.

The ion storage technique for studies of atomic spectra is actually quite general and could in principle be used on all atomic and molecular ions; in practice, however, we find that its applicability is more limited. The number of ions that can be stored is typically rather small (densities $\lesssim 10^6/cm^3$, trap volume $\lesssim 10\ cm^3$) and therefore the signal to noise ratio in many experiments is rather small. This problem is compounded if the ion population is distributed over many states as in the case of molecules, but in spite of these difficulties, trapped molecular ion spectra have been obtained by laser induced fluorescence[3]. The low densities of course yield the main advantage of the technique - that is, the perturbations on the ions' internal structure (due to ion-ion collisions for example) are extremely small. This coupled with long storage times and methods for obtaining cold samples can lead to very high resolution and accuracy.

## II. TRAPPING

The basic methods of trapping have been discussed in the various reviews referred to in the introduction. The Paul (or rf) trap is the most popular method; both it and the Penning trap can provide very long trapping times (> hours). The Kingdon trap is finding increased use (partially because of its simplicity) but the

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magnetostatic trap or magnetic bottle has not been used very much in spectroscopy because of the inhomogeneous fields required for trapping. Combinations of the above traps have been studied but not extensively used. A summary of trap methods has been given in a recent review[3] and in other papers in these proceedings.

## III. STATE PREPARATION AND DETECTION

### Optical Pumping/Double Resonance

In the past several years the dominant method of state selection and detection of stored atomic ions has been via optical means. More conventional optical pumping and detection with lamps[17] and lasers[18] has been used for example to measure hyperfine spectra[19]. In addition, some novel optical pumping and detection effects have been realized using lasers with trapped ions; we illustrate this with a few examples.

In Fig. 1, we show the $3^2S_{1/2}$ and $3^2P_{3/2}$ level structure of $^{24}Mg^+$ ions in a magnetic field. If a laser is tuned to the (-1/2) → (-3/2) transition (numbers in parentheses refer to the ground $3^2S_{1/2}$ and excited $3^2P_{3/2}$ values of $M_J$ respectively) then we note that ions must decay to the $M_J$ = -1/2 ground level because of the selection rule $\Delta M_J = 0,\pm1$. At first, one might think that after many photon scattering events the ions are gradually pumped from the $M_J$ = -1/2 to $M_J$ = +1/2 ground state level because of excitation in the wings of

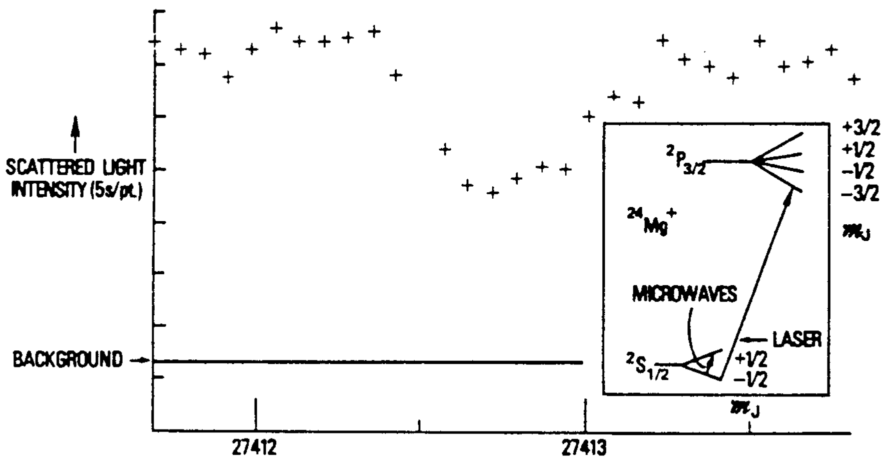


Fig. 1. Microwave/optical double resonance spectrum of $^{24}Mg^+$. Inset shows relevant energy levels of $^{24}Mg^+$ in a magnetic field. With the laser tuned to the transition shown, 16/17 of the ions are pumped into the $^2S_{1/2}$ ($M_J$ = -1/2) ground state and a quasi two level system is formed 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 state Zeeman transition, these levels are nearly equally populated which causes a decrease in fluorescence scattering from the ions. Transitions in other ions can be detected in a similar way. (From ref. 20).

other allowed transitions (Assume the laser is linearly polarized perpendicular to the magnetic field so that only $\Delta M_J = \pm 1$ transitions are allowed). In fact just the opposite occurs. Although excitation in the wings of the (-1/2) → (+1/2) transition pumps ions out of the (-1/2) ground state, excitation in the wings of the (+1/2) → (-1/2) transition also occurs which tends to pump ions from the (+1/2) to (-1/2) ground state. Since this latter transition is four times closer in frequency to the laser than the former one, the net result is that about 16/17 of the population is pumped into the (-1/2) ground state.[20] This pumping is very weak, but because of the very long relaxation times of the ions in the trap it can be very efficient. Similar optical pumping can also be observed when hyperfine structure is present; for example[21], in the case of $^{25}Mg^+$ and $^9Be^+$. Novel hyperfine pumping effects have also been observed[22] in the excited $^3S_1$ states of $Li^+$. This kind of pumping is far from universal. For example "depopulation" pumping occurs if one excites any of the $3^2S_{1/2} \rightarrow 3^2P_{1/2}$ transitions in $^{24}Mg^+$. In this case, which is perhaps more typical, one must redistribute or mix the ground state population in order to see additional scattering from the laser. In this instance one of the advantages of the traps for high resolution spectroscopy (weak relaxation) becomes a disadvantage in terms of observation. Solutions to this problem are: (1) provide a buffer gas for relaxation. For example, Ruster et al.[23], observed fluorescence from single $Ba^+$ ions in an rf trap by relaxing the ions against an $H_2$ buffer gas. (2) If the number of ground (and metastable) states is not too large, artificial relaxation can be provided by auxiliary microwave or laser radiation.

This kind of pumping described above is important for laser cooling and also establishes a population imbalance necessary to observe other internal transitions in the ions. In the $Mg^+$ example above, if the scattered fluorescence light from the ions is monitored, the ($M_J = -1/2$) to ($M_J = +1/2$) ground state Zeeman transition (induced by microwave radiation) can be detected by observing the decrease in fluorescence as the microwave oscillator is swept through resonance. (Fig. 1) An interesting feature of this optical pumping, double resonance detection scheme is that each microwave photon absorbed causes a change of about $\Delta N^* = 24B(-1/2,-3/2)/17B(-1/2,+1/2)$ in the number of scattered photons where $B(M_J,M_J')$ is the transition rate from the $M_J$ ground state to the $M_J'$ excited state.[20] For $Mg^+$ ions in a magnetic field of about 1 T, $\Delta N^*$ can be as high as $2 \times 10^6$. This technique has sometimes been referred to as "electron shelving" because the ion's electron is temporarily "shelved" in a state from which the laser scattering is essentially absent.[7] It has been used in all the optical pumping double resonance experiments on $Mg^+$ and $Be^+$ ions stored in Penning traps. Not only is the detection sensitivity increased by this photon number amplification effect but also by the photon energy upconversion. Perhaps noteworthy is the case of detecting absorbed 303 MHz photons in $Be^+$ hyperfine transitions (see below) where an energy enhancement factor of $\Delta N^* \lambda(303\ \mathrm{MHz})/\lambda(\mathrm{laser}) > 10^{12}$ is obtained. These impressive numbers are of course not realized in practice since fluorescence collection efficiencies are typically significantly less than 100%. However, a more important statement is that if (the absence of) enough scattered photons per ion (typically $\gtrsim 2$) are <u>observed</u> before repumping takes place, then the signal to noise ratio in such experiments need only be limited by the statistical fluctuations in the number of ions that make the transition[24]. This is the maximum signal to noise ratio possible.

