Reprinted from SPIE Vol. 426—Laser-based Ultrasensitive Spectroscopy and Detection V

Spectroscopy of stored ions using fluorescence techniques

D. J. Wineland, Wayne M. Itano, J. J. Bollinger,
J. C. Bergquist, and H. Hemmati

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

Abstract

Fluorescence light is used in spectroscopic experiments on stored ions. We discuss applications in (1) high resolution microwave and rf/optical double resonance spectroscopy, (2) single ion detection, (3) mass spectroscopy and (4) studies of stored ion clouds which exhibit properties of strongly coupled plasmas.

The stored ion method

Ions can be confined for long periods (as long as days) under ultrahigh vacuum conditions in ion "traps" using electric and magnetic fields. This trapping can be accomplished without the usual perturbations associated with confinement (for example the perturbations due to collisions with walls or buffer gases in a traditional optical pumping experiment.) Trapped ions are thus advantageous for high precision spectroscopy since long confinement times can yield high resolution and systematic shifts in observed spectra can be quite small.

Unfortunately (and necessarily), there is a price to be paid for this property of long storage times with small perturbations -- the number of particles that can be stored is typically small (approximately 10^6 or less for a "trap" with centimeter dimensions); the densities are ultimately governed by the competition between space charge repulsion and the confining electromagnetic forces obtained under normal laboratory conditions. We remark that if we could obtain the high trapping fields necessary to obtain high densities, then we would lose one of the advantages of the technique because, for example, Stark shifts due to confinement would cause problems in very high resolution work. As a consequence of the low numbers of trapped ions, many types of experiments may be precluded -- for example spectroscopic experiments on complex molecular ions where only a small fraction of the ions are in a given state. However, in spite of the low numbers obtained, sensitive techniques have been developed so that single atomic ions can be observed.

Here we will discuss only those experiments using the Penning[1] static trap. The more common Paul or rf trap is very similar in construction and is discussed elsewhere [2,3]. The electrode structure of a Penning trap is shown in Figure 1.

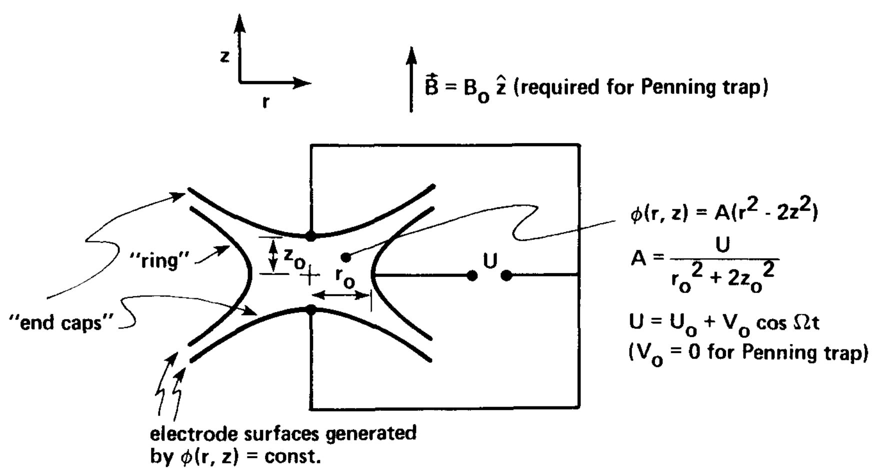

Figure 1. Schematic representation of Penning trap.
($V_o \neq 0$ for Paul trap)

The voltage U_o is used to bias the "endcaps" so that a harmonic electric potential well is created along the z or axial direction. This causes a repulsive potential in the x - y plane which can be overcome by superimposing a static magnetic field along z ($\vec{B}=B_o\hat{z}$). For a single ion in the trap (or neglecting space charge) the equations of motion are

$$\ddot{z} + \omega_z^2 z = 0,$$

$$\ddot{\vec{r}} = \tfrac{1}{2}\omega_z^2 \vec{r} - i\omega_c \dot{\vec{r}},$$

where $\vec{r} = x + i\,y$, $\omega_z^2 = 4qU_o/m(r_o^2 + 2z_o^2)$, and $\omega_c = qB/mc$. (1)

