Electric Quadrupole Shift Cancellation in Single-Ion Optical Frequency Standards

P. Dubé,* A. A. Madej, J. E. Bernard, L. Marmet, J.-S. Boulanger, and S. Cundy
Institute for National Measurement Standards, National Research Council, Ottawa, Canada K1A 0R6
(Received 17 December 2004; published 12 July 2005)

The electric quadrupole shift is presently the most significant source of uncertainty on the systematic shifts for several single-ion optical frequency standards. We present a simple method for canceling this shift based on measurements of the Zeeman spectrum of the clock transition. This method is easy to implement and yields very high cancellation levels. A fractional uncertainty of 5×10^{-18} for the canceled quadrupole shift is estimated for a measurement of the absolute frequency of the $5s\,^2S_{1/2}$–$4d\,^2D_{5/2}$ clock transition of $^{88}Sr^+$.

DOI: 10.1103/PhysRevLett.95.033001 PACS numbers: 32.10.Dk, 06.30.Ft, 32.80.Pj, 32.30.Jc

Atomic frequency standards are the basis for time and length measurements and are crucial to science and technology. Examples of applications include navigation systems, tests of physical theories, and measurements of fundamental constants [1]. A single, laser-cooled ion confined by a radio-frequency (rf) trap is a nearly ideal oscillator for an optical frequency standard [2]. Since the confining field vanishes at the center of the trap, the single cooled ion closely approximates a particle at rest in free space [3,4]. Very narrow optical atomic resonances with Q values greater than 10^{15} can be advantageously selected for the "clock" transition to make extremely accurate and stable oscillators. Currently, the lowest reported fractional inaccuracies for ion optical frequency standards are 1×10^{-14} for $^{199}Hg^+$ [5], $^{171}Yb^+$ [6], and 3.4×10^{-15} for $^{88}Sr^+$ [7]. It is expected that the systematic shifts can be reduced to levels of 10^{-17} to 10^{-18} [2,3,8–12], which would improve on the present best cesium fountain frequency standards [13–16] by more than 2 orders of magnitude.

The main source of systematic error in several single-ion systems is the electric quadrupole shift caused by the interaction between the quadrupole moment of the upper level of the clock transition and a residual electric field gradient at the trap center [5–7,9,12,17–20]. Such electric field gradients are difficult to control and vary widely from system to system. They are most likely caused by patch potentials due to contamination on the surfaces of the trap electrodes. A method for canceling the quadrupole shift that has been used in the past consists of measuring the clock transition frequency for three mutually orthogonal directions of an applied magnetic field, and taking the average of the values obtained [9]. The level of cancellation with this method is degraded by the inaccuracy in setting the magnetic field directions [7,8,17,19,20]. We present a new method which relies on the frequency dependence of the clock transition Zeeman spectrum for cancellation of the quadrupole shift without any change of an applied magnetic field. The practical realization of this new method is simple and yields a very high level of cancellation. Our method has recently been applied to make the most accurate optical frequency measurement to date [7].

The expression for the electric quadrupole energy shift, H_Q, of a state $|\gamma IJFM_F\rangle$ of an atom in an electric field gradient was derived by Itano [9]:

$$\langle \gamma IJFm_F|H_Q|\gamma IJFm_F\rangle = \frac{-2A[3m_F^2 - F(F+1)](\gamma IJF \,\|\, \Theta^{(2)} \,\|\, \gamma IJF)}{[(2F+3)(2F+2)(2F+1)2F(2F-1)]^{1/2}}[(3\cos^2\beta - 1) - \epsilon\sin^2\beta(\cos^2\alpha - \sin^2\alpha)]. \tag{1}$$

This result from first order perturbation theory makes the usually valid assumption that the linear splitting of the magnetic sublevels caused by an applied magnetic field is much greater than the quadrupole energy shifts. The quantum numbers have the usual meanings: γ specifies the electronic configuration of the atom, I the nuclear spin, J the total electronic angular momentum, F the total angular momentum, and m_F the projection of F on the quantization axis. $(\gamma IJF \,\|\, \Theta^{(2)} \,\|\, \gamma IJF)$ is the reduced matrix element of the electric quadrupole moment operator. α and β are two of the three Euler angles that take the principal-axis frame of the electric field gradient to the quantization-axis frame defined by the applied magnetic field. In particular, β is the angle between the electric field gradient principal axis and the magnetic field. A is an amplitude parameter for the electric potential causing the field gradient. Finally, ϵ is an asymmetry parameter of the electric potential function [21]. It is usually small in ion traps and can be ignored [12,17].

