Efficient quenching of population trapping in excited Yb$^+$

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(Received 14 October 1994)

We report on a study to determine the efficiency of various buffer gases in quenching the population trapping states of laser-excited ytterbium ions. The ions were confined in an rf-dc hybrid trap, and their $^2S_{1/2} \leftrightarrow {}^2P_{3/2}$ transition was excited with 329-nm laser light. Buffer gases used include H_2, N_2, CO_2, Ar, and He at several different pressure regimes. We have identified N_2 to be highly efficient in quenching the population of the trapping states and thus be the most suitable buffer gas to use with ytterbium for the development of a trapped-ion microwave frequency standard.

PACS number(s): 32.80.Bx, 32.50.+d, 32.30.Bv, 34.50.Ez

Optical and microwave spectroscopy of ions in radio-frequency (Paul) traps has been of much interest in recent years primarily due to the small size of the inherent perturbations that confined ions experience in rf traps. The relatively benign environment of these traps has also led researchers to exploit them, along with the appropriate choice of ions, as ultrastable frequency standards in both the microwave and the optical frequency regime [1–7]. A trapped mercury-ion standard has recently demonstrated unsurpassed stability of parts in 10^{16} at several thousand seconds of averaging time, with a reported drift less than 2×10^{-16}/day [5].

Despite the superior stability demonstrated by the mercury-ion standard the realization of the ultimate potential of trapped-ion frequency standards depends on the ability to use lasers for excitation and interrogation of the active ions [1,2,6–9]. The 171 isotope of ytterbium is a particularly attractive choice for frequency standards applications. This ion has a nuclear spin $I = 1/2$ and thus a simple hyperfine-level structure with an energy splitting of 12.64 GHz. The lower-lying excited electronic states of singly ionized ytterbium are accessible from the ground state with light generated by frequency-doubled semiconductor lasers [10,11]. This is a particularly useful feature of the ytterbium ion in connection with the development of practical standards.

The presence of low-lying metastable levels in the electronic structure of the ytterbium ion, however, has been the subject of much study and concern [9,12–16]. Such long-lived states can "trap" the excited population of ions involved in the optical pumping of the clock transition. The observation of a "dark" state with estimated lifetime exceeding several days has been associated with population trapping in the $4f^{13}6s^2$ $^2F_{7/2}$ state [15] and has been examined in several investigations [7,10,12,13]. Initial studies of the F state have resulted in some unanswered questions concerning the mechanism for its population; these studies have not identified an efficient scheme to deexcite the ions back to the ground state. Until now the only effective approach to avoid population trapping in the dark state has involved using additional lasers to depopulate the metastable D states [7–9,12,13,17], which are believed to be the intermediary path to the excitation of the F state.

In this paper we examine the efficacy of several different buffer gases (including H_2, N_2, CO_2, He, and Ar) in quenching the population of the "dark" state in the ytterbium ion. Nitrogen is found to be extremely efficient at quenching the dark state with an estimated quenching rate of 3.78×10^4/s Pa for pressures less than 2.66×10^{-4} Pa. While the influence of nitrogen on the depletion of the population of the "dark" state will be the primary focus of this paper, we will also present results obtained with other gases that point to a possible path for population trapping due to molecular formation with laser-excited ions.

Buffer-gas studies were performed with naturally abundant ytterbium, as well as with isotopically enriched ytterbium 171 ions confined in a hybrid linear rf-dc trap [18]. The isotopically enriched ytterbium 171 study was performed to examine the effect of collisions with the buffer gas on the coherence of the microwave transition between the hyperfine levels. The trap is housed in a stainless steel vacuum chamber evacuated to a background pressure below 7×10^{-7} Pa. H_2, N_2, CO_2, He, and Ar were introduced from a manifold connected with a high-precision sapphire variable leak to the vacuum chamber.

Ytterbium ions were generated by the collision of counterpropagating beams of ytterbium atoms from a tantalum tube and electrons from a hot filament. The beam directions were perpendicular to the trap axis. During ion loading, a background buffer-gas pressure of 6.7×10^{-4} Pa, as read on the ion gauge, was maintained. Once a sufficiently large cloud of ions was loaded ($\sim 10^6$) both the electron beam and the atom beam were turned off. After a short relaxation time the pressure was reduced to 6.7×10^{-5} Pa and the steady-state fluorescence was measured as a function of buffer-gas pressure.