Therefore $z = z_o \cos \omega_z t$ and $\vec{r} = \vec{r}_c e^{-i\omega'_c t} + \vec{r}_m e^{-i\omega_m t}$,

where $\omega'_c = \tfrac{1}{2}\omega_c + [(\omega_c/2)^2 - \omega_z^2/2]^{\frac{1}{2}}$

$$\omega_m = \tfrac{1}{2}\omega_c - [(\omega_c/2)^2 - \omega_z^2/2]^{\frac{1}{2}}$$

Thus the motion of a single ion in the trap is composed of a harmonic oscillation along z and a superposition of two circular motions in the x-y plane at the shifted cyclotron (ω'_c) and magnetron (ω_m) frequencies. From the 3 oscillation frequencies we can derive the free space cyclotron frequency ω_c of the ions from the expression: [4]

$$\omega_c = \left[(\omega'_c)^2 + \omega_m^2 + \omega_z^2\right]^{\frac{1}{2}} \quad (2)$$

Typical experimental parameters are such that $B_o \cong 1T$, $U_o \cong 1V$, $r_o \cong \sqrt{2}\, z_o \cong 1$ cm. Atomic ions can usually be loaded by directly ionizing the parent neutral atom with an electron beam which is externally injected through the trap.

Microwave and rf/optical double resonance experiments on laser cooled ions

The principle of these experiments is perhaps best illustrated by an early experiment on $^{24}Mg^+$ ions.[5] Small clouds ($10^2 \lesssim N \lesssim 10^4$; cloud diameter ~200μm to ~1mm) of Mg^+ ions are stored in a trap. The confining axial (z) magnetic field (B_o=0.978 T) splits the $^{24}Mg^+$ energy levels, as shown in the inset in Figure 2.

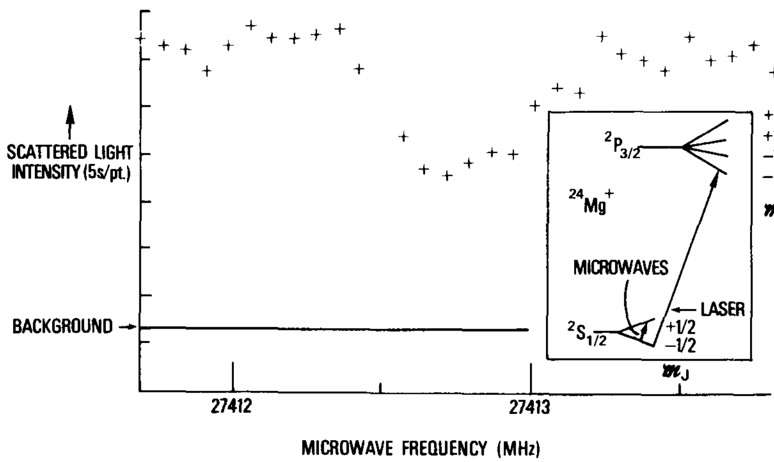

Figure 2. Microwave/Optical double resonance spectrum of $^{24}Mg^+$. Inset shows relevant energy levels and microwave and optical pumping transitions.

Light (~5 μ W focused to a spot diameter ≅100μm; λ ≅280 nm) from a frequency-doubled dye laser incident along the x axis and polarized in the y direction is tuned to the (3p $^2P_{3/2}$ M_J = −3/2) ↔ (3s $^2S_{\frac{1}{2}}$ M_J = −1/2) transition frequency. This pumps the ions into the M_J = −1/2 ground state. This repopulation pumping can be explained as follows: Ions in the M_J = +1/2 ground state are driven weakly in the wings of the (−1/2) ← (+1/2) transition (we denote the excited and ground state M_J values by the numbers in the first and second parentheses, respectively). On re-emission, the ion decays with 2/3 probability to the (−1/2) ground state, which tends to populate this state. Once in the (−1/2) ground state, the ion is driven with high probability to the (−3/2) excited state, from which it can only decay to the (−1/2) ground state level. Depopulation of the (−1/2) ground state can occur because we are pumping in the wings of the (+1/2) ← (−1/2) transition. Even though this transition frequency is about 36.6 GHz away from the laser frequency, it is driven at a rate that far exceeds the nonradiative relaxation rate in the ground state. However, the (−1/2) ← (+1/2) transition frequency is only about 9.15 GHz away from the laser frequency, and therefore from a simple rate equation analysis, we should expect the population in the (-1/2) ground state to be about 16 times larger than that in the (+1/2) ground state.