The electric quadrupole shift of Eq. (1) has a zero for $m_F^2 = F(F+1)/3$. Since ion optical clock transitions usually have a lower S state, only their upper D or F state has an electric quadrupole shift which needs to be canceled. If one measures the clock line center frequency $\nu_{\rm ion}$ at two or more values of $m_{F'}^2$ for the upper state (labeled with a prime symbol), then the quadrupole-shift-free frequency ν_0 at $m_{F'}^2 = F'(F'+1)/3$ can be interpolated from a plot of $\nu_{\rm ion}$ vs $m_{F'}^2$. Note that the analysis is simplified if F' is equal to a half integer since then the average of the frequencies measured for all possible values of $m_{F'}^2$ gives the same result as the intercept at $F'(F'+1)/3$.

A line center is found by measuring either a single component with $m_{F'} = 0$ (integer F' only), or the average of two symmetric Zeeman components with upper sublevels $\pm m_{F'}$. The second order quadrupole shift term is thus canceled for each line center determination because it is an odd function of $m_{F'}$ [22]. For $m_{F'} = 0$ the second order shift is zero, and for $m_{F'} \neq 0$ the symmetric components are shifted by equal and opposite amounts. The cancellation method presented here is thus exact to second order in the perturbation theory. The third order term is about 8 to 10 orders of magnitude smaller than the first order term for our $^{88}Sr^+$ ion (Larmor frequency of 10–100 kHz and quadrupole shift of ≈ 1 Hz). In what follows, we illustrate the electric quadrupole shift cancellation method applied to the $^{88}Sr^+$ ion optical frequency standard.

Our single ion is confined in an rf Paul trap [12]. The optical frequency reference is provided by the 0.4 Hz wide ($Q = 1 \times 10^{15}$) quadrupole-allowed $5s\,^2S_{1/2} - 4d\,^2D_{5/2}$ transition at 674 nm (445 THz). This transition is probed with a diode laser that is stabilized and frequency narrowed to <100 Hz using a cascade of two Fabry-Perot resonators [23]. The ion is cooled on the strong $5s\,^2S_{1/2}$–$5p\,^2P_{1/2}$ transition with radiation at 422 nm [24]. Fluorescence at 422 nm is monitored for detection of the probe-induced quantum jumps between the S and D states of the clock transition [12,25]. Decay from the $^2P_{1/2}$ state to the metastable $^2D_{3/2}$ state during the cooling pulse is prevented with polarization-switched laser radiation at 1092 nm [26].

The 422 and 1092 nm beams are pulsed with an open-blade mechanical chopper while the probe laser beam is pulsed by modulating the rf power driving a double-pass acousto-optic modulator (AOM). Insignificant amounts of 422 or 1092 nm radiation reaches the ion when blocked by the blade. For the present data, an interrogation cycle lasts 40 ms, with 20 ms for cooling and 16 ms for probing.

The 96 MHz gap between the ultrastable resonator and the ion clock transition is bridged by shifting the probe frequency with the double-pass AOM. An unshifted portion of the probe beam is sent via an optical fiber to a femtosecond laser frequency comb for absolute frequency measurements [27]. The data of the probe frequency lock to the ion was compared to a linear fit of the frequency comb measurements during the course of a measurement day [23]. Both the frequency comb and the synthesizer driving the AOM are referenced to a National Research Council of Canada (NRC) hydrogen maser, itself referenced to the ensemble of NRC cesium atomic clocks. The estimated fractional uncertainty of the maser frequency is 1×10^{-14}, or 5 Hz at 445 THz.

