Precision determination of the ground-state hyperfine splitting in $^{137}Ba^+$ using the ion-storage technique

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The ground-state hyperfine splitting of the $^{137}Ba^+$ ion has been measured with a precision of 4.6×10^{-11}. About 10^5 ions were confined in a rf quadrupole trap for many hours. Hyperfine pumping was achieved by a pulsed tunable dye laser and transitions between the Zeeman sublevels were induced by microwaves, locked to a primary frequency standard. The transitions were detected via changes in the ionic fluorescence perpendicular to the laser beam. The final result is $W_{hfs}=8\,037\,741\,667.69$ (0.36) Hz. The uncertainty stems in about equal parts from the extrapolation to zero electric and magnetic field strength.

I. INTRODUCTION

The confinement of charged particles by electromagnetic forces for very long times to a small volume almost free of perturbations has found a variety of applications during the past decade. It has been used, e.g., as a high-resolution mass spectrometer, which recently provided new values for the ratio of electron and proton mass,[1,2] served to determine the anomalous magnetic moment of electron and positron with unprecedented accuracy,[3] and allowed the measurement of lifetimes of very-long-lived metastable states.[4,5,6] In microwave spectroscopy the pioneering experiment on $^3He^+$ by Dehmelt and co-workers[7] was followed by measurements of the hyperfine splitting of $^{199}Hg^+$.[8,9,10] While the first one used spin exchange and spin-dependent charge exchange between He^+ and Cs atoms for polarization and detection of Zeeman resonances, the optical double-resoance experiment on $^{199}Hg^+$ relied on a fortuitous matching of spectral lines of different Hg^+ isotopes.

The use of a tunable laser for optical pumping allows more general applications in spectroscopy on ions and at the same time increases the signal-to-noise ratio substantially. Recently, the first experimental results have been obtained on Mg^+ and Ba^+ ions. In the first case[11] a cw dye laser was employed, which served for optical pumping and optical sideband cooling of the ions at the same time and required a sophisticated sequence of optical and microwave transitions. The experiment on $^{137}Ba^+$ was performed using a pulsed dye laser to change state populations and to detect microwave transitions. Preliminary results have been published elsewhere.[12]

The ground-state hyperfine separation of (nominal) 8 GHz of $^{137}Ba^+$ has been determined previously on ions in a buffer gas cell.[13] Light shift, pressure shift, and coherence-time effects limited the accuracy in this experiment to 7.5 parts in 10^8. It seems worthwhile to improve the accuracy, since ion storage is being discussed for frequency-standard applications,[14,15] and because of its large hyperfine splitting, its high mass, and its resonance lines in the reach of available dye lasers, $^{137}Ba^+$ may be a suitable candidate.

II. APPARATUS

A. Ion storage

The principle of ion storage has been treated extensively by several authors,[14–16] so we restrict ourselves to a brief outline. The ions are confined in a rf quadrupole trap (Paul trap). A dc voltage U_0 and an ac voltage $V_0\cos\Omega t$ are applied between a ring electrode (radius r_0) and two endcaps (half distance $z_0=r_0/\sqrt{2}$) of hyperbolic shape to create the potential

$$\Phi=(U_0+V_0\cos\Omega t)(x^2+y^2-2z^2)/r_0^2\ . \tag{1}$$

Under the action of the inhomogeneous force, the ions follow trajectories given by the solution of a differential equation of the Mathieu type. A class of solution, depending on two parameters a and q,

$$a_z = -8eU_0/mr_0^2\Omega^2 = -2a_r \ , \qquad (2)$$
$$q_z = 4eV_0/mr_0^2\Omega^2 = -2q_r \ ,$$

leads to finite amplitude of the ion motion, i.e., to confinement. Following the notation of Ref. 14, we can describe this motion in first order by a harmonic oscillation at a frequency ω whose amplitude is modulated at the frequency Ω of the trapping field:

$$x_i(t) = A_i(1 + 1/2q_i\cos\Omega t)\cos\omega_i t, \quad i = r,z$$
$$\omega_i = \beta_i\Omega/2 \ , \qquad (3)$$
$$\beta_i^2 = a_i + (1/2)q_i^2 \ .$$