If we now drive a high-Q transition (here called a clock transition), which has as its ground state the same repopulated level from the optical pumping described above, this level will be depleted and the transition will be indicated by a decrease in the fluorescence scattering from the optical pumping transition. This simple double-resonance principle is illustrated in our experiments, in which the clock transition is represented by the ground-state Zeeman transition (Fig. 2). In these experiments, we observed the backscattered light in an f/4 cone; the net collection efficiency was 3×10^{-5}. The poor resolution in this experiment is due to poor magnetic-field stabilization, that is, the field fluctuates about 10 ppm in about 1s. We note however, that in spite of the low ion numbers and poor collection efficiency, it is possible to achieve adequate signal to noise because it is possible to scatter many optical photons (or observe the absence of scattering) for each microwave photon absorbed. In these experiments the absorption of one microwave photon resulted in the absence of 10^6 scattered optical photons giving a quantum enhancement factor of 10^6.

In these experiments we are also able to reduce the kinetic energy of the ions by a process called laser cooling or optical sideband cooling. This is important in very high resolution work where residual first order and second order Doppler effects can cause systematic shifts in spectra. Laser cooling is a method by which a beam of light can be used to damp the velocity of an atom or ion. The basic mechanism for cooling of a trapped ion by a laser beam tuned slightly lower in frequency than a strongly allowed resonance transition is as follows: when the velocity of the ion is directed against the laser beam, the light frequency in the ion's frame is Doppler shifted closer to resonance so that the light scattering takes place at a higher rate than when the velocity is along the laser beam. Since the photons are reemitted in random directions, the net effect, over a motional cycle, is to damp the ion's velocity, due to absorption of photon momentum. If the laser frequency is tuned above resonance, it causes heating. The effects of frequency detuning, orientation, and intensity profile of the laser beam on laser cooling of an ion in a Penning trap have been calculated[6]. In these experiments, laser cooling and optical pumping are obtained with the same laser beam.

These same basic techniques have now been applied to high resolution rf/optical double resonance experiments which measure nuclear spin flip hyperfine transitions. Figure 3 shows the ground state $(M_I, M_J) = (-3/2,1/2) \leftrightarrow (-\frac{1}{2},\frac{1}{2})$ hyperfine resonance obtained on a small cloud of $^{25}Mg^+$ ions.[7] The

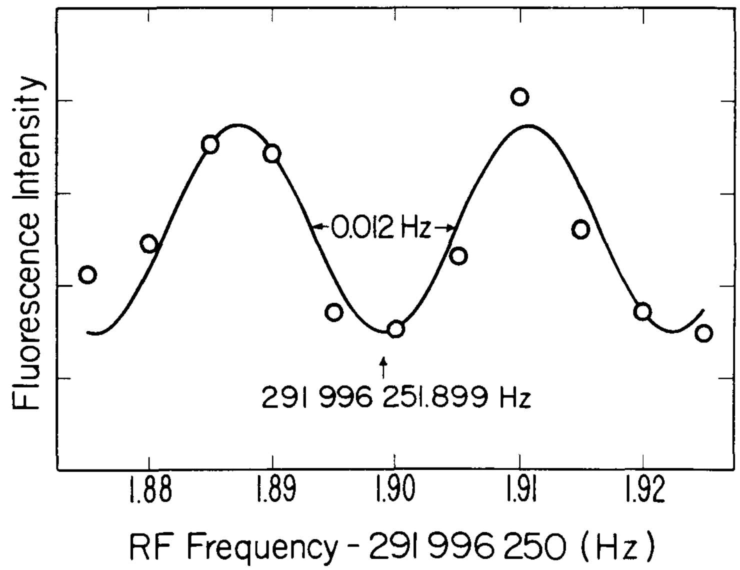

Figure 3. $^{25}Mg^+$ hyperfine resonance.

oscillatory lineshape results from the use of the Ramsey separated oscillatory field technique, applied in the time domain. Two coherent 1.02 s rf pulses separated by 41.4 s were used to drive the transition. This resonance demonstrates the long relaxation times possible with stored ions. Line broadening due to magnetic field variations was eliminated by operating the trap near a magnetic field at which the derivative of the transition frequency with respect to field is zero. Light shifts were avoided by turning the laser off during the 43.44 s rf period.