The fluorescence measurements were made by exciting the $4f^{14}(^1S)6s^2S_{1/2} \leftrightarrow 4f^{14}(^1S)6p^2P_{3/2}$ transition using 328.9-nm laser radiation directed along the trap axis. The fluorescence rate from the decay of the excited $4f^{14}(^1S)6p^2P_{3/2}$ level was monitored perpendicular to the trap axis. The fluorescence was monitored for 30 s, followed by blocking the laser for another 30-s interval; during this time the buffer-gas pressure was manually adjusted from 6.7×10^{-5} to 1.3×10^{-4} Pa. After this period the laser was unblocked again and fluorescence vs time was monitored for another 30-s interval. This procedure was continued until the fluorescence rate was measured for each of the following nine buffer-gas pressures (6.7×10^{-5}, 1.3×10^{-4},
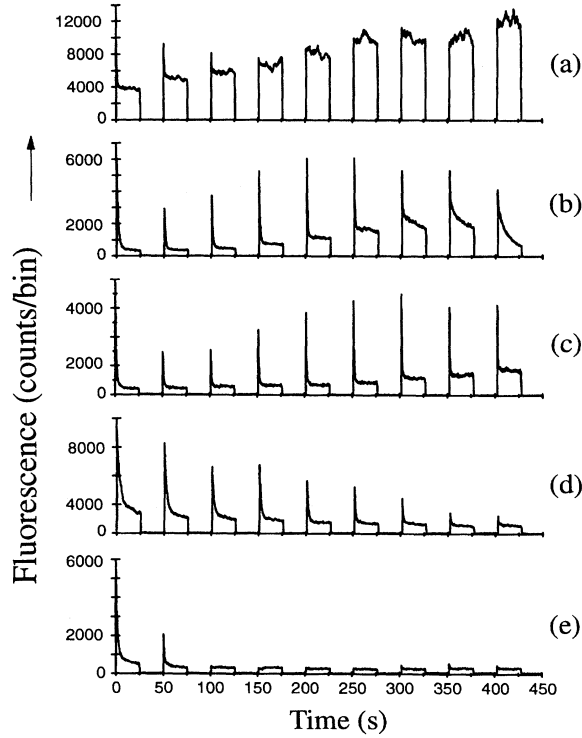
FIG. 1. Steady-state fluorescence spectrum for (a) nitrogen, (b) helium, (c) argon, (d) carbon dioxide, and (e) hydrogen. The fluorescence rate was recorded on a multichannel scaler with a 110-msec bin width.

FIG. 2. (a) Partial-energy-level diagram showing Yb^+ levels involved in the present study. (b) Further simplification where the D and F states have been combined into one state, which we call the "dark" or "trap" state.

2.7×10^{-4}, 6.7×10^{-4}, 1.3×10^{-3}, 2.7×10^{-3}, 6.7×10^{-3}, 1.3×10^{-2}, 2.7×10^{-2}) Pa. Once the steady-state fluorescence measurement was completed, the ions were reloaded, to replace the ions lost at very high buffer-gas pressures, and a measurement of the ion temperature was performed by scanning the laser 40 GHz at a rate of 7.63 GHz/s to obtain the Doppler profile of the transition. The temperature measurements were performed at the same nine buffer-gas pressures, each measurement comprising 50 scans summed to improve the signal-to-noise ratio. The resonance spectrum obtained in this manner was then fitted to a sum of five Voigt profiles, corresponding to the five dominant peaks present in naturally abundant ytterbium, using a commercial curve-fitting program. Using the ratio of the peak fluorescence together with the temperature measurements, a quenching rate for the "dark" state can be determined.