Because of the extremely high detection sensitivity in such quasi-two level systems, the ability to detect very small numbers of ions exists; in fact single ions have been detected by several groups[23,25-28]. This is perhaps not so surprising if we consider for example a $Mg^+$ ion which is cooled down (see below) to where the Doppler broadening is smaller than the natural width and is localized to say less than a few μm in the trap. In this case, a 0.05 μW laser beam ($\lambda$ = 280 nm) focused to a beam waist $\omega_o$ = 5 μm can scatter about $10^7$ photons/s - an easily detectable signal even with modest collection efficiency.

Recently, another interesting optical pumping scheme has been developed for trapped negative ions[29-31]; here a population imbalance in Zeeman substates has been created using polarization dependent photodetachment. In these experiments, changes in trapped ion number were detected by driving the ion motions and detecting the induced currents. This method of state selection and detection is similar to that used in past experiments on $H_2^+$ where polarization dependent photodissociation was employed[5].

## Cooling

The technique of radiation pressure[32] or sideband[33] cooling was first demonstrated[34,35] in 1978 (see also refs. 27 and 36). It has become a key element in experiments whose goal is high resolution spectroscopy because both first and second order Doppler effects are suppressed. Frequency shifts in spectra due to the second order Doppler effect (time dilation of the ions which are moving with respect to the lab) have historically been the main limitation to obtaining high accuracy because of the relatively high temperatures of the ions in the trap - up to about 1 eV for ions in an rf trap. A kinetic energy of 1 eV for ions with mass M = 50 u (atomic mass units) yields a fractional second order Doppler frequency shift of 2 x $10^{-11}$. The kinetic energy of the ions can be determined by observing first order Doppler effect generated sidebands in microwave spectral lines[37-42]. It can be reduced by cooling the ions with a light buffer gas such as He[4,5,7,23,43-51]. With these techniques, accuracies near one part in $10^{13}$ should be obtained[40,42] but if one hopes to obtain an accuracy significantly better than the best existing frequency standards ( a few parts in $10^{14}$ for cesium beams) laser cooling may be necessary.

The best experimental results on laser cooling (and those most easily compared to theory) have been obtained using single ions. This is because for many trapped ions, rf heating in Paul traps (due to the driven motion) and the kinetic energy in the magnetron motion for Penning traps gives rise to higher effective temperatures. In the first single ion experiments, done at Heidelberg on $Ba^+$ ions, photographs were made of the trapped ion[25]. 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 kinetic energy in the driven motion will be approximately the same[4,52]. Laser cooling of single $Mg^+$ ions in Penning[26] and rf[27] traps has also been accomplished. The lowest temperatures measured are those of the Seattle group[27] where the temperature for at least two directions of the pseudopotential motion was determined to be less than 20 mK (Fig. 5). (Cooling in all directions will be straightforward). In both of the magnesium experiments, the temperature was determined from the observed Doppler broadening on optical transitions. For temperatures below about 0.1 K this Doppler broadening contributes only a small part of the total linewidth which is now primarily due to radiative decay. Therefore, very low temperature becomes difficult to measure. In the future this problem can be circumvented by measuring the first order Doppler effect generated sidebands in optical spectra as was done for microwave spectra above. In any case, for $Mg^+$ ions cooled to 20 mK, the second order Doppler effect is only about 2 parts in $10^{16}$!

The theory of laser cooling of trapped ions has been elaborated for a large number of cases, starting with the original proposal[33], which introduced the "optical sideband" picture. Calculations based on this picture are included in refs. 25, 35, and 53. The fundamental process is the absorption of a photon with frequency less than that of an optical transition, followed by the emission of a photon whose frequency, on the average, is about equal to the transition frequency, the deficit coming out of the kinetic energy of the ion. Some of the more recent general discussions of the state of the theory are given by Javanainen[54] and Stenholm[55]. For reasons of theoretical simplicity, the ions are usually considered to be two-level systems confined by harmonic potentials, and interactions between ions are generally ignored. This situation corresponds fairly closely to the experiments carried out with a single ion in an rf trap.

Of particular interest from an experimental point of view is the Lamb-Dicke regime or limit, which corresponds to the ion being confined to dimensions much less than an optical wavelength. In this limit, the broadening of the optical transition due to the first-order Doppler effect disappears.

Wineland and Itano[53] calculated cooling rates and limiting temperatures using perturbation theory and rate equations. They considered the limiting cases of the trap oscillation frequency being much greater than or much less than the natural linewidth ($\gamma$) of the optical transition, calling them the "strong binding" and "weak binding" cases, respectively. Experiments, so far, correspond to the weak binding case. In this limit, the minimum temperature is on the order of $\hbar\gamma/2k_B$. They also treated laser cooling in a Penning trap for the weak binding case and compared the results with experiment[56]. All of these calculations were limited to low laser intensities.

André et al.[57] calculated numerically the equilibrium energy distributions for the weak binding case. In later work[58], the kinetic energy due to the micromotion in an rf trap was included, using a semiclassical method.

In a series of papers, Javanainen and Stenholm[59-61] and Javanainen[62-64] have used quantum statistical methods to study various limiting cases. The Fokker-Planck equation for the Wigner function was solved in the "heavy particle" limit, which corresponds roughly to the weak binding case, for one-dimensional[59] and three-dimensional[62] traps. The "fast particle" limit, which corresponds to high excitation of the ionic motion, was treated by solving a Fokker-Planck equation in the n (harmonic oscillator quantum number) representation, for both the strong binding and weak binding cases[60]. The Lamb-Dicke limit was treated by solving the coupled rate equations for the populations, for both the strong binding and weak binding cases[61]. Recently, results have been obtained for the steady state[65] and the dynamics[66], which are exact in the Lamb-Dicke limit. These results extend and correct the earlier work.

Laser Sources

A troublesome obstacle that is generally encountered in optical studies of atomic ions is the radiation source. This is because the wavelength of the requisite radiation frequently lies in the ultraviolet (UV). While reliable continuous-wave (cw) lasers are readily available throughout the visible, there are but a few cw lasers in the U.V. region. Presently, most of the narrowband cw UV sources are generated by some nonlinear process that requires high powers at the fundamental wavelength(s) in order to reach useful levels of UV power. And so it is only with the development of high power tunable dye lasers and power enhancement cavities that narrowband and tunable UV sources with useable powers are possible[67]. Fortunately, very little power is required to radiatively cool ions that are confined in electromagnetic traps at high vacuum; usually no more than several microwatts.

