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M. H. Prior and R. D. Knight

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Fluorescence of optically pumped trapped ions

M.H. Prior and R.D. Knight*

Materials and Molecular Research Division, Lawrence Berkeley Laboratory
and Department of Physics, University of California, Berkeley, California
94720

ABSTRACT

Narrow bandwidth laser excitation of the $2\ ^3S_1 \rightarrow 2\ ^3P_J$ ($J = 0, 1, 2$) transitions near 5485 Å from $2\ ^3S_1\ Li^+$ ions confined in an rf quadrupole trap has produced novel fluorescence response curves (fluorescence vs. laser frequency) characteristic of optical pumping in the absence of strong hyperfine relaxation. The $2\ ^3S_1 \rightarrow 2\ ^3P_{2,1}$ transitions in $^7Li^+$ were extensively studied. The observations are consistent with predictions of a rate equation model which treats the ions as a gas in temperature equilibrium. A narrow bandwidth pumping source (linewidth < Doppler width and hyperfine splittings) produces a response curve narrower than the Doppler blended hyperfine complex. Frequency scanning elicits hysteresis effects when the scan rate exceeds the response rate of the pumped ions.

In the course of preparations to conduct radio-frequency and microwave studies of the hyperfine levels of metastable $1s2s\ ^3S_1\ Li^+$ ions, and as an outgrowth of our previous measurement of the radiative lifetime of this state,¹ we have made a number of observations of the fluorescence from these ions when pumped by a narrow bandwidth laser beam tuned to

one of the $3S_1$ to $1s2p\ 3P_J$ transitions. The relevant energy levels of Li^+ are shown in Fig. 1. In this work we report studies of the fluorescence from the $3P_{1,2}$ states of $7Li^+$ ions. The transition to the $3P_2$ state lies about 60 GHz higher in frequency than that to $3P_1$; the nominal wavelength for either transition is 5485 Å.

1. EXPERIMENTAL CONFIGURATION

Excitation of the $3P_{1,2}$ states has been observed by detecting the weak XUV fluorescence at 202 Å produced when these states decay directly to the ground state ($1s^2\ 1S_0$). In the case of $3P_1$, this occurs with a branching ratio² of 1/1200 (versus decay back to $3S_1$) via E1 intercombination radiation caused by a small mixture of $1P_1$ character in the " $3P_1$ " wavefunction. For $3P_2$, however, a combination of hyperfine induced E1 and pure M2 amplitudes result in a much smaller branching ratio ($\sim 1.5 \times 10^{-5}$) for decay to the ionic ground state. We also detect excitation of these states by observation of the scattered laser photons ("visible" fluorescence); because of the weak XUV decay of $3P_2$, this is the preferred method for this state, yielding a count rate of some 10^4 times higher than the XUV rate.

The metastable Li^+ ions were confined inside a radio-frequency quadrupole trap (see Refs. 1,3) with a collision dominated lifetime of about 5 seconds. The XUV photons were detected by windowless CuBe venetian blind electron multipliers which viewed the trap through 800 Å Al foils. A fraction of the 5485 Å laser photons scattered about the trap midplane was detected by a photomultiplier located outside the vacuum chamber containing the ion trap. A lens mounted inside the chamber focused light from the trap volume out through a viewport onto an interference

filter placed over the photocathode of the photomultiplier. Careful focusing and steering of the linearly polarized laser beam, together with a light baffle system in the entrance and exit arms of the chamber, reduced the scattered light from the entrance and exit windows to an acceptable level ($\sim 500 \text{ sec}^{-1}$ photomultiplier count rate at a laser power $\sim 10 \text{ mW}$). The frequency of the laser was scanned at variable rates over a range of 30 GHz under control of a computer based data collection system. The residual scattered light signal, collected when the trap was empty, was subtracted in alternate cycles from data collected with Li^+ ions stored.

