PHYSICAL REVIEW A, VOLUME 63, 051802(R)

High-resolution spectroscopy of a single In^+ ion: Progress towards an optical frequency standard

Th. Becker, J. v. Zanthier, A. Yu. Nevsky,* Ch. Schwedes, M. N. Skvortsov,* H. Walther, and E. Peik
Max-Planck-Institut für Quantenoptik and Sektion Physik der Ludwig-Maximilians-Universität München, Hans-Kopfermann-Strasse 1, 85748 Garching, Germany

(Received 16 August 2000; published 16 April 2001)

The $5s^2\,{}^1S_0 \rightarrow 5s5p\,{}^3P_0$ transition of a single laser-cooled $^{115}In^+$ ion in a miniature radiofrequency trap is investigated as a possible optical frequency standard. This line at a frequency of 1267 THz (wavelength 236.5 nm) is highly immune to frequency shifts due to external perturbations so that the expected systematic uncertainties can be reduced to the millihertz level. Experimentally, we obtained a fractional resolution $\Delta\nu/\nu = 1.3\times10^{-13}$ (linewidth 170 Hz), limited by the frequency instability of the laser used for excitation. The g factor and the lifetime of the metastable $^3P_0$ level were measured as $g(^3P_0) = -9.87(5)\times10^{-4}$ and $\tau(^3P_0) = 0.195(8)$ s. Both values are in good agreement with perturbative calculations, based on hyperfine mixing between the ^1P and ^3P levels.

DOI: 10.1103/PhysRevA.63.051802 PACS number(s): 42.62.Fi, 06.20.Fn, 32.70.Cs, 32.80.Pj

A single ion, localized in a radiofrequency trap and laser-cooled to a microkelvin temperature, possesses unique properties for high-resolution spectroscopy. It is practically a motionless pointlike absorber in a nearly perturbation-free environment, not limited by finite interaction times, Doppler shifts, or collisional broadening. A narrow optical resonance of such an ion, e.g., with a linewidth of 1 Hz at a frequency of 10^{15} Hz, can consequently serve as a reference in an atomic clock or frequency standard of very high accuracy [1]. With a laser of sub-Hertz linewidth [2,3] it seems possible to achieve a frequency stability of 10^{-15} for 1 second and a long-term accuracy of 10^{-18} after several days of averaging. Such an accurate frequency standard, combined with recently developed precision techniques to measure and compare optical frequencies [4], will be useful to test fundamental physics, improve metrology, and serve technological applications [5]. At present, several candidate ions are being investigated and high-resolution spectroscopy of forbidden optical transitions has yielded sub-kHz linewidths in Hg^+ [6], Ba^+ [7], Sr^+ [8], Yb^+ [9], and In^+. Indium is the first alkaline-earth-like ion that has been studied for this purpose. It offers quite a few advantages compared to the alkalinelike ions, as will be discussed in this paper. It should also be mentioned that recently absolute frequency measurements of high precision have been made for the indium clock transition, the latest result being 1 267 402 452 899.92 (0.23) kHz [10].

Here we report ultrahigh-resolution spectroscopy of the $5s^2\,{}^1S_0 \rightarrow 5s5p\,{}^3P_0$ transition of $^{115}In^+$ at a wavelength of 236.5 nm. This type of forbidden transition between states with vanishing total electronic angular momentum $J=0$ in a two-electron atom promises lower systematic frequency shifts in the coupling to the electric field of the trap than quadrupole or higher-order multipole transitions in the alkalinelike ions [1]. In this respect In^+ is unique among the ions now being investigated. The dominant source of uncertainty for the In^+ frequency standard will most likely be the Zeeman shift. With the high resolution available in our experiment it has been possible to measure this shift for small magnetic fields. We also measured the radiative decay rate of the $^3P_0$ state, which is important for determining the achievable short-term stability of the standard.