At present the most prominent method of generating UV radiation is by the interaction of high power laser radiation with an optically transparent material presenting a non-linear response. The two dominant methods are second harmonic generation (SHG), which is the doubling of laser radiation, and sum frequency mixing (SFM), which is the generation of a higher frequency source by the mixing of the outputs of two lower frequency lasers[71]. The phase matching condition

$$n_3\omega_3 = n_1\omega_1 + n_2\omega_2$$

must be met in order to efficiently produce radiation at $\omega_3$ by mixing lasers at frequencies $\omega_1$ and $\omega_2$ ($\omega_3 = \omega_1+\omega_2$). $n_i$ is the refractive index of the nonlinear medium for the frequency $\omega_i$. For second harmonic generation, $\omega_1 = \omega_2$ and the phase matching condition reduces to $n(\omega) = n(2\omega)$. Since all optical materials have spectral dispersion, properly oriented uniaxial or biaxial crystals are required to satisfy the phase matched condition to give efficient mixing. In experiments on the ions $Mg^+$ and $Be^+$, tunable UV radiation has been generated near the first resonance lines (280 nm & 313 nm respectively) by SHG in KDP isomorphs (AD*P & RDP respectively). These crystals were temperature tuned to phase match the UV and fundamental indices (90° phase matched). In both cases the conversion efficiency exceeded $5 \times 10^{-4}$ $W^{-1}$ so that tens of microwatts of UV radiation could be obtained by single-passing the light from the tunable dye laser through the crystal. For radiation pressure cooling and optical pumping of trapped mercury ions, narrowband and tunable radiation near the 6s $^2S_{1/2}$ - 6p $^2P_{1/2}$ first resonance line at 194 nm is required. One method for producing cw radiation at 194 nm is by SFM in a potassium pentaborate (KB5) crystal, the 257 nm second harmonic of the output of a cw 515 nm argon-ion laser with the output of a tunable cw dye laser in the 792 nm region[68] (Fig. 2). The 257 nm second harmonic is generated in a ADP crystal that is placed in an external ring cavity which is held in resonance at the fundamental frequency[69]. To amplify the 194 nm power, the KB5 crystal is placed into two intersecting power enhancement cavities. One of these cavities increases by 15 the circulating 792 nm power and the second cavity increases by 7 the 257 nm power. By this method 8-10 microwatts of tunable cw 194 nm power has been generated. Thermal lensing caused by heating in the KB5 crystal due to absorption of light at 792 nm is the present limit to achieving higher powers at 194 nm[70].

Sympathetic Cooling

So far, optical pumping and laser cooling have been achieved on only a few different ions. Laser cooling could be extended to certain other ions but in practice this may be difficult to accomplish because of the required laser wavelengths or "trapping" in metastable states. Ions which are difficult to cool directly can be cooled by collisional coupling with other stored ions which are easy to cool[34]. This has been demonstrated[72] in experiments on $Mg^+$ where $^{24}Mg^+$ was laser cooled and by collisions "sympathetically" cooled $^{25}Mg^+$ and $^{26}Mg^+$. (We note that in subsequent experiments at NBS, it was possible to sympathetically cool $^{24}Mg^+$ by laser cooling $^{25}Mg^+$; this result is more definitive because the laser was tuned to the heating side of the $^{24}Mg^+$ transition.) For ions in a Penning trap, lighter ions should be held near the center of the trap by heavier ions which are laser cooled [73]. Qualitatively, this should occur because the magnetron frequency is slightly higher for heavy mass

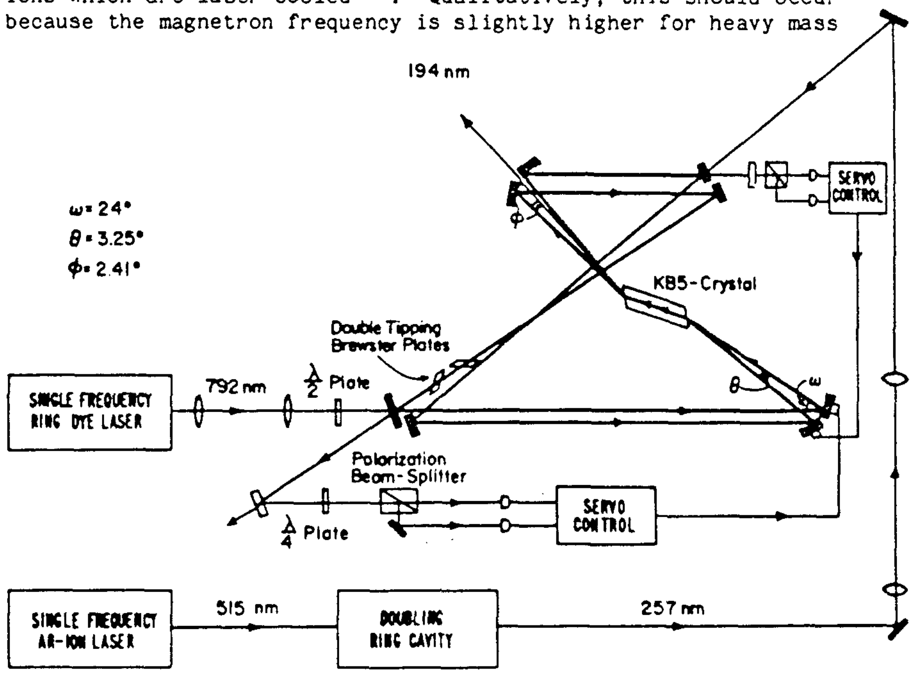


Fig. 2. 194 nm laser source. (From ref. 68)

ions; this causes a friction force on the lighter ions which should push them towards the center of the trap[56,73]. At low temperatures, the separation between species should be nearly complete[73]. As an example, spectroscopy could be done on $^9Be^+$ ions which are held at the center of the trap and sympathetically cooled by an outer annulus of $^{24}Mg^+$ ions which are laser cooled. The cooling laser could be applied so that it would not spatially overlap the $^9Be^+$ ions and therefore light shifts on the $^9Be^+$ energy levels could be avoided. In this way, extremely narrow linewidths (<< 1 mHz) and high accuracy spectra on $Be^+$ (or other ions) might be obtained. For ions in an rf trap, sympathetic cooling may be limited by rf heating.

## IV. rf AND OPTICAL SPECTRA

### Radiofrequency Spectra

The ion storage method is capable in principle of achieving extremely narrow resonance linewidths on either rf or optical transitions. It is much easier experimentally to observe narrow lines on rf transitions because the natural linewidths are negligible and because stable, tunable oscillators are readily available. Sub-hertz linewidths on hyperfine transitions have been observed on several different atomic ions.

Early work on the hyperfine structures of $H_2^+$ and the 1s and 2s states of $^3He^+$ has been reviewed previously[5,6]. Recent work on the determination of ground state hyperfine structure separations by microwave-optical double resonance is reviewed elsewhere in these Proceedings[19]. We restrict our discussion to studies of negative ions and to the high-accuracy work at the National Bureau of Standards (NBS) on laser cooled ions.