The most striking result of these studies is the narrow fluorescence response curves produced (fluorescence signal versus laser frequency). These curves can be considerably narrower than the complex of blended Doppler broadened hyperfine lines one would expect from a normal absorption spectrum of a Li^+ "gas" at the equivalent temperature of the trapped ions. Consider the $^3\text{S}_1$ to $^3\text{P}_1$ transition complex in $^7\text{Li}^+$ (nuclear spin $I = 3/2$). There are three hyperfine levels with total angular momentum quantum numbers $F = 5/2, 3/2, 1/2$ in both the $^3\text{S}_1$ and $^3\text{P}_1$ states. This produces seven optical hyperfine transitions extending over a range of about 30 GHz. The trapped ions have a Maxwell-Boltzmann distribution of energies characterized by a temperature of several thousand degrees Kelvin, yielding a Doppler width of $\sim 10 \text{ GHz}$ for each hyperfine line (the natural width is $\sim 3.5 \text{ MHz}$). Thus one might expect a fluorescence response over a range of some $\sim 50 \text{ GHz}$ in laser frequency (the laser "linewidth" was $\sim 50 \text{ MHz}$). In fact we observe a single near-Gaussian shaped signal with a full width of 5 to 10 GHz (depending on trap parameters). This effect is the result of optical pumping of

the 3S_1 hyperfine states in an environment (the ion trap and residual background gas) where the relaxation rate among the hyperfine levels is weak in comparison to the pumping rate.

II. THREE LEVEL MODEL

This behavior can be understood by considering a simpler system which would exhibit the same effect. Figure 2 shows the hypothetical spectrum appropriate to an ion with a single level in the excited state. Allowed optical transitions connect each lower level to the excited state. The rest spectrum would consist of two lines as shown in the left portion of the figure. An ion confined inside a trap will execute a complex periodic motion; this is a superposition of harmonic motions in the rf quadrupole trap, but the component of motion along the laser beam can be approximated as simple harmonic motion at a frequency and amplitude dependent upon the trap parameters, ion charge-to-mass ratio, and total energy. The resultant frequency modulation of the absorption spectrum for a particular ion energy is shown in the right half of Fig. 2.

For the rest ion, a laser beam tuned to either transition frequency would quickly empty the corresponding lower level, transferring its population to its non-resonant companion. The system would be optically pumped and no more photons would be scattered unless the initial state were repopulated by some other mechanism or the laser were tuned to the opposite transition. Depending upon the relative strengths of the two transitions, only a few transient photons would be scattered during the pumping time.

For the oscillating trapped ions, the same brief pumping transient would occur over much of the range of laser frequencies between the two

rest values, yielding near zero time-averaged scattering rate. It is clear, however, that there is a range between the two rest frequencies where the laser may cause sequential alternative pumping of each lower level, yielding a non-zero average scattered signal. This region is just the overlap region of the Doppler shifted resonant frequencies. The signal from a collection of such oscillators would be given by an average over the Maxwell-Boltzmann distribution of ion energies capable of interacting with the laser beam when in either lower level. This produces a fluorescence response curve centered between the rest frequencies with a width which can be narrower than the Doppler width of either transition and the separation of the two rest frequencies.

III. RATE EQUATION TREATMENT

A quantitative treatment of the fluorescence from an ensemble of atomic absorbers can be made by solving a set of rate equations for the populations of the levels involved. We have found this useful for the case of the $\text{Li}^+ 3S_1 - 3P_J$ pumping cycle. The equations are

$$\dot{N}_i = \sum_j [A_{ji}X_j - I_\nu \delta\nu B_{ij}(\nu)N_i] - r(N_i - w_i n)$$

$$\dot{X}_j = -AX_j + \sum_i I_\nu \delta\nu B_{ij}(\nu)N_i$$

where the N_i and X_j are populations of the $3S_1$ and $3P_J$ levels, respectively. A_{ji} is the spontaneous emission rate for the $j \rightarrow i$ transition ($A = \sum_i A_{ji}$). $B_{ij}(\nu)$ is proportional to the absorption coefficient multiplied by the fraction of ions in state i capable of absorbing a photon of frequency ν to make the $i \rightarrow j$ upward transition. I_ν is the laser spectral intensity (intensity per unit bandwidth) and $\delta\nu$ is the laser