In thermal equilibrium the ions assume a Maxwell-Boltzmann velocity distribution, whose mean energy is approximately one-tenth of the trap-potential well-depth D, given by

$$D = (1/8)m\Omega^2(\beta_r^2 r_0^2 + \beta_z^2 z_0^2) \ . \qquad (4)$$

The spatial ion distribution around the trap center is found to be Gaussian, the width being proportional to the mean energy.[17,18] In our experiment a layer of less than 0.5 mg of isotope separated Ba on a hot Pt filament placed near the inner surface of the lower endcap electrode served as the ion source. About 2% of the ions, created by surface ionization at moderate temperatures, were confined, yielding approximately 10^5 trapped ions after a few seconds. The storage time usually exceeded several hours at background pressures between 10^{-5} and 10^{-9} mbar. Trap parameters and typical operating conditions are listed in Table I.

TABLE I. Trap parameters and typical operating conditions.

trap dimensions:	$r_0 = 20$ mm
	$z_0 = 14.14$ mm
typical confinement data:	$a_z = -0.012$
	$q_z = 0.56$
	$\beta_r = 0.21$
	$\beta_z = 0.38$
drive frequency	$\Omega/2\pi = 490$ kHz
applied potential	$V_{dc} = 8$ V
	$V_{ac} = 756$ V
potential depth	$D_z = 48.8$ eV
	$D_r = 30.4$ eV
ion cloud diameter:	$d_c = 12$ mm
laser beam diameter:	$d_L = 4$ mm
laser pulse duration:	$\tau = 6$ nsec
laser repetition frequency:	$0 \le f_L \le 50$ Hz
laser power/pulse:	$P_L > 10$ kW

B. Optical pumping

The ground-state hyperfine splitting of 8 GHz, which is larger than the optical Doppler width of 3 GHz (at typical mean ion energies of 2 eV), allows easy hyperfine pumping by tuning a laser to one of the hyperfine components of the resonance line at 493.4 nm (Fig. 1). The splitting of the excited $6P_{1/2}$ state of 0.74 GHz can be neglected. The excited P state partially decays into the metastable $5D_{3/2}$ state (branching ratio 2.8). Since the radiative decay time of this state is 17.5 s (Ref. 5) the ions would accumulate there, being lost for the pumping cycle. Therefore we introduced He buffer gas at about 10^{-7} mbar into our system for collisional quenching. The hyperfine density shift at this pressure amounts to $\delta\nu/\nu = 5\times10^{-16}$ (Ref. 13) and is negligible at our level of accuracy. We employed a pressure-tuned pulsed dye laser (bandwidth 1 GHz) which was operated well above saturation intensity. Solution of the rate equations for the pumping cycle shows that equilibrium of state population is achieved after about 10 laser pulses. The pulse rate can be varied between 0 and 50 Hz.

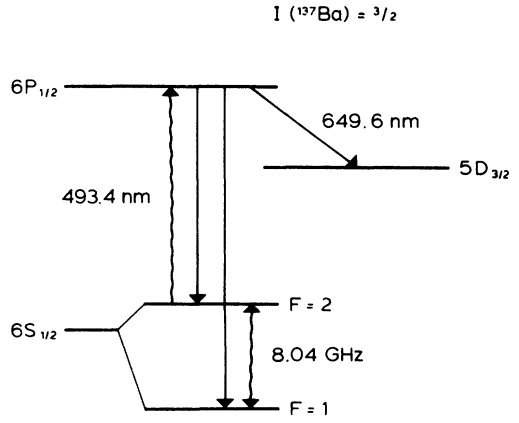

FIG. 1. Part of the energy diagram of Ba^+ and optical pumping scheme. The hyperfine-structure (hfs) splitting of excited states is neglected.