In our experiment the indium ion is trapped in a quadrupole radiofrequency trap of the Paul-Straubel type [11,12]. The ring electrode is made of copper beryllium and has an inner diameter of 1 mm. A radiofrequency voltage with an amplitude of 1 kV at 10 MHz, together with DC voltage of 30 V applied to the ring result in oscillation frequencies in the time-averaged pseudopotential of 1.4 MHz in the axial and 0.9 MHz in the radial direction. Electric stray fields are compensated with adjustable static potentials, minimizing the strength of the motional sidebands at the trap frequency [13]. Sideband cooling [1] is done by laser excitation of the $5s^2\,{}^1S_0 \rightarrow 5s5p\,{}^3P_1$ intercombination line (natural linewidth: 360 kHz) at a wavelength of 230.6 nm using a frequency-doubled dye laser. The laser is frequency-stabilized to a reference cavity, resulting in a laser linewidth below 10 kHz. In^+ is most efficiently laser-cooled in a zero magnetic field: The hyperfine level $F=I+1=11/2$ of the $^3P_1$ state (where $I=9/2$ denotes the nuclear spin and F the total angular momentum) is excited with circularly polarized light so that optical pumping between the Zeeman sublevels results in a closed two-level system. Since the ground state is a singlet, no hyperfine repumping is required. For optimized cooling conditions (i.e., weak laser excitation of the first motional sideband), the ion is cooled to the ground state of the trap and temperatures as low as 60 μK have been measured [13]. In the experiments reported here, the laser intensity was higher and the detuning to the carrier was decreased to obtain a stronger fluorescence signal. This leads to a slightly increased temperature of about 150 μK, as measured from the strength of the vibrational sidebands in the spectrum of the $^1S_0 \rightarrow {}^3P_0$ transition.

The laser system used for excitation of the $^1S_0 \rightarrow {}^3P_0$ clock transition is described in Ref. [14]. It is based on a diode-pumped Nd:YAG laser emitting at 946 nm. The fourth harmonic of this line is coincident with the In^+ transition. The laser contains the necessary tuning elements and is

*Permanent address: Institute of Laser Physics, 630090 Novosibirsk, Russia.

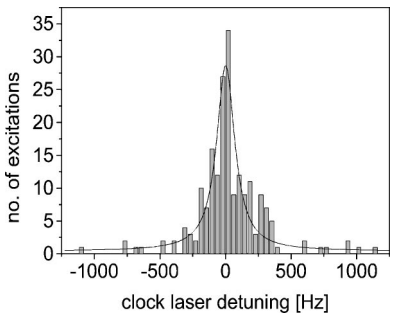

FIG. 1. High-resolution spectrum of the In^+ clock transition $^1S_0 \rightarrow {}^3P_0$, obtained with a single ion. The linewidth of the fitted Lorentzian is 170 Hz FWHM. The peak excitation probability is about 10% and the total measuring time is 30 minutes.

frequency-stabilized to a Fabry-Perot resonator of high finesse by the Pound-Drever phase modulation technique [2]. The reference resonator consists of two highly reflecting mirrors, optically contacted to a spacer made from ultralow expansion glass (ULE) spacer suspended in a temperature-stabilized, vibration-isolated vacuum chamber. A second diode-pumped Nd:YAG laser, containing only a Nd:YAG crystal and a $KNbO_3$ crystal, is used for power amplification and intracavity frequency doubling. Infrared light from the stable master laser is coupled into this laser to transfer the frequency stability via injection locking. The second frequency doubling, converting the blue light at 473 nm to UV radiation at 236.5 nm, is performed with a BBO crystal in an external enhancement cavity. Recent improvements to the system include locking of the master laser to the reference cavity with sub-Hertz stability, better vibrational isolation, and active stabilization of the path length between the laser and the cavity, of the laser power, and of the residual amplitude modulation in the phase modulator of the Pound-Drever lock [17].