We apply a dc magnetic field to split the Zeeman sublevels and define the quantization axis. The resulting spectrum is composed of ten lines, grouped into five symmetric pairs, between the $^2S_{1/2}$ and $^2D_{5/2}$ states [7]. To find the line center, $\nu_{\rm ion}$, the probe frequency is tuned in sequence to the four half-intensity points of one symmetric pair of components and the quantum jump rates are measured. Imbalance in the jump rates provides the correction signal for locking the shifted laser light into resonance with the Zeeman components [28].

An ion temperature of (16 ± 8) mK was determined for the data presented here from a measurement of the sideband intensities caused by thermal secular motion [29]. The radial secular frequencies are $f_x \simeq 950$ kHz and $f_y \simeq 975$ kHz, and the axial frequency is $f_z \simeq 1930$ kHz. These results are in agreement with the relation $f_x = f_y = f_z/2$ [30], indicating that the rf Paul trap is not perturbed by strong field gradients [17].

Micromotion at 12 MHz, caused by stray electric fields and other trap imperfections which move the ion away from trap center, is detected for motion along the direction of the 422 nm beam using the technique of fluorescence correlation [31]. The micromotion is minimized by adjusting two dc trim voltages, one between the two end cap electrodes and the other between the ring electrode and the Sr oven.

To demonstrate that the technique is independent of the quantization-axis direction, $\nu_{\rm ion}$ was measured as a function of $m_{F'}^2$ of the $^2D_{5/2}$ state for three different directions of the magnetic field. The results are shown in Fig. 1. Since

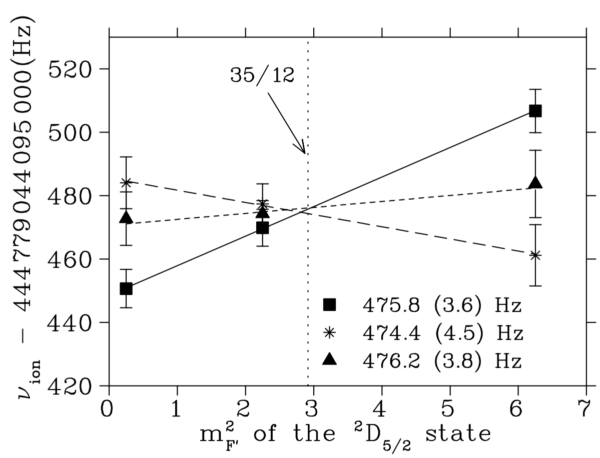

FIG. 1. Clock transition frequency of $^{88}Sr^+$ as a function of the square of the magnetic quantum number in the $^2D_{5/2}$ state for three orientations of the magnetic field. The legend gives the frequency intercepts at $m_{F'}^2 = 35/12$, and their standard deviations.

$^{88}Sr^+$ has a quadratic Zeeman shift on the order of 1 mHz for our operating conditions [12], changes in the magnitude of the magnetic field between the various directions produce a negligible shift.

The $m_{F'}^2$ dependence observed in Fig. 1 contains contributions from both the tensor terms of quadratic Stark shifts and from electric quadrupole shifts. Both effects have the same dependence on $m_{F'}^2$ and on the angle β between the quantization axis and a perturbing field [12].

For $^{88}Sr^+$ where $F' = J' = 5/2$, the frequency ν_0 at which both the quadrupole shift and the tensor terms of Stark shifts are canceled occurs for $m_{F'}^2 = 35/12$. This value is shown in Fig. 1 by the vertical dotted line. The ν_0 frequencies for all our measurements are summarized in Fig. 2. They were determined primarily from the inner $(\pm 1/2, \pm 1/2)$, second $(\pm 1/2, \pm 3/2)$, and fourth $(\pm 1/2, \pm 5/2)$ pairs of components which represent all possible values of $m_{F'}^2$.

The data, composed of 17 independent determinations of ν_0, has a standard deviation of 4.3 Hz. The first three data points have larger uncertainties because they were measured with only two values of $m_{F'}^2$.