Microwave spectra of negative atomic ions have been obtained in a series of experiments by Larson and coworkers. These experiments were carried out with Penning traps in magnetic fields of about 1 T. State preparation and detection were carried out by utilizing the polarization dependence of the photodetachment cross section. Microwave transitions between Zeeman components of the ground $^2P_{3/2}$ states of $^{32}S^-$ and $^{16}O^-$ were observed[29,30] (Fig. 3). The observable transitions were from $M_J = +1/2$ to $M_J = +3/2$ and from $M_J = -1/2$ to $M_J = -3/2$. The two transition frequencies are separated due to the perturbation by the $^2P_{1/2}$ state. The average of the two transition frequencies yields the atomic $g_J$ factor, while the frequency splitting yields an indirect value for the fine structure separation. The magnetic field was calibrated by detecting the cyclotron resonance of electrons in the same trap. The accuracy obtained for the $g_J$ factors was sufficient to show the deviations from the Landé value after correction for the anomalous moment of the electron. In further studies, different $M_I$ components of the $M_J = -3/2$ to $M_J = -1/2$ transition in the $^2P_{3/2}$ state of $^{33}S^-$ were observed[31]. The dipole and quadrupole hyperfine parameters were determined from the frequency splittings.

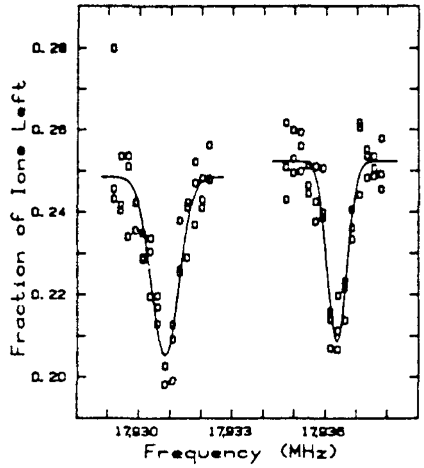


Fig. 3. Microwave resonances between magnetic sublevels of the $^2P_{3/2}$ ground state of $^{32}S^-$ at about 0.96 T. (From ref. 29).

The ground state hyperfine constants (A) and nuclear-to-electronic g factor ratios ($g_I/g_J$) of $^{25}Mg^+$ and $^9Be^+$ have been measured with high accuracy in a series of experiments at NBS. In these experiments, the ions were stored for long periods (hours) in Penning traps. The ions were optically pumped and laser cooled by light from a frequency-doubled dye laser. Radiofrequency transitions between ground-state hyperfine Zeeman sublevels were detected by a change in the fluorescence intensity. In most cases, the resonances are broadened by magnetic field instabilities and inhomogeneities. However, for certain transitions, and at certain values of the magnetic field, the first derivatives of the transition frequencies with respect to the field are zero. If the magnetic field is sufficiently close to one of these values, a resonance can be observed with a linewidth limited only by the finite observation time.

In $^{25}Mg^+$, the first derivative of the ($M_I$ = -3/2, $M_J$ = 1/2) to ($M_I$ = -1/2 , $M_J$ = 1/2) transition goes to zero at a value of the magnetic field near 1.24 T. Near this field, a resonance with a width of 0.012 Hz and a center frequency of 291.996 251 899(3) MHz was observed[21] (Fig. 4). A and $g_I/g_J$ were determined with much less accuracy, because the other transitions observed were field-dependent. The results are A = -596 254 376(54) Hz and $g_I/g_J$ = 9.299 484(75) x $10^{-5}$.

Similar spectroscopy has been performed with $^9Be^+$ ions with an even higher degree of accuracy[75]. Two field-insensitive transitions have been observed. They are ($M_I$ = -3/2, $M_J$ = 1/2) to ($M_I$ = -1/2, $M_J$ = 1/2) at about 0.82 T and ($M_I$ = 3/2, $M_J$ = -1/2) to ($M_I$ = 1/2, $M_J$ = -1/2) at about 0.68 T. The first of these has been used as a reference for a frequency standard. The results for the constants are A = -625 008 837.048(4) Hz and $g_I/g_J$ = 2.134 779 853(1) x $10^{-4}$. The accuracy of these constants is currently limited by the theoretical uncertainty of the diamagnetic shift of the hyperfine structure. The determination of the actual values (as opposed to the ratios) of the g factors by measuring the cyclotron frequency of the ions is discussed in the section on mass spectroscopy.

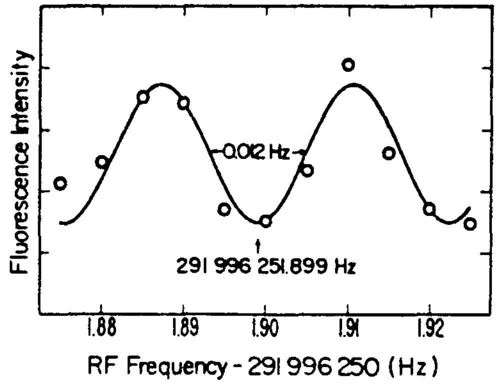


Fig. 4. The ($M_I$ = -3/2, $M_J$ = 1/2) to ($M_I$ = -1/2, $M_J$ = 1/2) resonance in $^{25}Mg^+$ at about 1.24 T. The oscillatory lineshape results from the use of the Ramsey separated oscillatory field method, implemented by applying two phase-coherent rf pulses 1.02 s long, separated by 41.4 s. (From ref. 21).

The repeatability from run to run of the frequency standard based on the $^9Be^+$ hyperfine transition is less than 1 part in $10^{13}$. Possible sources of systematic errors have been carefully investigated. At present, the largest source of error is the second-order (relativistic time dilation) shift, equal to $-(1/2)\langle v^2\rangle/c^2$. While the cooling laser is on, this shift is only about $-3 \times 10^{-15}$. However, the light and the state-preparation microwaves must be shut off while the rf resonance is driven, in order to prevent resonance shifts and broadenings. The ions heat up during this period, which is typically 20 s. The average shift is about $-3 \times 10^{-13}$ and can be calibrated by optical Doppler width measurements of the ion temperature. The magnetic field instability of a few parts in $10^6$ leads to a random error of about $3 \times 10^{-14}$. Shifts due to thermal radiation, electric fields, and microwave switch leakage are estimated to be below $10^{-14}$. Shifts due to collisions with residual gas molecules are estimated to be below $10^{-15}$. A light shift can exist, even though the light is shut off during the rf resonance period, if coherence survives the optical pumping period. In order to eliminate a shift of this type, the rf phase is randomized before the beginning of each rf resonance period.

Even better frequency standard performance might be expected if a hyperfine transition in $^{201}Hg^+$ were used, because of the higher transition frequency[24]. As a preliminary step toward this goal, the ground-state Zeeman resonance of $^{198}Hg^+$ ions stored in a Penning trap has been observed at NBS by microwave-optical double resonance. The value obtained for the g factor is 2.003 1743(74), which agrees with a theoretical calculation[131].

Optical Spectra

In this section we review optical spectroscopy that has been performed with atomic ions in traps. Very few such studies have been performed, if spectroscopy is narrowly defined as the determination of energy level separations. The first observation of laser-induced fluorescence of trapped ions was made by Iffländer and Werth[18]. They observed the 493 nm 6 $^2S_{1/2}$ to 6 $^2P_{1/2}$ (D1) line of $Ba^+$ ions in an rf trap, using a pulsed tunable dye laser as a source. In later work, they observed a saturation dip in the D1 fluorescence when the ions were illuminated by counterpropagating laser beams[76]. This feature is not broadened nor shifted by the first-order Doppler effect. The hyperfine splitting of the D1 line of the $^{137}Ba^+$ isotope was resolved by Blatt et al.[77]. The average kinetic energy of the trapped ions in these experiments was a few eV, so the first-order Doppler broadening was large (typically about 5 GHz).