Spectroscopy of the narrow $^1S_0 \rightarrow {}^3P_0$ line is performed in optical-optical double resonance using the detection of quantum jumps [1,16]: Excitation of the metastable $^3P_0$ level leads to cessation of the single-ion fluorescence signal on the cooling transition until the level decays. This method allows detection of transitions to the metastable state with practically 100% efficiency. In order to avoid any light shift and line broadening of the clock transition due to the radiation of the cooling laser, the two laser beams are applied alternately by means of mechanical shutters. After a clock-laser pulse of 20 ms duration, the cooling laser is turned on and the fluorescence photons are counted in a 40 ms time interval. Typically 18 fluorescence photons are detected in one time interval, with a background of less than one count on the average from laser stray light and photomultiplier dark counts. If fluorescence photons are detected, the excitation attempt of the clock transition is regarded as unsuccessful. If the ion is not fluorescing, an excitation of the clock transition is recorded, and the cooling laser is kept switched on to wait for the decay of the metastable state. Typically, the frequency of the clock-laser radiation is changed in steps of 8 Hz and four excitation attempts are made at each frequency.

A high-resolution spectrum of the clock transition is shown in Fig. 1. The clock-laser power was reduced to 30 nW to avoid saturation broadening. Twenty unidirectional scans over the resonance are superimposed after correction for a linear drift of the reference cavity of 7.1 Hz/s (all frequencies refer to the UV light). The cavity drift was controlled by repeatedly taking excitation spectra of the ion at higher laser power and thus with a higher excitation rate. The drift was found to be linear on the timescale of an hour. Both the shift and the expansion of the frequency scale due to the drift were corrected for. Fitting the spectrum with a Lorentzian curve results in a linewidth of 170 Hz full width at half maximum (FWHM), corresponding to a fractional resolution $\delta\nu/\nu$ of 1.3×10^{-13}. A spectral window of width 200 Hz contains 50% of all excitations. According to our present experimental control of the ion temperature, electromagnetic fields, and vacuum conditions, no significant Doppler, Zeeman, Stark, or collisional broadening of the absorption spectrum of the ion is expected beyond the level of 1 Hz. The linewidth is determined by the frequency instability of the laser and the lineshape is not exactly Lorentzian but reflects the fluctuations of the laser frequency, which arise mainly at low modulation frequencies in the range 1–15 Hz. Measurement of the frequency stability of the laser using a second independent high-finesse optical cavity gives a consistent result. Improvements of the vibrational isolation of the reference cavity that is used for the frequency stabilization will probably enable us to resolve the natural linewidth of the ion (0.82 Hz), leading to a resolution of 6×10^{-16}. The measurements described here are done with a laser setup made from discrete optical elements [14], but in the future a monolithic ring laser [18,19] may be used to achieve high intrinsic stability and compact design.

The efficient laser excitation and the high resolution of double resonance spectroscopy allow us to study the properties of the metastable $^3P_0$ level. In the absence of a nuclear spin, the $^1S_0 \rightarrow {}^3P_0$ transition would be forbidden as a one-photon process in all multipole orders of the electromagnetic field, and both states would not couple to an external magnetic field to first order. The $^{115}In^+$ ion, however, possesses a nuclear spin $I=9/2$ and its $5s5p\ {}^3P_0$ state is not a pure $J=0$ state, but contains small admixtures of the $5s5p$ levels $^3P_1$ and $^1P_1$ caused by the magnetic dipole hyperfine interaction. (The same holds for ^{113}In, the less abundant stable indium isotope.) These perturbations are responsible for the nonvanishing electric dipole moment between $^1S_0$ and $^3P_0$ and also for a small deviation of the g factor of the $^3P_0$ state from the nuclear g factor of the $^1S_0$ ground state [15,20,21], leading to a weak anomalous Zeeman effect of the $^1S_0 \rightarrow {}^3P_0$ transition. The admixtures to the $^3P_0$ level can be written in terms of the states $|{}^3P_1'\rangle$ and $|{}^1P_1'\rangle$ in intermediate coupling or the pure LS coupled states $|{}^3P_1\rangle$ and $|{}^1P_1\rangle$:

$$|{}^3P_0'\rangle = |{}^3P_0\rangle + \alpha_0 |{}^3P_1'\rangle + \beta_0 |{}^1P_1'\rangle \tag{1}$$

$$= |{}^3P_0\rangle + (\alpha_0\alpha - \beta_0\beta)|{}^3P_1\rangle + (\alpha_0\beta + \beta_0\alpha)|{}^1P_1\rangle. \tag{2}$$

The mixing coefficients α_0, β_0 of hyperfine mixing and α, β of intermediate coupling have been calculated semi-