bandwidth. n is the total number of ions in the 3S_1 levels, and w_i is the statistical weight of level i ($\sum w_i = 1$). Γ is a relaxation rate which forces the populations to statistical equilibrium in the absence of laser pumping. We have found it is appropriate to use in the $B_{ij}(\nu)$, a Doppler profile to represent the fraction of ions resonant with the laser frequency for each $i \rightarrow j$ transition. The true absorption line shape for an ensemble of ions confined in a radio-frequency quadrupole trap consists of the rest spectrum together with a comb of Doppler side bands extending on either side of each absorption line.⁴ These sidebands are offset from the rest frequencies by harmonics of the trap drive frequency and the ion secular frequencies (1 MHz and ≈ 100 kHz in this work). The envelope of these sidebands is very well approximated by a Gaussian shape when the Doppler width (≈ 10 GHz for the Li^+ ions), corresponding to the average ion energy, is large compared to the sideband spacing. Additionally, the 3.5 MHz natural width of each sideband and the ≈ 50 MHz laser frequency jitter effectively average out any sideband structure in this work. The assignment of a Doppler profile to each absorption line is equivalent to averaging the system of Fig. 2 over the Maxwell-Boltzmann distribution with the additional proviso that the thermal relaxation of the oscillation energy is rapid compared to the pumping rate. This insures that a thermal distribution of oscillator energies is maintained for the collection of ions in each lower level separately.

Once the 3P_j level populations are determined, the fluorescence signal is given by

$$S = \sum_{jk} x_j A_{jk} R_{jk}(\Delta\Omega),$$

where the subscript k indicates that the observed photons may result from transitions to a system of levels other than the i levels (such as in the XUV emission from the $^3P_{1,2}$ states in decay to the $1s^2\ ^1S_0$ ground state). The k levels are omitted from the rate equations because we deal always with $(A_{jk}/A_{ji}) \ll 1$. $R_{jk}(\Delta\Omega)$ is an angular factor giving the relative intensity emitted into solid angle $\Delta\Omega$.

IV. OBSERVATIONS AND ANALYSIS

For $^7\text{Li}^+$ pumped by the transition to 3P_1 and observed via the 202 Å intercombination emission, the results of the steady state rate equation solution (all time derivatives set to zero) are shown in Fig. 3 for various values of Γ . The calculation was done for conditions (trap parameters, laser power) similar to a case experimentally studied, and plotted on the same figure are those results. Because absolute measurements of the fluorescence rate and laser frequency are not made, the amplitude and line center of the data have been adjusted to best agree with the calculated shape; this occurs for small Γ . The frequency scale is known and no adjustment to it was made. The vertical lines indicate the locations and relative absorption strengths of the seven hyperfine lines. The normal absorption line shape would be that obtained in the limit $\Gamma \rightarrow \infty$; this curve would lie off the figure, however, one can see the marked narrowing of the fluorescence signal by comparing the shape of the observed response to the curve for $\Gamma = 10^4\ \text{sec}^{-1}$.

In Fig. 4 we present the 5485 Å fluorescence (scattered laser photons) from the 3P_2 state of $^7\text{Li}^+$ when held in a 10 eV effective spherical potential well. The curves are the steady state rate equation solutions for three values of Γ . The curve for $\Gamma = 10^6\ \text{sec}^{-1}$ is essentially the normal absorption line shape. The data shown has been adjusted as was

done for Fig. 3 and agrees best with the lowest relaxation rate curve. In Fig. 5 the same data are shown in the upper portion with the curve for $\Gamma = 1$. The lower portion shows the corresponding variation of the 3S_1 hyperfine state populations. For this case a special role is played by the $^3S_1, F = 5/2$ to $^3P_2, F = 7/2$ transition. This transition does not contribute to the optical pumping since $^3P_2, F = 7/2$ can only decay back to $^3S_1, F = 5/2$. One notes that the peak of the fluorescence response curve (Fig. 5) is at the frequency of the $5/2 - 7/2$ transition and that for frequencies greater than this value, the $^3S_1, 5/2$ state is fully populated ($3/2, 1/2$ are empty). It follows that the high frequency half of the response curve is due only to the $5/2 - 7/2$ transition and should be that of the Doppler profile of this transition alone. In fact the high frequency half of the observed line shape is indistinguishable from a Doppler profile characterized by a temperature of 3100 K. This temperature is in agreement with results obtained previously³ from studies of the spatial density distribution of the Li^+ metastable ions. The fall off of the data and rate equation solution below the Doppler shape (dashed curve) on the low frequency side is due to the switching of the 3S_1 hyperfine populations as shown in the lower portion of Fig. 5.