An rf oscillator has been locked to the $(-3/2,1/2) \leftrightarrow (-\frac{1}{2},\frac{1}{2})$ transition in $^9Be^+$ ions to illustrate the potential of stored ions as a frequency standard[8]. Stabilities comparable to those of a commercial cesium clock were obtained and systematic frequency shifts were determined to be below one part in 10^{13}. The present best frequency standard is based on the ground state hyperfine transition in neutral cesium and has an inaccuracy slightly less than 1 part in 10^{13}. Eventually,[9] the ground state hyperfine transition in Hg^+ ions might be used to obtain a frequency standard with inaccuracy less than 1 part in 10^{15}.

Single ion detection

The extreme sensitivity of the fluorescence techniques is illustrated by the ability to detect single ions as shown in Figure 4.

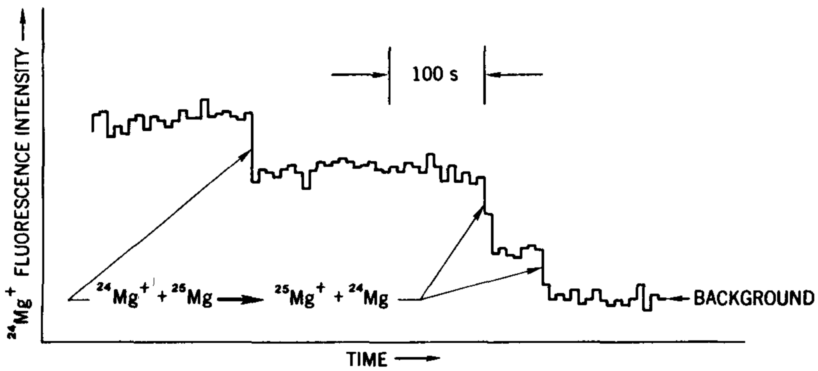

Figure 4. Fluorescence vs. time from a small group of $^{24}Mg^+$ ions. The three large steps are due to the loss of individual ions by charge exchange with ^{25}Mg.

The four plateaus are due to the presence in the trap of three, two, one, and zero $^{24}Mg^+$ ions, which were neutralized, one by one, by ^{25}Mg atoms coming from an oven[10]. Similar experiments have also been performed at Heidelberg[11] and the University of Washington[12]. In the Heidelberg experiments single cold ions were actually photographed[11]. This ability to detect single ions is not surprising when one realizes that an individual ion can scatter photons at nearly half the spontaneous decay rate (10^7/s - 10^8/s) when the laser beam is of saturating intensity.

Mass spectroscopy

The possibility of performing high resolution mass spectroscopy in a Penning trap has been realized for some time. At present, the best experiment compares the cyclotron frequencies of electrons and protons which are alternately stored in the trap; this yields a direct value for the electron-proton mass ratio[13]. In these experiments[13] the ion motion is detected by observing the induced currents in the Penning trap electrodes. In our experiment[14] we measure the axial (ω_z), magnetron (ω_m), and electric-field-shifted cyclotron (ω_c') frequencies of a small cloud of atomic ions stored in a Penning trap by observing the changes in ion fluorescence scattering from a laser beam which is focused onto the ion cloud as shown schematically in Figure 5. 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 laser fluorescence due to a decrease in overlap between the ion cloud and focused laser beam. To a good approximation, the electric field excites only the collective center of mass modes, whose frequencies are equal to those of a single isolated ion in the trap[15]. By measuring ω_c', ω_m and ω_z in this way, eq. (2) can be used to determine the cyclotron frequency ω_c of the ion in the magnetic field B_o. One obvious application of the method is to measure ω_c for different ions in the same magnetic field and thereby make direct mass comparisons.