C. Hyperfine transitions

The $\Delta F=1$, $\Delta m_F=0,\pm 1$ selection rule allows, for a nuclear spin of $\frac{3}{2}$, nine different transitions between the hyperfine Zeeman sublevels. The microwaves to induce those transitions were created by a klystron, thermally isolated and phase-locked to the 17th harmonic of a 500-MHz frequency synthesizer, whose time base was supplied by a Rb frequency standard (short-term stability 5×10^{-11}/s). As a reference for long-term stability we used the broadcast 77.5-kHz signal of the Physikalisch-Technische Bundesanstalt locked to a primary cesium standard (Fig. 2). The microwaves were fed into the trap by a hairpin antenna, placed between the ring and the lower endcap electrode. This caused only a slight distortion of the trapping field and did not affect the storage time at all.

We observed the hyperfine Zeeman transitions by a change in the fluorescence intensity perpendicular to the laser beam. The *P-D* decay photons at 649.6 nm were monitored in a time interval of about 20 ns, triggered by the laser pulse. This assured complete absence of stray light caused by the laser beam. The efficiency of the optical detection system was 2×10^{-3} (5% solid angle, 75% filter and surface transmission, 5% photomultiplier efficiency). Typical count rates off resonance were 17 photons per laser pulse, at resonance 24 photons per pulse. For statistical averaging we usually summed over 10–30 pulses.

III. MEASUREMENTS

The measurements were performed according to the following sequence:

(1) The ions were created by surface ionization and confined usually for one day.

(2) The dye laser was pressure-tuned to the lower hyperfine component of the optical resonance transition (starting from $F=2$). Since the laser wavelength was not stabilized, we had to slightly readjust the wavelength a few times a day. The laser pulse rate could be varied between 0 and 50 Hz. Although the width of the resonance decreases with lower pulse rate we usually chose 20 Hz for reason of signal-to-noise ratio.

(3) The klystron output frequency was swept across the hyperfine transition and the fluorescence count rate at 649.6 nm was sampled and stored in a multichannel analyzer (MCA) for further data handling.

We observed all possible $\Delta F=1$, $\Delta m_F=0,\pm 1$ transitions. Apart from the $F=1$, $m_F=0-F=2$, $m_F=0$ transition, which showed a weak quadratic magnetic field dependence only and which we call "field independent", the width of the remaining lines was determined by the inhomogeneity of the residual magnetic field inside the trap. It could be varied by three pairs of Helmholtz coils between 10^{-2} and 10 G. Typical linewidths were 2–10 kHz, which was sufficient to determine the magnetic field to about one part in 10^4.

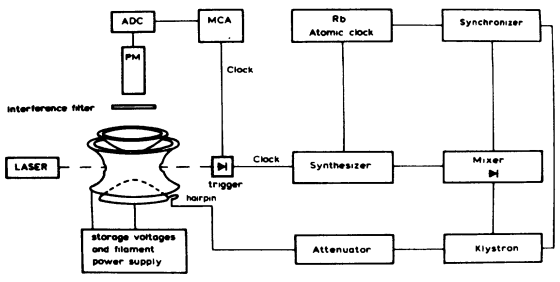

FIG. 2. Experimental arrangement. Not shown is the broadcast Cs reference (DCF 77) for long-term frequency stability of the Rb clock.

A. Line shape and linewidth of the 0-0 resonance

There are different relaxation mechanisms, which might contribute to the linewidth of the "field-independent" transition.

a. Collisions with neutral He atoms. The cross section of alkali atoms with noble gases for hyperfine relaxation is typically smaller than 10^{-16} cm^2. Assuming a similar order of magnitude for the alkalilike Ba^+ ion, we have for He pressures of 10^{-7} mbar and average ion velocities of 10^5 cm/s relaxation constants of 30 s.

b. Magnetic field inhomogeneity. From the linewidth of the magnetic field dependent lines we deduce a typical field inhomogeneity $\delta H/H$ over the active trap volume of about 1×10^{-3} at field strength of 1 G. This value leads to a linewidth of 1 Hz in the "field-independent" resonance. Motional narrowing may further reduce this value.

c. Ion loss from the trap. Since the storage time of many hours exceeds the time for one sweep across the resonance by many orders of magnitude, we do not regard it as a significant contribution to the linewidth. We take into account any possible

ion loss during one microwave sweep by a linear term $-C(\omega-\omega_0)$ in the final line-shape formula whose amplitude C has to be determined experimentally.