The effect of varying the orientation of the laser polarization with respect to the trap axis (along which there existed a ≈ 50 Gauss magnetic field) was studied for the steady state fluorescence from the 3P_1 and 3P_2 levels. The polarization orientation angle had negligible effect on the shape of the response curves; this observation and the overall change of fluorescence intensity were in agreement with the rate equation solutions.

The data and calculations of Figs. 3, 4, and 5 have all been addressed to the case of steady state fluorescence. That is, the laser frequency is steady, and its beam has interacted with the trapped ions long enough to establish a static population distribution. Experimentally this is carried out by holding the laser frequency constant for a fixed number of trap cycles (fill, store, dump), collecting fluorescence counts and stepping to the next laser frequency. The storage time is long (~ 1 sec) compared to the pumping time (~ 1 msec) so the steady state solutions are appropriate. In Fig. 6 we show data collected from the 5485 Å fluorescence from 3P_2 $^7Li^+$ ions when the laser frequency is scanned rapidly up and down during the storage period. A marked hysteresis is observed in the fluorescence response curves which increases as the rate of scan is increased. This is a reflection of the inability of the 3S_1 level populations to reach the steady state distribution during the dwell time of the laser at each frequency. In this domain one cannot ignore the transient solution to the rate equations.

We have not carried out the complete transient solution to the rate equations for the $^7Li^+$ 3S_1 to 3P_2 transition complex, but the results of a simpler calculation for an artificial but analogous problem are shown in Fig. 7. The level system includes a non-pumping transition, $3/2 \rightarrow 5/2$, analogous to the $5/2 \rightarrow 7/2$ transition in $^7Li^+$. Since the 5/2 level does not participate directly in the pumping process, the results can be derived from the solution for the three level systems $1/2, 3/2 \rightarrow 1/2$, for laser powers such that the population of the 5/2 level is always small compared to that of the 3/2 lower level.

The dwell time, Δt , at each frequency is measured by the dimensionless quantity $\Delta x = PA\Delta t$, where A is the total decay rate of each of the

upper levels. P is a dimensionless measure of the laser intensity,

$$P = \frac{1}{4\pi} \left(\frac{\ln 2}{\pi} \right)^{\frac{1}{2}} \frac{\lambda^3}{hc} \frac{I}{\Delta\nu_D}.$$

I is the laser intensity and $\Delta\nu_D$ is the Doppler width of the absorption lines. The ordinate in Fig. 7 is the dimensionless fluorescence rate $r = s/\Delta x$ where s is the number of photons scattered per ion in the dwell time Δt . The calculations were carried out for $\Gamma = 0$, $\Delta\nu_D = 10.0$ GHz and a lower level spacing of 20 GHz; these values approximate those appropriate to ${}^7\text{Li}^+$.

At small dwell times ($x = 0.1$), there is little hysteresis and the response approaches the normal absorption profile appropriate to no optical pumping (the lower levels were given statistical equilibrium initial populations). Also, at large dwell times ($x = 100.$) there is little hysteresis and the response approaches the steady state rate equation solution. For intermediate dwell times, however, there can be substantial differences in the response depending upon the direction of frequency sweep. One sees that the contribution of the pumping transitions to the net fluorescence response decreases as the dwell time increases and the signal becomes totally dominated by the non-pumping transition. The curves for $x = 10.0$ are quite similar to the observations shown in Fig. 6.

V. DISCUSSION

Recently Pinard et al.⁵ reported a Doppler free spectroscopic technique based upon velocity selective laser optical pumping of metastable Ne atoms, contained in a buffered discharge cell, and absorption of a weak counter propagating probe beam. The broad (but sub-Doppler) structure, upon which was superimposed the narrow resonance observed by these

authors, is closely related to the narrowed fluorescence response spectra reported here. This is particularly so for their observations on the $1s_3, J = 0 \rightarrow 2p_5, J = 1$ transition in ^{21}Ne . The important role of velocity changing collisions in the work of Pinard et al. is played, in the case of the trapped Li^+ ions, by "collisions" with the rf-quadrupole fields.