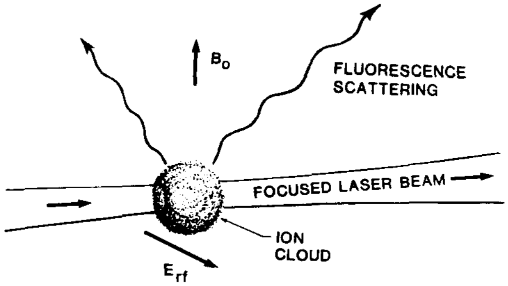

Figure 5. A small sample of ions is confined by static magnetic and electric fields (not shown.) A laser beam is focused onto the sample and the fluorescence scattering is observed. When the cyclotron motion is excited by an externally applied electric field ($\vec{E}_{rf}$) the ion orbits increase in size which results in a decrease in fluorescence due to a decrease in overlap between the laser beam and ion cloud.

As a demonstration of the basic technique, in our experiments we compared the cyclotron frequency of $^9Be^+$ ions to the electron spin flip frequency of the outer electron in the same $^9Be^+$ ions. This yielded the quantity $g_J(^9Be^+)\, m(^9Be^+)/m_e$ to a precision of 0.15 ppm. From a theoretical calculation of $g_J(^9Be^+)$ and an auxiliary value of $m(^9Be^+)/m_p$ where m_p is the proton mass, we obtained a value of m_p/m_e to 0.34 ppm limited by the theoretical calculation. The precision in our measurements was limited by magnetic field fluctuations and rather large anharmonic terms in the electric potential. Using a trap with electrodes designed to null the higher order anharmonic terms, a similar experiment done on single ions should yield precisions near 1 part in 10^{13}.

Studies of one component plasmas

In our experiments, when space charge can be neglected, a cloud of ions will rotate at the frequency ω_m given in eq. (1). In general, however, space charge cannot be neglected and the cloud will rotate at a frequency ω_m' given by

$$\omega_m' = \frac{\omega_c}{2} - \left[\left(\frac{\omega_c}{2}\right)^2 - \frac{\omega_z^2}{2} - \frac{4\pi q^2 na}{3m}\right]^{\frac{1}{2}} \qquad (3)$$

where we approximate the cloud as a uniformly charged ellipsoid[16,17]. The constant a has a value near 1 and is related to the shape of the ellipsoid and n is the ion density. In a frame rotating at ω_m' the cloud of ions looks like it is embedded in a uniform background of negative charge with density n; therefore this cloud of ions in a Penning trap might be viewed by a plasma physicist as a one component non neutral ion plasma[18,19].

We can probe the properties of this plasma with the following optical/optical double resonance fluorescence technique. This method is essentially the same as was described earlier to measure the ground state Zeeman resonance in $^{24}Mg^+$. Instead of the microwave oscillator, we use a second lower power, focused probe laser beam incident in the x direction and tuned to an optical transition (for example $^2P_{3/2}(M_J = +\frac{1}{2}) \leftrightarrow {}^2S_{\frac{1}{2}}(M_J = -\frac{1}{2})$) which depopulates the $^2S_{\frac{1}{2}}(M_J = -\frac{1}{2})$ state, causing a decrease in fluorescence. The width of the observed double resonance fluorescence "dips" can be used to determine the Doppler broadening of the optical transition and therefore the ion temperature. By moving the probe laser beam in the y direction we can measure ω_m' from the rotation induced first order Doppler shifts of the optical transitions; from eq. 3 we can then derive the density n. From these kinds of measurements on Be^+ ions we can determine the plasma coupling constant Γ and we measure values as high as 10. Γ is the ratio of Coulomb energy to kinetic energy per particle[20]. A plasma usually exhibits liquid properties for $\Gamma \cong 2$. Eventually it may be possible to observe "Wigner crystallization"[20,21] in a similar system ($\Gamma \cong 155$).

Acknowledgments

The authors wish to acknowledge the support of the Office of Naval Research and the Air Force Office of Scientific Research in this work.

References

1. Penning, F. M., "The Glow Discharge of Low Pressure between Coaxial Cylinders in an Axial Magnetic Field," Physica, Vol. 3, pp. 873-894, 1936.

2. Dehmelt, H. G., "Radiofrequency Spectroscopy of Stored Ions, I: Storage", Adv. Atom. Mol. Phys. Vol. 3, pp. 53-72, 1967; Dehmelt, H. G., "Radiofrequency Spectroscopy of Stored Ions, II: Spectroscopy" Adv. Atom. Mol. Phys. Vol. 5, pp. 109-154, 1969.