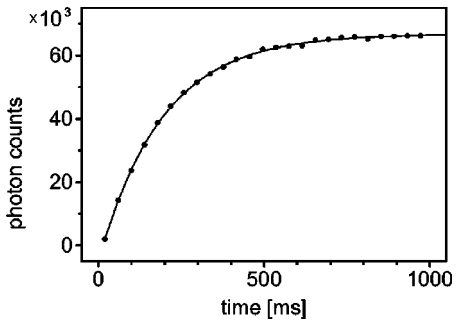

FIG. 2. Lifetime measurement of the $^3P_0$ level: accumulated fluorescence signal on the $^1S_0 \rightarrow {}^3P_1$ transition of a single ion after excitation of the $^3P_0$ state (3600 events).

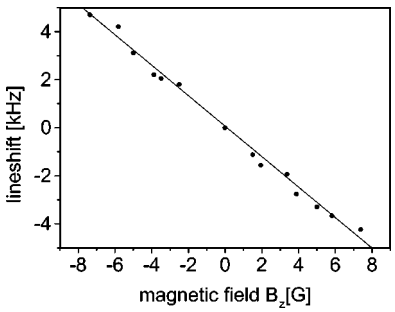

FIG. 3. Zeeman shift of the $|^1S_0, F=\frac{9}{2}, m_F=\frac{9}{2}\rangle \rightarrow |^3P_0, \frac{9}{2}, \frac{7}{2}\rangle$ transition as a function of the axial magnetic field B_z (parallel to the circularly polarized laser beam).

empirically [15]: $\alpha = 0.997$, $\beta = -0.079$, $\alpha_0 = -1.1 \times 10^{-3}$, $\beta_0 = 3.5 \times 10^{-5}$. From them it is possible to relate the lifetime of the $|^3P_0'\rangle$ state to that of $|^3P_1'\rangle$ via

$$\tau(^3P_0) = \left[\frac{E(^3P_1)}{E(^3P_0)}\right]^3 \frac{\beta^2}{(\alpha_0\beta + \beta_0\alpha)^2}\,\tau(^3P_1), \qquad (3)$$

where E denotes the energies of these levels relative to the ground state. With the value $\tau(^3P_1) = 0.44(4)$ μs, the result for $\tau(^3P_0)$ is 0.20(3) s [15]. The g factor of the perturbed $^3P_0$ state is given by

$$g(^3P_0) = g(^1S_0) + \frac{\sqrt{8}}{\sqrt{3I(I+1)}}\,(\alpha_0\alpha - \beta_0\beta) \qquad (4)$$

to first order in α_0 and β_0. This calculation predicts a difference in the g factors of $\Delta g_{00} = g(^3P_0) - g(^1S_0) = -3.5(2) \times 10^{-4}$, where the g factor of the ground state is $g(^1S_0) = -6.6647 \times 10^{-4}$ [22]. The stated uncertainties in the theoretical values reflect those of the experimental parameters entering the calculation.

Experimentally, the lifetime of the $^3P_0$ state can be determined from the duration of the dark periods in the fluorescence on the cooling transition after excitation of the metastable state. The laser radiation that is resonant on the $^1S_0 \rightarrow {}^3P_1$ transition has no effect on the decay of the $^3P_0$ level, since it is far detuned from any resonance connected to that level. Such a lifetime measurement has already been made by taking advantage of the excitation of the metastable state via the weak decay of $5s5p\,{}^3P_1$ to $5s5p\,{}^3P_0$, but was limited by the small number of only 150 observed events. The result was 0.14(2) s [15]. In the present experiment more than 20 000 records of the fluorescence of the ion after direct laser excitation of the $^3P_0$ state have been analyzed. Each individual event resembles a step function, comprising a dark period of variable duration followed by a fluorescence signal until the end of the detection cycle. Photons were counted in time intervals of 40 ms. Summing all the photon counts measured at a fixed delay after the clock laser excitation pulse and plotting the sums as a function of the delay time t gives an exponential curve $\propto [1 - \exp(-t/\tau)]$, where τ is the lifetime of $^3P_0$. Figure 2 shows a sample of the data including 3600 excitations. Analysis of all data gives the result $\tau(^3P_0) = 0.195(8)$s, in excellent agreement with the theoretical estimate.