It is interesting to consider the fluorescence to be expected if the ions were excited by counter propagating laser beams. Extending the simple arguments associated with Fig. 2, modulation of the absorption spectrum would be phase shifted by 180° for the counter propagating beam and, with beams of equal intensity, a general frequency would provide double the single beam fluorescence rate. However, near the mean frequency of the two unmodulated lines, the rate should increase sharply since simultaneous frequency matching would occur for ions in either level. In this situation, each beam undoes the pumping of the other and the average number of fluorescent photons emitted by an ion, at each coincidence with the laser frequency, is not limited to that required to achieve the pumped condition (as is the case for single beam excitation). The linewidth of this sharp resonance, under appropriate conditions, could be less than the excited state natural width. This effect would be the analog of the cross-over resonances observed by Pinard et al.

It is reasonable to expect that effects similar to those reported here could be observed in atomic vapor (e.g., Na) cells. The case of optical pumping effects on saturation spectroscopy of Na and Ba vapors has been reported recently by Feld et al.⁶ In contrast, effects reported

here, in common with those observed by Pinard et al., do not require saturation, optical coherence is negligible, and populations develop according to simple rate equations.

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*Present address: Center for Astrophysics, 60 Garden St., Cambridge, MA
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FIGURE CAPTIONS

Figure 1 Energies and decay modes of Li^+ levels relevant to this work.

Figure 2 Absorption spectrum for three level ions at rest and undergoing simple harmonic oscillation parallel to the laser beam with velocity amplitude v_{max} . The Doppler effect modulates the absorption spectrum and allows quasi-continuous interaction with the laser when its frequency ν_L lies between the horizontal dashed lines. The solid portion of the modulated absorption spectrum indicates the lower level populated by complete laser pumping at each coincidence with ν_L .

Figure 3 Fluorescence response from observation of the 202 Å intercombination decay of $3P_1$ $^7\text{Li}^+$ ions. The curves are the steady state solutions for various hyperfine relaxation rates Γ . The spherical effective well depth for the ions was 20 eV, and the ion temperature used in the calculations was 6440 K. The vertical lines indicate the location and relative strengths of the $3S_1 \rightarrow 3P_1$ hyperfine lines.

Figure 4 Fluorescence response from observation of 5485 Å scattered laser photons following excitation of $^7\text{Li}^+$ ions to the $3P_2$ hyperfine level in a 10eV spherical well. The curves are steady state rate equation solutions for various amounts of relaxation among the $3S_1$ levels. The shape of the observed response (points) is in agreement with the smallest hyperfine relaxation rate. The location of the $3S_1 \rightarrow 3P_2$ hyperfine lines are indicated at the top of the figure.

Figure 5 The data of Fig. 4 and the $\Gamma = 1 \text{ sec}^{-1}$ curve replotted (upper) together with the corresponding $3S_1$ hyperfine level populations (lower) predicted by the steady state solution. The location of the hyperfine lines is shown in between. A prominent role is played by the non-pumping $5/2 - 7/2$ transition which contributes nearly all the signal and whose

Doppler profile (frequencies > 0) is eroded by the pumping process for frequencies < 0 . The dashed line is an extension of the Doppler profile matched to the high frequency side of the observed response.

Figure 6 Hysteresis in the 5485 Å fluorescence from ${}^7\text{Li}^+ {}^3\text{P}_2$ ions for two different laser frequency scan rates. The laser frequency was held at each point for the dwell time shown. The direction of sweep was down for the solid circles and up for the crosses.

Figure 7 Fluorescence response calculated for the simple level system shown in the inset for various values of the dimensionless dwell time x . The calculation begins at the high frequency side with statistical population fractions ($2/3, 1/3$ in the $3/2, 1/2$ lower levels). The vertical lines indicate the location of the three transitions; their height is the absorption rate from the initial population distribution.

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Fig. 1

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Fig. 2

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Fig. 3

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Fig. 4

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Fig. 5

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Fig. 21

Fig. 7

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