d. Pulsed laser excitation. The ions interact essentially freely with the applied microwave field during the time T between two consecutive laser pulses, while the short (6 ns) and intense (~ 10 kW) pulse destroys coherence. Since the linewidth of the 0-0 transition is many orders of magnitude smaller than the energy distance to any neighboring state, we can deal satisfactorily with a two-level system. The well-known transition probability for this case, neglecting relaxation, is

$$P=\frac{\gamma_m^2}{(\omega-\omega_0)^2+\gamma_m^2}\times\sin^2\left[\frac{T}{2}[(\omega-\omega_0)^2+\gamma_m^2]^{1/2}\right], \tag{5}$$

where γ_m is the hyperfine transition rate, proportional to the microwave amplitude, ω the microwave frequency, and ω_0 the resonance frequency. This transition rate, however, has to be modified due to the fact, that the ion cloud width is somewhat larger than the laser beam diameter. Thus, there is a finite chance for an ion to escape one or even more laser pulses, which extends the free interaction time to multiples of T. Accordingly the transition rate is given by

$$P=\frac{\gamma_m^2}{(\omega-\omega_0)^2+\gamma_m^2}\times\sum_{k=1}^{n}a_k\sin^2\left[k\frac{T}{2}[(\omega-\omega_0)^2+\gamma_m^2]^{1/2}\right], \tag{6}$$

where $k=1,2\ldots$. The amplitudes a_k are determined purely by geometry and are normalized to $\sum_{k=1}^{n}a_k=1$.

In the process of fitting the line-shape formula to our data it turned out what we had to add a term symmetrically around ω_0 in order to get satisfactory agreement. For purposes of simplicity we chose

$$B\exp[-(\omega-\omega_0)^2/\gamma_m^2], \tag{7}$$

whose amplitude B is small, possibly attributed to residual phase noise in our microwave oscillator. Later measurements on the $^{135}Ba^+$ isotope, which resulted in narrower lines, indicate that under the given experimental conditions and the present level of accuracy, relaxation due to collisions with background molecules can be neglected.[19]

To summarize, the line-shape formula $F(\omega)$, which we used to fit our data, consists of different terms as described above:

$$F(\omega)=AP+B\exp[-(\omega-\omega_0)^2/\gamma_m^2]-C(\omega-\omega_0)+D, \tag{8}$$

where D is a constant background. We checked this formula by comparison to experimental lines, taken with high spectral resolution (Fig. 3) and at different microwave amplitudes (Fig. 4). Without exception, all experimental curves could be fitted with a constant set of parameters $a_1,\ldots,a_5$, A, B, C, and D. Apart from normalization, the only parameter which could not be determined independently was the microwave power inside the trap. It was used as a free parameter in the fitting process. We found however, that instead of Eq. (6) we had to use

$$P'=\frac{\gamma_m^2}{(\omega-\omega_0)^2+\gamma_m^2}\times\sum_{k=1}^{n}a_k\sin^2\left[k\frac{T}{2}[(\omega-\omega_0)^2+\gamma_m'^2]^{1/2}\right], \tag{9}$$

with different values of γ_m,γ_m' to obtain satisfactory agreement. This is not understood so far. Although the line shape might not be completely understood, we have some confidence in the determination of the line centers because of the apparent high degree of symmetry in the lines.

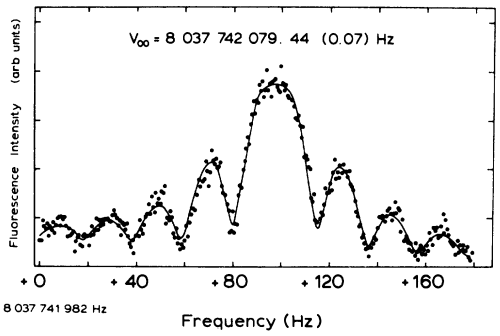

FIG. 3. $F=2$, $m=0\rightarrow F=1$, $m=0$ hyperfine transition in $^{137}Ba^+$. The full line represents a least-squares fit according to Eq. (8) to the experimental points. Frequency steps 0.6 Hz, laser repetition rate 20 Hz, averaging time 15 s/channel. Statistical error of center frequency 0.07 Hz.