Experiments at several laboratories have now demonstrated the Doppler narrowing that can be achieved by laser cooling[14,27,36,72]. We note again that laser cooling, unlike some other Doppler reduction techniques, can be used to eliminate second-order as well as first-order Doppler effects. Optical transitions have been observed for which the widths are dominated by the natural linewidths, due to the reduction of the first-order Doppler broadening by laser cooling. This degree of line narrowing has been observed on single $Mg^+$ ions in a Penning trap at NBS[26] and on single $Mg^+$ and $Ba^+$ ions in rf traps at the University of Washington (U.W.)[27,28]. The U.W. group obtained a value for the natural linewidth of the 280 nm 3 $^2S_{1/2}$ to 3 $^2P_{3/2}$ (D2) line, which agreed with previously published Hanle-effect measurements, by fitting the observed resonance profiles. (Fig. 5)

A narrow spectral feature in a single, trapped $Ba^+$ ion due to two-photon excitation of the 6 $^2S_{1/2}$ - 6 $^2P_{1/2}$ - 5 $^2D_{3/2}$ Raman resonance was first observed in experiments at the University of Heidelberg[14]. This feature is potentially very narrow, since its natural linewidth is on the order of the inverse of the 5 $^2D_{3/2}$ lifetime, which has been measured to be 17.5 (4.0) s[78].

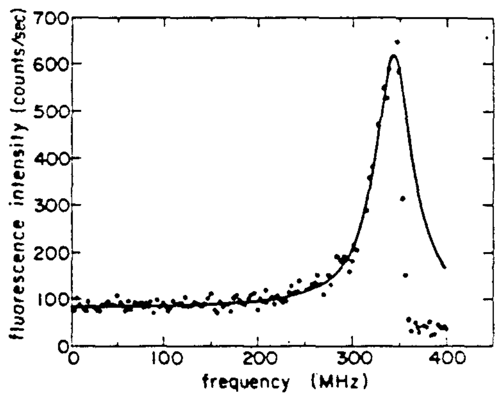


Fig. 5. Fluorescence of a single laser-cooled $^{24}Mg^+$ ion in an rf trap as a function of the relative optical frequency. The sharp decrease in signal above the line center is due to laser-induced heating. The fitted linewidth is equal to the natural linewidth to within the measurement error. (From ref. 27)

In recent work at U.W. this feature has been observed with greatly increased resolution[28]. In these experiments, the blue (493 nm) laser is tuned to the low side of the 6 $^2S_{1/2}$ to 6 $^2P_{1/2}$ transition and the red (650 nm) laser is swept across the 5 $^2D_{3/2}$ to 6 $^2P_{1/2}$ transition while fluorescence at the blue wavelength is observed. What is observed is a broad resonance due to the one-photon transition centered at the 5 $^2D_{3/2}$ to 6 $^2P_{1/2}$ transition with a narrow dip which occurs at the two-photon resonance (i.e., when the frequency difference between the blue and red lasers is equal to the 6 $^2S_{1/2}$ to 5 $^2D_{3/2}$ transition frequency). The two-photon resonance is broadened, but to a high degree not shifted by the laser intensities[132]. The observed linewidth of the dip is about 5 MHz and is due to the laser frequency widths. This is less than the natural linewidth of the 6 $^2P_{1/2}$ state, which is about 21 MHz. This type of two-photon resonance has been observed previously in other atomic systems[79].

The isotope and hyperfine shifts of the D2 line of $Mg^+$ were measured in experiments at NBS[72]. In these experiments, which were carried out in a Penning trap, one laser was tuned to the low side of the $^{24}Mg^+$ component, to continuously cool the ion cloud, while the fluorescence induced by a lower-power laser was observed as its frequency was swept. Laser cooling was particularly useful for this measurement because it allowed full resolution of the optical isotope structure which is normally obscured by the room temperature Doppler width. These measurements are in agreement with those made by other methods.

The first measurement of the magnetic dipole hyperfine constant of the 2 $^2P_{1/2}$ excited state of $^9Be^+$ was made recently at NBS[75,80].

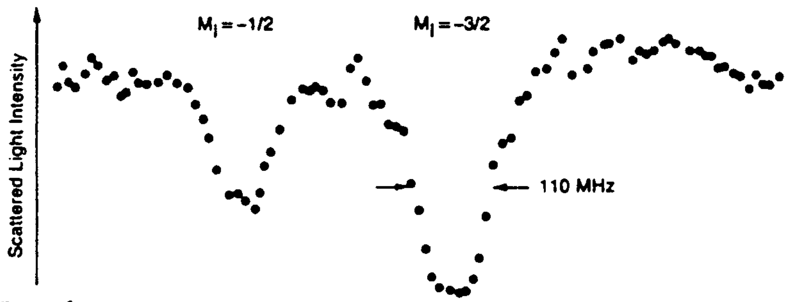


Fig. 6. Optical-optical double resonance signals corresponding to the 2 $^2S_{1/2}$ ($M_I$ = -3/2, $M_J$ = -1/2) to 2 $^2P_{1/2}$ ($M_I$ = -3/2, $M_J$ = +1/2) and the 2 $^2S_{1/2}$ ($M_I$ = -1/2, $M_J$ = -1/2) to 2 $^2P_{1/2}$ ($M_I$ = -1/2, $M_J$ = +1/2) transitions at about 1.14 T in a cloud of laser-cooled $^9Be^+$ ions. The signal observed is the fluorescence due to a laser tuned to the 2 $^2S_{1/2}$ ($M_I$ = -3/2, $M_J$ = -1/2) to 2 $^2P_{3/2}$ ($M_I$ = -3/2, $M_J$ = -3/2) transition as a function of the frequency of another, lower-power laser. Note that the room temperature Doppler width would be about 4 GHz. (From ref. 80)

The ions were confined in a Penning trap at a magnetic field of about 1.14 T and laser-cooled to about 0.5 K by excitation of a hyperfine-Zeeman component of the 313 nm $2\ ^2S_{1/2}$ to $2\ ^2P_{3/2}$ (D2) line with a frequency-doubled dye laser. Several hyperfine-Zeeman components of the $2\ ^2S_{1/2}$ to $2\ ^2P_{1/2}$ (D1) line were probed with a second frequency-doubled dye laser (Fig. 6). The resonance frequencies of these components were measured by comparing the dye laser frequencies to the frequencies of $^{127}I_2$ hyperfine components. The relative frequencies of the $^{127}I_2$ components were determined by laser heterodyne measurements. The laser cooling was required in order to resolve the hyperfine components of the D1 line. The value obtained for $A(2\ ^2P_{1/2})$ was -118.3(3.6) MHz, which is in good agreement with theoretical calculations.

Certainly, the few experiments described here have only just begun to exploit the possibilities for high resolution optical spectroscopy with trapped ions. The fundamental advantages are the same as for microwave spectroscopy (long observation times with small perturbations and elimination of Doppler effects by laser cooling). There is the additional advantage of higher fractional resolution for a given measurement period, due to the higher transition frequencies.