Steady-state fluorescence and resonance spectra were obtained for each of the five buffer gases examined in this study. Figure 1 shows the fluorescence measurements for all five buffer gases. It is clear from the figure that N_2 is the most efficient of the buffer gases studied in its ability to quench the dark state. In order to obtain a more quantitative measurement of the influence of N_2 on the ytterbium ion, fluorescence vs time measurements were repeated with higher resolution and at lower pressures. Fifteen values of N_2 pressures between 6.7×10^{-5} and 1.3×10^{-3} Pa were used to study its quenching efficacy.

Figure 2(a) shows a partial energy level diagram for Yb^+ and 2(b) shows a further simplification where we have combined the $^2D_{3/2}$, $^2D_{5/2}$, and $^2F_{7/2}$ metastable states into
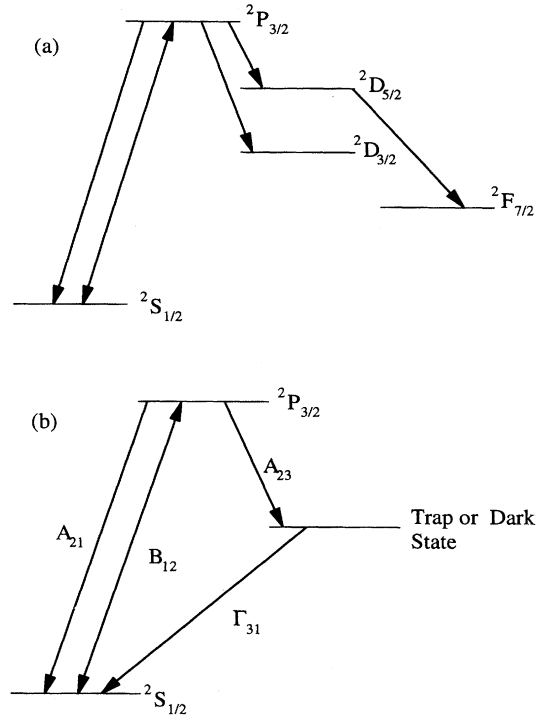
a single dark state. This procedure is justified since the dark state is presumed to result from population trapping via a mechanism that involves the D states, or the F state, which is populated through the D states, or the combination of all three states.

Using the oscillator strengths and branching ratios quoted in Fawcett and Wilson [19] we set up a three-level rate equation.

$$\dot{\mathcal{N}}_1 = -\rho(f_{12})g(f_{12})B^f_{12}\mathcal{N}_1 + \rho(f_{12})g(f_{12})B^f_{12}\mathcal{N}_2$$
$$+ A_{21}\mathcal{N}_2 + \Gamma_{31}\mathcal{N}_3, \tag{1}$$

$$\dot{\mathcal{N}}_2 = \rho(f_{12})g(f_{12})B^f_{12}\mathcal{N}_1 - \rho(f_{12})g(f_{12})B^f_{12}\mathcal{N}_2$$
$$- A_{21}\mathcal{N}_2 - A_{23}\mathcal{N}_2, \tag{2}$$

$$\dot{\mathcal{N}}_3 = A_{23}\mathcal{N}_2 - \Gamma_{31}\mathcal{N}_3, \tag{3}$$

$$\mathcal{N}_0 = \mathcal{N}_1 + \mathcal{N}_2 + \mathcal{N}_3, \tag{4}$$

where A and B are the Einstein coefficients, Γ_{31} is the quenching rate of the dark state, and $g(f_{12})$ is the line-shape factor given as the convolution of the Doppler broadening, lifetime broadening, and the laser linewidth. Since the laser linewidth (~ 1 MHz) is much smaller than either the Doppler broadening (~ 1 GHz) or the lifetime broadening (~ 19 MHz) of the S to P transition, we assumed the laser to be

perfectly monochromatic, reducing $g(f_{12})$ to a convolution of only the lifetime and Doppler broadening. The resulting Voigt profile is given by

$$\mathcal{V}(f,f',\Delta f_{lt},\Delta f_d)= \frac{1}{2\pi}\sqrt{\frac{4\ln2}{\pi}}\frac{\Delta f_{lt}}{\Delta f_d}$$
$$\times \int_{-\infty}^{+\infty}\frac{e^{-4\ln2\left(\frac{f'-f_0}{\Delta f_d}\right)^2}}{(f_0-f)^2+\left(\frac{\Delta f_{lt}}{2}\right)^2}\,df_0.$$