It is important for further analysis to determine the relative contributions of the Stark shifts and of the electric quadrupole shift to the observed $m_{F'}^2$ dependence. A convenient measure of the interaction strength is the maximum slope, $k_{\max}$, of ν_{ion} vs $m_{F'}^2$. This value is found by fitting the data to $k_{\max}(3\cos^2\beta - 1)/2$. The parameter $k_{\max}$ and the direction of the perturbing field, which affects the angle β, are the variable parameters in this fit. The magnetic field vector was characterized with measurements of the Zeeman splittings made with three pairs of Helmholtz coils. The result is shown in Fig. 3. The direction of the perturbing field is found to be approximately in the plane of the ring electrode.

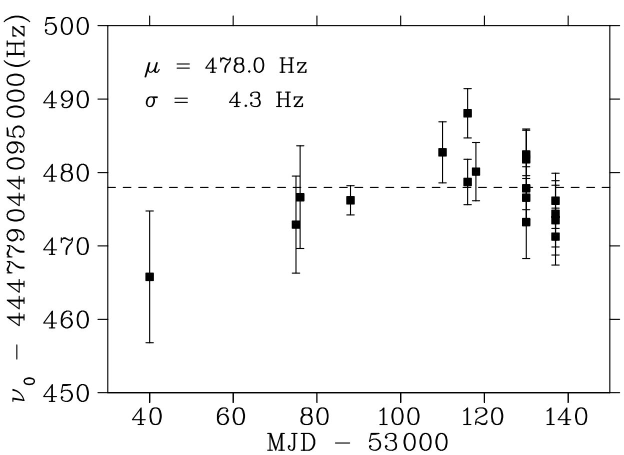

FIG. 2. Measured clock transition frequencies of $^{88}Sr^+$ after cancellation of the electric quadrupole shift and of the tensor terms of the Stark shifts as a function of time (MJD = modified julian day). The dashed line represents the mean frequency; its value and standard deviation are given on the figure. These data were taken between 2004-02-05 (MJD = 53 040) and 2004-05-12 (MJD = 53 137).

A simple model, consisting of a patch potential on the ring electrode, indicates that the observed slope is caused predominantly by a tensorial Stark shift associated with micromotion, with a contribution of $\approx 5\%$ from the quadrupole shift. According to the model, the quadrupole shift slope is $k_Q \simeq 0.6$ Hz and the field gradient is $A \simeq -56$ V/cm^2 [17], giving a shift of -1.6 Hz for the inner components. The slope contributed by Stark shifts, $k_S \simeq k_{\max} \pm k_Q = (13.4 \pm 1.5)$ Hz, corresponds to an electric field of $E_{\text{rms}} = (92 \pm 14)$ V/cm. The uncertainty in the current knowledge of the tensor polarizability α_2 [12] is the main source of error for E_{rms}.

The large "micromotion" Stark shift observed is a consequence of micromotion cancellation in a single direction. When electrodes and viewing ports are available for 3D cancellation, micromotion Stark shifts on the order of 10 mHz are obtained [7,31].

Although the cancellation method for electric quadrupole shifts is rigorous, possible drifts in the magnetic field direction, or in the amplitude and direction of the electric field gradient during a measurement interval Δt could lead to a bias in the frequency. Changes in the magnetic field strength B were calculated from changes in the Zeeman splittings. The observed drifts in B were taken as representative of the drifts in the direction that affects the angle β: $\Delta\beta/\Delta t \simeq (\Delta B/B)/\Delta t$. We obtain $(\Delta\beta/\Delta t)_{\text{rms}} \simeq 0.65$ mrad/h, which results in an uncertainty of 1 mHz for a 1 h measurement. The slow drift in the bias voltage for micromotion cancellation gives an indication of the stability of the electric field gradient. For an estimated linear drift in A of ≈ 2 V/(cm^2 h), the rms uncertainty in the frequency is 10 mHz. It is assumed that the direction of