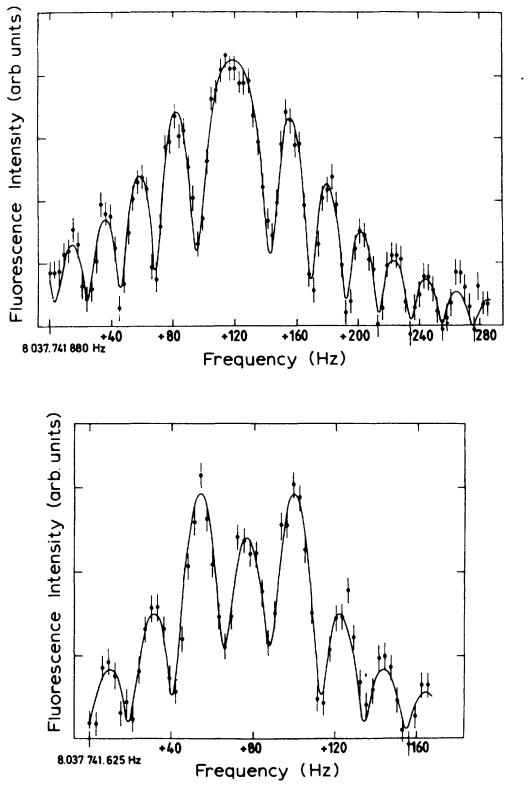

FIG. 4. Examples of "field-independent" hfs transition and fits according to Eq. (8).

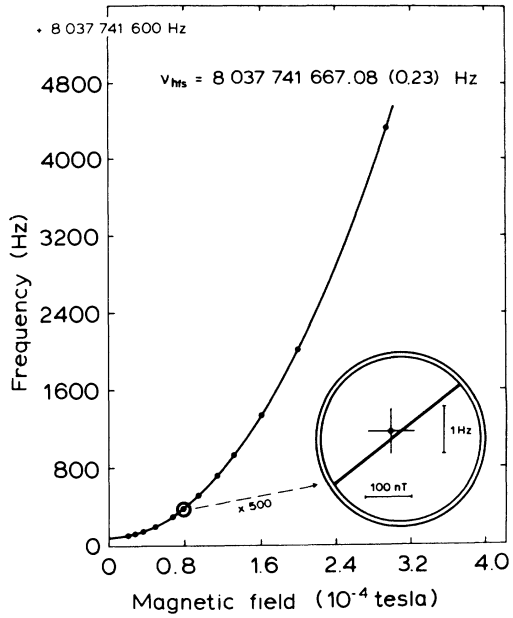

FIG. 5. Magnetic field dependence of the 0-0 transition. The magnetic field was determined by the $\Delta m_F = \pm 1$ transitions. Least-squares fit according to the Breit-Rabi formula [Eq. (10)].

B. Magnetic field dependence

In order to determine the magnetic field inside the ion trap all other hyperfine transition frequencies were measured. Because of insufficient shielding, stray and 50 Hz fields in the lab caused a residual linewidth of a few kHz. Thus, it was possible to determine the applied magnetic field with an uncertainty of 1×10^{-4}.

The magnetic field dependence of the 0-0 transition is given by the Breit-Rabi formula, which yields

$$\nu_{00}(B)=\nu_{00}(0)+487.7B^2 \qquad (10)$$

(B in 10^{-4} tesla), if we take the g_J value from the isoelectronic Cs. Figure 5 shows the corresponding fit. The total error in the extrapolation to zero field is 0.23 Hz. To give an idea of the error at a single data point, the insert is 500 times enlarged.

C. Doppler Shift

Since the ion motion is limited to dimensions which are smaller than the observed wavelength, the first-order Doppler shift plays no role.[17] However, because of the ion energy of several eV the second-order Doppler shift is of importance at our level of accuracy.