(5)

Here Δf_d is the Doppler full width at half maximum, which we are able to obtain through the resonance fluorescence data fitted with the sum of five Voigt profiles, as previously discussed. Δf_{lt} is the lifetime width and is given by $A_{12}/2\pi$. f' is the center of the Doppler broadened transition where we have shifted the origin to set $f'=0$ and also set the laser frequency f to overlap the center of this transition. Throughout the experiment the laser frequency is monitored with the aid of the ytterbium hollow cathode lamp. With $f'=0$ and $f=0$ the line-shape factor $g(f)=g=\mathcal{V}(f,f',\Delta f_{lt},\Delta f_d)$ in Eqs. (1) and (2). Steady-state solutions of Eqs. (1)–(4) may be obtained by letting $\dot{\mathcal{N}}_1=\dot{\mathcal{N}}_2=\dot{\mathcal{N}}_3=0$ and by rearranging the equations to get

$$\mathcal{N}_2=\frac{pgB_{12}^f\Gamma_{31}\mathcal{N}_0}{pgB_{12}^f(2\Gamma_{31}+A_{23})+\Gamma_{31}(A_{21}+A_{23})},$$

(6)

The $\mathcal{N}_2$-level population is the only one of importance since the observed fluorescence level is directly proportional to this population. Several time constants are necessary to fit the fluorescence rise and decay curves. The initial peak fluorescence is dominated by a very fast time constant in which an equilibrium is reached between the ground-state population depleted by the laser and the decay of the P state via the various available decay channels. This peak fluorescence is proportional to the maximum value of $\mathcal{N}_2$ ($\mathcal{N}_2^{max}$) given by setting $A_{23}/\Gamma_{31}=0$ in Eq. (6). This is justified since the ratio between A_{21} and A_{23} is large (66:1), which in turn implies that the peak population in level 2 is approximately equal to the steady-state population in that level if Γ_{31} is very large. This is followed by a much slower time constant in which fluorescence is lost due to ions getting shelved into a metastable state. The steady-state level beyond several seconds is determined by the actual value of Γ_{31}. The measured ratio $\mathcal{R}$ of the steady-state fluorescence vs the peak height is therefore equal to $\mathcal{N}_2/\mathcal{N}_2^{max}$, from which we can determine Γ_{31} as follows:

$$\Gamma_{31}=\frac{pgB_{12}^f A_{23}\mathcal{R}\mathcal{N}_2^{max}}{pgB_{12}^f-(2pgB_{12}^f+A_{21}+A_{23})\mathcal{R}\mathcal{N}_2^{max}}.$$

(7)

A plot of Γ_{31} vs pressure is shown in Fig. 3. The data fit well a polynomial of order 2 reflecting thermalizing effects [20,21] and multiple collisional effects that may be present. We have fit the first seven data points to a straight line to obtain a quenching rate $\Gamma_{31}=(3.78\pm0.99\times10^4)$/s/Pa at low
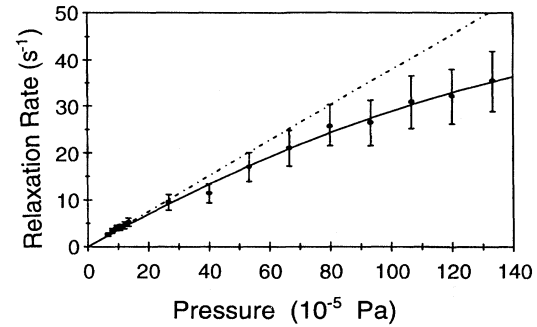

FIG. 3. Quenching rate of ytterbium's trap state vs N_2 buffer-gas pressure. The curved line represents a least-squares fit of the data to the polynomial $\Gamma_{31}=aP+bP^2$; $a=3.63\pm0.12\times10^4$/s Pa and $b=-7.45\pm1.15\times10^6$/s Pa^2, while the straight line represents a linear least-squares fit to pressures $\leqslant26.6\times10^{-5}$ Pa.

pressures ($P\leqslant2.66\times10^{-4}$ Pa). The uncertainty corresponds primarily to fluctuations in the laser power.