## V MASS SPECTROSCOPY

In addition to the study of spectra due to the internal energy levels in atomic ions, the possibility also exists to perform mass spectrum analysis using the traps. The Paul (or rf) trap is the three dimensional analogue of the Paul rf quadrupole mass spectrometer which is commonly used for residual gas analysis. For high resolution studies, measuring mass ratios by comparing the cyclotron frequencies of different ions in the same magnetic field has been more successful.

For several years, trapped ion cyclotron resonance (ICR) spectrometers have been used by chemists to yield mass spectra[81-84]. Trapped ICR spectrometers are basically Penning traps with rectangular shaped electrodes. If semiempirical fits are made to the cyclotron resonances in order to account for ion number dependent effects such as space charge, mass determinations near 1 ppm accuracy are possible[85]. However, Penning traps with hyperbolic electrodes would seem to be better for very high resolution work for the following reason: To the extent that the electric potential inside the trap is quadratic and the magnetic field (B) homogeneous, the (modified) cyclotron, axial, and magnetron motions are harmonic (neglecting relativistic effects) and their frequencies ($\nu_c'$, $\nu_z$ and $\nu_m$ respectively) are related by[86]:

$$\nu_c^2 = \nu_c'^2 + \nu_z^2 + \nu_m^2. \qquad (1)$$

where $\nu_c$ is the "unmodified" cyclotron frequency in a magnetic field B. In principle, a quadratic electric potential is guaranteed if the electrodes are equipotentials of the function $\phi = A(r^2 - 2z^2)$. This case is more nearly satisfied for the Penning traps with hyperbolic electrodes than for the typical ICR cells. Therefore, we could expect higher resolutions and accuracy in the Penning traps because the higher order terms in the potential (which give rise to anharmonic frequency shifts and corresponding uncertainties) would be less. Additionally, sample sizes for ions and electrons in Penning traps can be quite small ($\ll mm^3$), therefore suppressing the effects of magnetic field inhomogeneities and electric field imperfections.

Five recent experiments have demonstrated the usefulness of the Penning trap for mass spectroscopy. In the three experiments of refs.87-89, direct measurements of the electron/proton mass ratio ($m_e/m_p$) were made by comparing the cyclotron frequencies of electrons and protons in the same Penning trap apparatus; this direct measurement of such widely different masses would be nearly impossible in a more conventional mass spectrometer[90].

These three experiments are very similar in principle; they differ in the method of detection. For example Gärtner and Klempt (2.9 ppm accuracy) detect electron/ion cyclotron resonance by measuring electron/ion loss from the trap after resonant excitation[87]. In the work of Gräff et al. (0.6 ppm accuracy), resonant excitation of electron/proton cyclotron motion is detected by the increase of the electron/proton orbital magnetic moment; this appears as a change in the time of flight spectrum when the electrons/protons are ejected out one endcap into an axially symmetric inhomogeneous magnetic field.

The most accurate measurements (0.04 ppm) are those of Van Dyck et al.[89,91]. This accuracy comes about primarily because the experiment is more sensitive to cyclotron excitation, therefore anharmonic and relativistic effects in the spectra are less. In this experiment, $\nu_c'$, $\nu_z$ and $\nu_m$ are separately determined yielding $\nu_c$ via Eq. 1. $\nu_z$ is measured by observing the spectrum of induced currents in the endcap electrodes. The proton cyclotron resonance is observed by splitting the ring electrode into quadrants, exciting the cyclotron motion by applying ac voltage across two of the quadrants and detecting the induced currents in the other two quadrants in a bridge arrangement. A resulting 76.4 MHz synchronously detected signal is shown in Fig. 7 where the line is only 0.2 Hz (2.5 ppb) wide. Recently linewidths on the order of 30 mHz have been observed[91]. Electron cyclotron resonance is detected using the magnetic bottle technique[92] and $\nu_m$ is measured via sideband structure on the $\nu_z$ and $\nu_c'$ spectra[89]. The present uncertainty in $m_e/m_p$ (0.04 ppm) is limited by the uncertainty in the respective positions of the electrons and protons (and therefore the respective average magnetic field) when they are alternately stored in the trap.

In the experiments of Wineland et al.[93], $\nu_c'$, $\nu_z$ and $\nu_m$ for $^9Be^+$ ions in a Penning trap were determined by observing the changes in ion fluorescence scattering from a laser beam which is focused onto the cooled ion cloud. That is, when the ion motional frequencies are excited by an externally applied oscillating electric field, the ion orbits increase in size causing a decrease in ion cloud/laser beam overlap which results in a decrease in laser fluorescence. In these experiments, the resulting value of $\nu_c$ (from Eq. 1) was compared to the $^9Be^+$ electron spin flip frequency to 0.15 ppm accuracy, limited by a rather large anharmonic term in the electric potential. This result could be viewed as giving an indirect measurement of $m_e/m_p$ (to 0.2 ppm) if a theoretical value of $g_J(^9Be^+)$ is assumed or it could be viewed as yielding a measurement of $g_J(^9Be^+)$ (to 0.15 ppm) by using the Van Dyck et al., measurement of $m_e/m_p$.

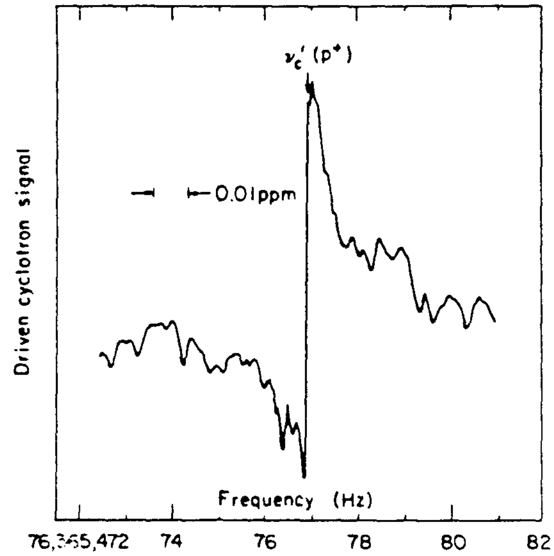


Fig. 7. Graph of proton cyclotron resonance in a Penning trap. This narrow dispersion-shaped curve is the result of direct synchronous detection of the resonance at $\nu_c'(p^+) = 76{,}365{,}476.9$ Hz using the split quadring design in a well-compensated Penning trap (for $V_0 = 54.4$ V). The linewidth, limited primarily by observation time, represents fewer than 40 protons. (From ref. 89)

In the experiments of Schwinberg et al.[94] the electron/positron mass ratio was measured to a precision of about 0.1 ppm. The cyclotron frequency detection method is the same as for the g-2 experiments.[92]

Discussion

It appears that several orders of magnitude improvement can be expected if the effects of magnetic and electric field imperfections can be reduced. (Relativistic effects can also be very important; see Van Dyck, these proceedings). Two ways this can be done are (1) directly reduce the field imperfections. Higher order terms in the electric potential can be reduced by using compensation electrodes and magnetic bottles could be eliminated[92]. One must worry about distortions of the magnetic field by the electrodes; these could be suppressed by appropriate machining[95]. (2) Increase the sensitivity to ion motion. If much smaller ion motions can be detected, the ions sample field imperfections to a lesser extent. These effects usually scale as some high power ($\geq 2$) of the ion amplitude so that improvement here could be substantial. (Frequency shifting effects of third and fourth order anharmonic terms have been discussed by Landau and Lifshitz[96]; these arguments can be extended to higher order terms). Ideally, one would like to use single ions at very low temperature since the extent of ion orbits can be extremely small. Detection sensitivity to induced currents can be increased by using SQUID amplifiers[97] and therefore can be extended to heavier ions (including molecular ions) which are more difficult to detect. Accuracies near 1 part in $10^{13}$ are not unrealistic for the laser fluorescence method[93]; this is primarily a statement that if the ions can be laser cooled, they can be confined (and detected) in extremely small regions of space where field imperfection effects are minimized.