3. Wineland, D. J., Itano, Wayne M., Van Dyck, Jr. R. S., "High Resolution Spectroscopy of Stored Ions", Adv. Atom. Mol. Phys. Vol. 19, to be published.

4. Brown, L. S. and Gabrielse, G., "Precision Spectroscopy of a Charged Particle in an Imperfect Penning Trap" Phys. Rev., Vol. A25, pp. 2423-2425, 1982.

5. Wineland, D. J., Bergquist, J. C., Itano, Wayne M., and Drullinger, R. E., "Double-resonance and Optical Pumping Experiments on Electromagnetically Confined, Laser Cooled Ions," Opt. Lett. Vol. 5, pp. 245-247, 1980.

6. Itano, Wayne M., and Wineland, D. J., "Laser Cooling of Ions Stored in Harmonic and Penning Traps" Phys. Rev. Vol. A25, pp. 35-54, 1982.

7. Itano, Wayne M., and Wineland, D. J., "Precision Measurement of the Ground-State Hyperfine Constant of $^{25}Mg^+$" Phys. Rev., Vol. A24, pp. 1364-1373, 1981.

8. Bollinger, J. J., Itano, Wayne M., Wineland, D. J., "Laser Cooled $^9Be^+$ Accurate Clock" to be published.

9. Wineland, D. J., Itano, Wayne M., Bergquist, J. C., Walls, F. L. "Proposed Stored $^{201}Hg^+$ Ion Frequency Standards" Proc. 35th Ann. Symp. on Freq. Control, (Copies available from Electronic Industries Ass., 2001 Eye St. NW, Washington, D.C., 20006) Philadelphia, Pa. p. 602-611, 1981.

10. Wineland, D. J., and Itano, Wayne M., "Spectroscopy of a Single Mg^+ Ion, Phys. Lett. Vol. 82 A, pp. 75-78, 1981.

11. Neuhauser, W., Hohenstatt, M., Toschek, P., Dehmelt, H., "Localized Visible Ba^+ Mono-Ion Oscillator" Phys. Rev. Vol. A22, pp. 1137-1140, 1980.

12. Nagourney, W., Janik, G., and Dehmelt, H., "Linewidth of Single Laser Cooled $^{24}Mg^+$ Ion in Radiofrequency Trap" Proc. Nat. Acad. Sci. USA Vol. 80, pp. 643-646, 1983.

13. Van Dyck, Jr., R. S. and Schwinberg, P. B., "Preliminary Proton/Electron Mass Ratio Using a Compensated Quadring Penning Trap" Phys. Rev. Lett. Vol. 47, pp. 395-398, 1981. and Van Dyck, Jr., R. S. Moore, F. L., and Schwinberg. P. B., "New Measurement of the Proton-Electron Mass Ratio" Bull. Am. Phys. Soc. Vol. 28, p. 791, 1983.

14. Wineland, D. J., Bollinger, J. J., and Itano, Wayne M., "Laser-Fluorescence Mass Spectroscopy" Phys. Rev. Lett. Vol. 50, pp. 628-631, 1983 and Vol 50, p. 1333, 1983.

15. Wineland, D. J., and Dehmelt, H. G., "Principles of the Stored Ion Calorimeter" J. Appl. Phys. Vol. 46, pp. 919-930, 1975.

16. Wineland, D. J., "Spectroscopy of Stored Ions", in Precision Measurements and Fundamental Constants II, Eds. B. N. Taylor and W. D. Phillips, NBS Special Publ. 617, in press.

17. Bollinger, J. J., and Wineland, D. J., to be published.

18. Davidson, R. C., Theory of Non-neutral Plasmas, Benjamin, 1974.

19. Driscoll, C. F. and Malmberg, J. H., "Length-Dependent Containment of a Pure Electron-Plasma Column" Phys. Rev. Lett. Vol. 50, pp. 167-170, 1983.

20. Ichimaru, S., "Strongly Coupled Plasmas: High-Density Classical Plasmas and Degenerate Electron Liquids", Rev. Mod. Phys., Vol. 54, pp. 1017-1059, 1982.

21. Malmberg, J. H., and O'Neil, T. M., "Pure Electron Plasma, Liquid and Crystal" Phys. Rev. Lett., Vol. 39, pp. 1333-1336, 1977.