Different measurements[18,20] have shown that the average ion energy varies linearly with the trap-potential depth D. This provides a means to change the ion temperature. We were able to vary our operating point to a certain extent, limited by the loss of ions near the boundary of the stable trapping region. The observed shift of the transition frequency can be fitted by a straight line for extrapolation to zero energy (Fig. 6). The experimental value

$$\delta\nu/\nu=-2.5(1.1)\times10^{-12}D\ ,$$

with D expressed in eV, is somewhat larger than the calculated value of $-7.8\times10^{-13}D$ from the second-order Doppler effect, assuming that the average ion energy is $\frac{1}{10}$ of the potential depth as in Ref. 19. The total correction from our usual operating point to zero energy amounts to 0.61 (0.27) Hz.

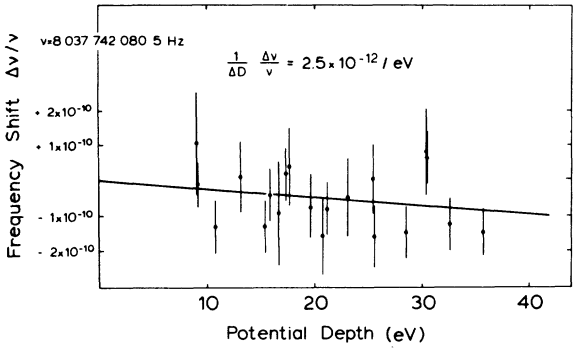

FIG. 6. Frequency of the 0-0 transition vs trap-potential well depth. The line is a linear least-squares fit.

D. Stark effect

Stark shifts of the ground-state hyperfine splitting have been observed only on a few neutral atoms. As an example, for the strongly polarizable Cs atom, the shift is

$$\delta\nu/\nu = -2.8\times10^{-16}E^2$$

with E in V/cm[21]. From this we estimate for our operating conditions a maximum frequency shift of 0.3 Hz. A possible effect of this kind would be included in the shift observed by variation of the trap-potential depth, since the electric-field strength cannot be changed independently. It might be the cause for the discrepancy between observation and calculation at the second-order Doppler effect, but we cannot totally exclude instrumental failure during the course of several runs, which could be responsible for that.

E. Other possible sources of frequency shifts

Light shifts do not occur in this experiment since the microwave frequency is always switched off when a laser beam passes through the ion trap. Measured values for the fractional density shift in the hyperfine structure of $^{137}Ba^+$ ions[13] give pressure shifts at most of 10^{-3} Hz. This is negligible at our level of accuracy as it is the Bloch-Siegert shift which contributes at most to an order of 10^{-6} Hz.

IV. RESULT

The final result of our measurements gives for the ground-state hyperfine splitting of $^{137}Ba^+$, including corrections to zero magnetic field and energy, a value of

$$W_{\rm hfs} = 8.037\,741\,667.69(0.36)\ \text{Hz}\ ,$$

with the following errors: statistical error of line center less than 0.1 Hz; magnetic field extrapolation, 0.23 Hz; and extrapolation to zero potential depth, 0.27 Hz. The uncertainty can be further reduced by improved design of the optical detection system to increase the signal-to-noise ratio, by better shielding of the magnetic field and by a different frequency standard, since the short-term stability of the applied frequency standard (5×10^{-11} sec^{-1}) can cause observable deviations at our level of accuracy.

V. CONCLUSION

The total relative uncertainty of 4.6×10^{-11} in this experiment demonstrates the high potential of the ion-storage technique for high-precision microwave spectroscopy. The use of a laser for optical excitation extends possible species to be investigated substantially, and at the same time leads to good signal-to-noise ratio and short measuring time in spite of the small ion number compared to experiments on neutral atoms. While pulsed lasers have the advantage of simplicity and can avoid any light shifts, cw lasers offer the possiblity to reduce the ion temperature substantially. In the case of Ba^+ ions, suspended in a rf quadrupole trap, this has been demonstrated by Toschek and coworkers.[22] This virtually eliminates all shifts caused by the ion motion. Relative accuracies of parts of 10^{-15} are discussed now,[23] which lead to new possibilities in frequency-standard applications.

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