For more than one ion in the trap, space charge effects can show up in several ways; for simplicity we only discuss the effect on the axial resonance here but similar arguments could be made for the other degrees of freedom. For a single ion species near the center of the trap where the coupling to the endcap electrodes for all ions is the same (i.e. the electric field from a voltage applied to one endcap is uniform over the cloud) no space charge shift in $\nu_z$ is observed since only the center of mass motion couples to the electrodes[98]. This was demonstrated in the work of Ref. 93 where for example, observed magnetron frequencies were consistent with the free space value (accuracy $\simeq$ 0.5%) but the magnetron frequency of individual ions was shifted by about a factor of 3 because of space charge[99]. If the cloud is spread out radially (e.g. shaped like a pancake whose diameter approaches the trap diameter) then the internal modes of oscillation in addition to the center of mass mode are observable because the z coupling to the endcaps depends on the ion's radius in the trap[100]. Internal modes also become observable if the ions are only weakly coupled together and the trap is imperfect so that for example $\nu_z$ depends on r. If two species of ions are present in the trap, different effects come into play. For dilute clouds the center of mass oscillation of one species is space charge shifted by the other ions[4]. This property was used in ref. 74 to measure ion density. In the experiment of ref.93, the presence of <u>single</u> $BeH^+$ ions would broaden the $Be^+$ cyclotron resonances by more than 100 ppm.

To further illustrate the above remarks, we present a simple example: that of two ions in a Penning trap. If the axial excursions of the ions ($z_1$ and $z_2$) are small compared to their separation r in the radial direction, then the equations of motion in the z direction can be approximately written

$$m_1 \ddot{z}_1 + k_1 z_1 = k_3(z_1 - z_2)$$

$$m_2 \ddot{z}_2 + k_2 z_2 = k_3(z_2 - z_1)$$

where $\omega_{zi} = (k_i/m_i)^{1/2}$ (i = 1,2) are the respective oscillation frequencies of the ions (with the other ion removed from the trap) and $k_3 = q_1 q_2 / r^3$. These equations can be solved exactly[101]. Some limiting cases are interesting to examine.

Case 1: $k_1 = k_2$, $m_1 = m_2$. The center of mass oscillates at the unshifted value $\omega_z = \omega_{z1} = \omega_{z2}$. If the coupling to the endcaps is different for the two ions (eg. suppose one ion is at the center of the trap and the other at a nominal radius r) then some current is induced at the internal mode frequency $\omega_z' = (\omega_z^2 - 2k_3/m)^{1/2}$. The strength of the induced current due to the internal mode will scale with the difference in endcap coupling between the two ions.

Case 2: $m_1 = m_2$, $k_1 \neq k_2$, $k_3 \ll |k_1-k_2|$ (weak coupling limit) Observed induced currents are at $\omega_{z1}' \cong (\omega_{z1}^2 - k_3/m_1)^{1/2} \cong \omega_{z1}$, ions are nearly independent.

Case 3: $m_1 = m_2$, $k_1 \approx k_2$, $k_3 \gg |k_1 - k_2|$ (strong coupling limit). Dominant part of the center of mass oscillation is at frequency $\omega_z' = (\omega_{z1} + \omega_{z2})/2$ ; particles appear locked together.

Case 4: $m_1 = m_2$, $k_1 \neq k_2$, $k_3 \approx |k_1 - k_2|$ (intermediate coupling). Oscillations near $\omega_{z1}$ and $\omega_{z2}$; qualitatively not significantly different than case 2.

The most straightforward solution to space charge problems is to use single ions. Short of this, different ion species can be eliminated from the trap by: (1) driving the unwanted ions out of the trap using strong motional excitation[89,93,102]. (2) Operate the trap in a mass selective mode. For rf traps both high and low masses can be excluded. For the Penning trap, particles with lower charge to mass ratio can be ejected by exceeding the critical voltage[3] for these ions. This was used in ref. 93 to eject ions with $M \geq 15$ u. (3) Selective ionization. In ref. 93, $Be^+$ ions were created but $H_2^+$ and $He^+$ formation was prevented by using an electron beam energy just slightly above the ionization potential of neutral Be.

The problem of space charge frequency shifts will depend on the particular experiment and can of course be quite complicated. In general, it will not be enough to consider the space charge frequency shift of one ion due to the other ions. For example, in the method of observing induced currents in the electrodes, the observable is the sum of the induced currents due to all ions. In the simple case of a small cloud of identical ions near the center of the trap, space charge frequency shifts in the spectrum of the total current are absent.

## VI APPLICATIONS

The ion storage technique will continue to find varied applications. We illustrate here with a few examples; other applications are mentioned in the reviews referred to in the introduction and in the accompanying papers[19,92,102].

### Frequency Standards and Clocks

In several laboratories, the primary motivation for doing high resolution spectroscopy is to use such spectra as references for frequency standards and clocks. Clocks are frequency standards where it is possible to count cycles of the radiation so that time intervals can be generated. This distinction is an important one in practice; for example, it will probably be much more difficult to obtain a laser "clock" than a microwave "clock" even though the performance of laser frequency standards should eventually be superior[103].

In a frequency standard or clock operating at frequency $\nu_0$, measurement imprecision $(\delta\nu_{error}/\nu_0)$ is approximately limited to $(Q \cdot S/N)^{-1}$ 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 linewidth is small enough then the experimental linewidth ($\Delta\nu_0$) is probably independent of the trapped ion that is used (eg. determined by interrogation time). Therefore we would like to use as high a frequency ($\nu_0$) as possible in order to increase Q. This is the single disadvantage of either $Mg^+$ or $Be^+$ ions since the interesting "clock" transitions are only around 300 MHz ($Q \gtrsim 10^{10}$). In spite of this limitation, the accuracy achieved with a beryllium clock[104] approaches that of the best cesium standards and significant improvement could be expected. A better ion for a laser cooled microwave clock[24] is perhaps $Hg^+$ ($\nu_0 \simeq 40$ GHz for $^{199}Hg^+$.) Very important frequency standard work has already been accomplished using this ion[19,40,105-107], but laser cooling is much harder to achieve than for $Be^+$ or $Mg^+$. A logical extension of this idea is to go to much higher frequency; for example, to use a narrow optical transition. A number of transitions in various ions have been proposed[3]; Dehmelt[108] was the first to suggest that such extremely high resolution spectroscopy could be carried out using single photon transitions in for example single group IIIA ions. For instance[108] the $6^1S_0 \leftrightarrow 6^3P_0$ transition in $Tl^+$ ($\lambda = 202$ nm) has a $Q \simeq 5 \times 10^{14}$. 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. In experiments at Heidelberg and Seattle, the present resolution of the two photon $6^2S_{1/2} \rightarrow 6^2P_{1/2} \rightarrow 6^2D_{3/2}$ stimulated Raman transition in $Ba^+$ is limited by laser linewidth broadening, but this transition could be extremely narrow[132]; the lifetime of the $^2D_{3/2}$ state in $Ba^+$ is 17.5 s which would give an intrinsic Q of $1.6 \times 10^{16}$.