To determine the difference in the g factors between the ground and metastable states, the Zeeman shift of the component $|^1S_0, F=\frac{9}{2}, m_F=\frac{9}{2}\rangle \rightarrow |^3P_0, \frac{9}{2}, \frac{7}{2}\rangle$ of the clock transition is studied in the experiment. The initial state is prepared by exciting the cooling transition $|^1S_0, F=\frac{9}{2}\rangle \rightarrow |^3P_1, \frac{11}{2}\rangle$ with circularly (σ^+) polarized light. After blocking the cooling laser the clock laser radiation is applied with circular polarization of the opposite helicity (σ^-). A pair of coils produces a variable, homogeneous magnetic field along the common axis of the two laser beams. The magnetic field at the position of the ion is calibrated with 1% uncertainty by measuring the splitting between the $^1S_0$ ground state Zeeman sublevels in RF-optical double resonance spectroscopy. Transverse magnetic fields are controlled by observing the ground-state Hanle effect [23] and are set to zero with about 10 mG uncertainty, with two more pairs of coils being used.

The experimental result for the Zeeman effect of the $|^1S_0, F=\frac{9}{2}, m_F=\frac{9}{2}\rangle \rightarrow |^3P_0, \frac{9}{2}, \frac{7}{2}\rangle$ transition is shown in Fig. 3. The data can be fitted by a linear shift of $-636(27)$ Hz/G, leading to $g(^3P_0) = -9.87(5) \times 10^{-4}$ or $\Delta g_{00} = -3.20(5) \times 10^{-4}$ in good agreement with the theoretical estimate. In a final realization of the indium frequency standard the $|m_F = \pm 1/2\rangle \rightarrow |m_F = \pm 1/2\rangle$ components of the clock transition can be used, which show a smaller Zeeman shift of ∓ 224 Hz/G and symmetric splitting, so that the unperturbed frequency at $B = 0$ can be determined as the average frequency of the two components. To obtain the anticipated uncertainty of 1 mHz, control of the magnetic field with a precision of several μG is required [24].

Finally, let us consider other expected line shifts and associated uncertainties of the indium frequency standard. The ion is localized to within a small fraction of the wavelength of the clock laser, so that a recoil-free and Doppler-free carrier is obtained. The second-order Doppler shift is proportional to the temperature and scales as 1.5 Hz/K. For a laser-cooled ion ($T \ll 1$ mK), this shift is reduced to below 1 mHz. Electric fields lead to a quadratic Stark shift of the transition frequency. In positive ions the static polarizabilities are generally smaller than in neutral atoms because the remaining valence electrons are more tightly bound. By comparison

with the Cd atom, which is isoelectronic to In^+, we estimate the quadratic Stark shift of the In^+ clock transition to be below 1 mHz/$(V/cm)^2$. The Stark shift induced by the trap field is proportional to the mean quadratic distance of the ion from the trap center and consequently proportional to the temperature of the ion. The shift is smaller than 0.1 Hz/K for our typical trap conditions and therefore negligible at the submillikelvin temperatures achievable with laser cooling. The electric field gradient of the trap has no influence, since both levels of the clock transition have vanishing quadrupole moment. As a single-photon transition without hyperfine splitting, the In^+ clock transition is immune to ac Stark shifts due to the exciting laser light. The averaged quadratic electric field strength of the black-body radiation emitted by the vacuum chamber is given by $\langle E^2\rangle = 69.2(\mathrm{V/cm})^2(T/300\ \mathrm{K})^4$. At room temperature, black-body radiation has its peak spectral density at a wavelength of 9 μm, whereas both the ground state and the metastable $^3P_0$ level of In^+ have strong electric-dipole-allowed transitions to the next-higher-lying states only at vacuum ultraviolet wavelengths (159 nm and 194 nm, respectively). Consequently, the influence of the thermal radiation can be estimated by using static polarizabilities. At a trap temperature of 300 K, control of the temperature to ± 1 K will be found sufficient to reduce the uncertainty in the black-body shift below 1 mHz.