Highly effective quenching of metastable states in many of the alkali atoms with N_2 as a buffer gas has been known for many years and has been attributed to large cross sections for energy transport between the alkali atoms' electronic energy into vibrational and rotational states of the nitrogen molecule [20–22]. We believe the same mechanism is responsible for quenching of the alkali-atom-like singly ionized ytterbium ion by the N_2 buffer gas.

As the data displayed in Fig. 1 show, He, Ar, and CO_2 exhibit a considerably smaller efficiency for depleting the population of the dark state as compared to N_2. The absence of quenching efficiency with argon and helium is not surprising since the noble gases do not have the vibrational and rotational structure of diatomic or polyatomic molecules and therefore may only collisionally transfer the electronic energy into kinetic energy, a process with a much smaller cross section. A previous study of the ytterbium ion's "trap" state lifetime as a function of buffer-gas pressure using He, Ne, and Ar indicated relaxation times on the order of minutes even at pressures approaching 1 Pa [15].

It was however surprising to see that neither CO_2 nor H_2 were efficient at quenching the dark state population. In fact, with hydrogen as the buffer gas the fluorescence quickly decayed to the level of the background light and could not be reestablished even after extremely long dark periods (approximately several hours). This would imply that either the trap time with hydrogen is short or hydrogen is particularly ineffectual in reducing the duration of the dark period. We verified that the trap time with hydrogen is quite long by waiting several hours, after initially loading the ions, before exposing the ions to the uv radiation. Since hydrogen is quite effective in quenching metastable states in other excited ions and atoms [14,20,23], and has been shown to be nearly an order of magnitude more efficient than nitrogen in quenching the $^2D_{3/2}$ state in Yb$^+$[14], we conjecture that molecular formation between hydrogen and excited ytterbium ions may be occurring. CO_2 proved to be a very ineffective buffer gas yielding very short trap times, thus being ruled out as a candidate buffer for use in the ytterbium-ion frequency standard.

A dual decay-time characteristic was exhibited when helium was used as the buffer gas at pressures of 6.7×10^{-3} Pa

and greater. A nonlinear behavior of the decay rate of the $^2D_{3/2}$ in Yb^+ at high He pressures has been previously observed [14,24] and discussed in detail in Ref. [24]. We also found that at very high He pressures the trap time was greatly reduced and a competing effect between quenching the "dark" state and loss of ions from the trap appeared to occur.

Since our main objective is to exploit the 12.64-GHz transition between the hyperfine levels of the ground state of $^{171}Yb^+$, we performed microwave optical double resonance spectroscopy using N_2 as a buffer gas and found no loss of coherence in the ground-state hyperfine levels due to the N_2 buffer gas. In fact, we were able to transfer the population of the ions between the lower and upper hyperfine states over a 25-s period using the Ramsey separated pulse technique, which yielded a linewidth of 20 mHz, corresponding to a line Q of 6.3×10^{11}. Furthermore, nitrogen was so efficient at quenching the "dark state" that we were able to obtain single-shot photon counts of 130 000 above a 50 000 count

background, corresponding to a signal-to-noise ratio exceeding 350:1 in the shot-noise limit. A potential stability of $1.8 \times 10^{-14}/\sqrt{\tau}$ is thus realizable with the present trapping configuration.

In summary we have determined a highly effective means for quenching the "trap" state in the ytterbium ion through introduction of N_2 into the vacuum system. A quenching rate of $(3.63 \pm 0.12 \times 10^4)/s/Pa - (7.45 \pm 1.15 \times 10^6)/s/Pa^2$ was determined by measuring the ratio of the peak fluorescence to the steady-state fluorescence level of naturally abundant ytterbium irradiated with 329-nm radiation. We found no loss of ion coherence due to the presence of nitrogen and were able to cool the ion temperature down to 600 K. This approach provides a simple solution to the problem of population trapping in a buffer-gas-cooled ytterbium-ion frequency standard.

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