The accuracy for optical frequency standards could be extremely high. As an example, in $In^+$, the linewidth of the $5^1S_0 \rightarrow 5^3P_1$ "cooling" transition is about 1.3 MHz, this implies a second order Doppler shift of $10^{-19}$ or lower. Other systematic shifts can occur[3-5,13,19,21,24,40,104-111] but it is not unreasonable to think they will be smaller than or 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, it may be that the accuracy and resolution will be limited by laser linewidth characteristics (linewidth and linewidth symmetry). However the potential for extremely narrow tunable lasers also exists[103,112,113].

## Search for Spatial Anisotropy

Frequency standards, including those based on atomic or nuclear (Mössbauer) transitions, have traditionally played an important role in testing gravitational theories. One example is measurements of the gravitational red shift. In addition, the very high resolution attained in trapped ion spectroscopy enables other sensitive tests of the Einstein Equivalence Principle (EEP). All metric theories of gravity (including General Relativity) are founded on the EEP, according to which, any nongravitational physics experiment done in a local freely falling frame near a strongly gravitating mass will have the same outcome when done in a freely falling frame far away from all such masses. Also included in the EEP is local Lorentz invariance which states that the outcome of the experiment is independent of the velocity of the freely falling frame[114,115]. In particular, two different atomic clocks (i.e., clocks based on transitions in two different kinds of atoms) located at the same point in space-time will have relative rates which are independent of (1) the velocity of the freely falling lab, and (2) the position and mass of strongly gravitating bodies. As a test of the EEP the frequency of the $^9Be^+$ "clock" transition ($M_J$ = 1/2, $M_I$ = -3/2) → ($M_J$ = 1/2, $M_I$ = -1/2) has been compared to the frequency of a passive hydrogen maser[133] to see if a correlation can be found with orientation in space.

Two gravitational interactions have been proposed which violate the EEP and shift the $^9Be^+$ "clock" transition relative to the hydrogen transition. The first is a direct coupling of a nucleon's spin to the gravitational field,[116].

$$U_g = U(r)\ \bar{I} \cdot \hat{r} = U(r)\ I_z P_1(\cos \beta),$$

where U(r) is the strength of the coupling, $\hat{r}$ is the unit vector pointing from the particle to the source of the field and β is the angle between the magnetic field used to confine the $^9Be^+$ ions (the quantization axis) and the direction $\hat{r}$. In the second model[117] the inertial mass of a nucleon in $^9Be^+$ depends upon the orientation of its orbit relative to the direction toward nearby massive bodies in the universe (e.g., the Milky Way Galaxy or the Virgo Supercluster of galaxies). This mass anisotropy is a quadrupolar effect and thus produces a shift of the $^9Be^+$ transition proportional to $P_2(\cos \beta)$. These experiments are also sensitive to a quadrupolar coupling between a nucleon's velocity (in the laboratory frame)and the velocity of the earth through the cosmic microwave background [114,118]. Thus it is possible to test local Lorentz invariance by investigating the extent to which the mean rest frame of the universe acts as a preferred frame.

These experiments have searched for a sidereal time variation in the $^9Be^+$ "clock" transition which is proportional to $P_\ell(\cos \beta)$ ($\ell$ = 1,2,3) for three directions of the unit vector $\hat{r}$: the direction of the galactic center, the direction of the Virgo supercluster center and the direction of motion through the apparent mean rest frame of the universe. Preliminary experiments have achieved resolution better than 1 mHz and see no such variation. These first results have decreased the limits set by Hughes[119] and Drever[120] on a $P_2(\cos \beta)$ variation by a factor of about 50. Ultimately, one could expect an increase in resolution of an additional factor of 100 or more.

Non Neutral Plasmas

At sufficiently high ion densities and sufficiently low ion temperatures such that the Debye length is small compared to the ion cloud dimensions, the ion cloud in a Penning or rf trap can be described as a non-neutral plasma[121]. Experiments on ions and electrons stored in Penning-type traps have studied a variety of plasma and cooperative effects. Examples include the spectra of plasma and diocotron waves in three dimensional plasmas[121-123] and the detection of waves similar to the drumhead modes of a vibrating membrane, in a nearly two dimensional cloud of ions stored in a hyperbolic Penning trap[100]. Radiation pressure from lasers can be used to cool and compress stored ions and study non-neutral plasmas in a state where the thermal energy per ion is less than the Coulomb energy per ion. Such a plasma is called strongly coupled[124]. A strongly coupled plasma is characterized by the Coulomb coupling constant $\Gamma \equiv q^2/ak_BT$ where $a = (4\pi n/3)^{-1/3}$, q is the ion charge, T is the ion temperature, and n is the ion number density. Extensive theoretical calculations exist for a strongly coupled one component plasma (OCP)[124]. An OCP consists of a single charge species embedded in a uniform density background of opposite charge. These calculations[124] predict that at $\Gamma \cong 2$, the pair correlation function should begin to show oscillations characteristic of a liquid, and at much larger values[125,126] of $\Gamma$ ($\Gamma \cong 170$), crystallization may take place. Crystallization has been observed[127] in a two dimensional OCP ($\Gamma \cong 137$) and in a system of charged aluminum particles (several microns in size) stored in an rf trap[128]. In a frame of reference rotating with the ($\vec{E}\times\vec{B}$) rotation frequency of an ion cloud in a Penning trap, the ions can be viewed as being embedded in a uniform charge distribution of opposite sign. Specifically, the spatial correlations and the values of $\Gamma$ for the onset of liquid and solid behavior are the same for the OCP and the non-neutral plasma in a Penning trap[129]. A value of $\Gamma$ on the order of 2 has been estimated for a pure electron plasma stored in a long cylindrical Penning trap and cooled to near the 4K temperature of its surroundings.[130] In a small plasma of laser cooled $^9Be^+$ ions stored in a Penning trap, a value of $\Gamma$ as large as 10 (indicating liquid behavior) has been measured[99]. In this latter experiment, a second laser was used to probe the ion plasma and measure the temperature of the ions from the Doppler broadening of the optical probe transition. The ion number density was determined by measuring the ($\vec{E}\times\vec{B}$) cloud rotation frequency. Because the trap electric field and magnetic field were known, the space charge electric field was extracted from the cloud rotation frequency and used to determine the ion number density. Ion number densities of $\approx 2 \times 10^7/cm^3$ and temperatures of $\lesssim 75$ mK produced values of $\Gamma \cong 10$. Values of $\Gamma$ large enough to observe a liquid-solid phase transition should be accessible in future versions of this experiment. If the theoretical cooling and density limits can be obtained, values of $\Gamma$ as large as 15,000 are perhaps possible for $Be^+$ ions. Because experimental information on three dimensional, strongly coupled plasmas is almost non-existent, these experiments can provide some useful tests of the theoretical calculations.

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