The combination of the very small systematic uncertainties in the transition frequency of the trapped indium ion and the availability of the technically convenient Nd:YAG laser to drive this transition makes this system a most promising candidate for a future optical clock.

J. Abel, S. N. Bagayev, M. Eichenseer, and M. Valentin are thanked for their contributions. This work was partly supported by the Volkswagen Foundation.

[1] H. Dehmelt, IEEE Trans. Instrum. Meas. **31**, 83 (1982).
[2] C. Salomon, D. Hils, and J. Hall, J. Opt. Soc. Am. B **5**, 1576 (1988).
[3] B. C. Young, F. C. Cruz, W. M. Itano, and J. C. Bergquist, Phys. Rev. Lett. **82**, 3799 (1999).
[4] J. Reichert, R. Holzwarth, Th. Udem, and T. W. Hänsch, Opt. Commun. **172**, 59 (1999); S. A. Diddams *et al.*, Phys. Rev. Lett. **84**, 5102 (2000); R. Holzwarth *et al.*, *ibid.* **85**, 2264 (2000).
[5] *Proceedings of the 5th Symposium on Frequency Standards and Metrology*, Woods Hole, MA, 1995, edited by J. C. Bergquist (World Scientific, Singapore, 1996).
[6] R. J. Rafac *et al.*, Phys. Rev. Lett. **85**, 2462 (2000).
[7] N. Yu, X. Zhao, H. Dehmelt, and W. Nagourney, Phys. Rev. A **50**, 2738 (1994).
[8] J. E. Bernard, L. Marmet, and A. Madej, Opt. Commun. **150**, 170 (1998); G. P. Barwood *et al.*, *ibid.* **151**, 50 (1998); J. E. Bernard *et al.*, Phys. Rev. Lett. **82**, 3228 (1999).
[9] Ch. Tamm, D. Engelke, and V. Bühner, Phys. Rev. A **61**, 053405 (2000).
[10] J. v. Zanthier *et al.*, Opt. Commun. **166**, 57 (1999); J. v. Zanthier *et al.*, Opt. Lett. **25**, 1729 (2000).
[11] N. Yu, W. Nagourney, and H. Dehmelt, J. Appl. Phys. **69**, 3779 (1991).
[12] C. Schrama, E. Peik, W. W. Smith, and H. Walther, Opt. Commun. **101**, 32 (1993).
[13] E. Peik, J. Abel, Th. Becker, J. v. Zanthier, and H. Walther, Phys. Rev. A **60**, 439 (1999).
[14] G. Hollemann, E. Peik, A. Rusch, and H. Walther, Opt. Lett. **20**, 1871 (1995).
[15] E. Peik, G. Hollemann, and H. Walther, Phys. Rev. A **49**, 402 (1994).
[16] J. C. Bergquist, W. M. Itano, and D. J. Wineland, Phys. Rev. A **36**, 428 (1987).
[17] J. v. Zanthier, E. Peik, H. Walther, A. Yu. Nevsky, M. N. Skvortsov, and S. N. Bagayev, in *Novel Lasers and Devices—Basic Aspects*, OSA Technical Digest (Optical Society of America, Washington, DC, 1999), p. 115.
[18] Th. J. Kane and R. L. Byer, Opt. Lett. **10**, 65 (1985).
[19] I. Freitag, R. Henking, A. Tünnermann, and H. Welling, Opt. Lett. **20**, 2499 (1995).
[20] M. C. Bigeon, J. Phys. (Paris) **28**, 51 (1967).
[21] B. Lahaye and J. Margerie, J. Phys. (Paris) **36**, 943 (1975).
[22] Y. Ting and D. Williams, Phys. Rev. **89**, 595 (1953).
[23] E. Peik, G. Hollemann, Ch. Schrama, and H. Walther, Laser Phys. **4**, 376 (1994).
[24] There is also the possibility of working at a high magnetic field of 2.5(5) T, where the transition frequency becomes independent of the magnetic field in first order. See D. Wineland and W. Itano, Bull. Am. Phys. Soc. **27**, 864 (1982).