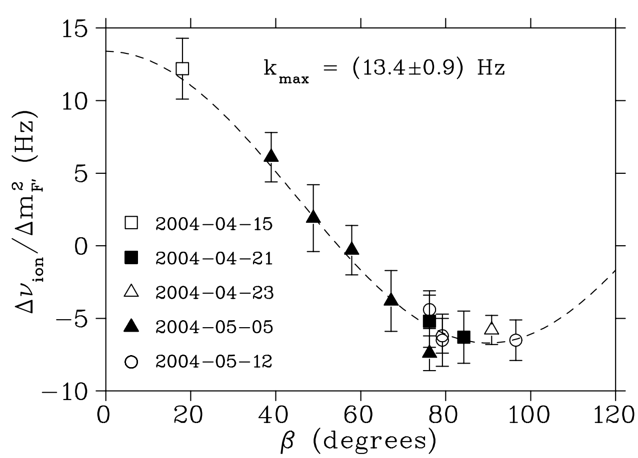

FIG. 3. Slope of the ion frequency dependence on $m_{F'}^2$ as a function of the angle β between the quantization axis and the perturbing field.

the electric field gradient does not change appreciably during the relaxation of the patch potential.

The above estimates added in quadrature give an uncertainty of 10 mHz on the canceled electric quadrupole shift for a typical 1 h measurement. The statistical uncertainty for 17 independent measurements is 2 mHz (5×10^{-18}). By measuring the three pairs of lines repeatedly during each run rather than on separate runs, it is possible to decrease the cancellation time scale from 1 h to a few minutes, thereby reducing the uncertainty by about an order of magnitude.

For our current ion experiment having $E_{\rm rms} = (92 \pm 14)$ V/cm, the scalar Stark shift is (38 ± 18) Hz and the time-dilation shift due to micromotion is (-44 ± 13) Hz. These partially correlated effects [31] have a net shift of (-6 ± 13) Hz, with an uncertainty caused primarily by current knowledge of the scalar polarizability of the $^2D_{5/2}$ state [12]. The uncertainties of the total estimated shift (13 Hz), of the frequency measurement (4.3 Hz), and of the maser (5 Hz), were added in quadrature to yield a total uncertainty of 15 Hz or 3.4×10^{-14}. Our new value for the ion frequency, including correction for the -6 Hz shift, is $(444\,779\,044\,095\,484 \pm 15)$ Hz. This value is in agreement with our previous determination of $(444\,779\,044\,095\,510 \pm 50)$ Hz [12], and with that of the National Physical Laboratory in the United Kingdom of $(444\,779\,044\,095\,484.6 \pm 1.5)$ Hz [7].

We have presented a method for canceling the electric quadrupole shift of single-ion optical frequency standards which relies on the Zeeman spectrum of the clock transition. The method requires measurement of the ion line center at different values of $m_{F'}^2$ in order to find the intercept at $m_{F'}^2 = F'(F'+1)/3$ where the quadrupole shift vanishes to second order in the perturbation theory. The cancellation level depends on the stability of β and of the magnitude of the electric field gradient during the measurement interval. We estimated that cancellation of the shift was good at a level of 2 mHz or 5×10^{-18} in the present experiments. The uncertainty in the quadrupole shift cancellation is expected to reach levels of $<10^{-18}$ by measuring the different line centers repeatedly during each run rather than on separate runs. Thus, once corrected for, the electric quadrupole shift is essentially eliminated from the error budget and is not expected to be an important factor in the selection of an ion optical frequency standard in the foreseeable future.

The authors are grateful to R. Pelletier and B. Hoger for their invaluable help with the construction of several electronic devices used in the present experiments.

*Electronic address: Pierre.Dube@nrc-cnrc.gc.ca

[1] *Proceedings of the 6th Symposium on Frequency Standards and Metrology*, edited by P. Gill (World Scientific, Singapore, 2002).
[2] H. G. Dehmelt, IEEE Trans. Instrum. Meas. **31**, 83 (1982).
[3] D. J. Wineland, W. M. Itano, J. C. Bergquist, and R. G. Hulet, Phys. Rev. A **36**, 2220 (1987).
[4] F. Diedrich, J. C. Bergquist, W. M. Itano, and D. J. Wineland, Phys. Rev. Lett. **62**, 403 (1989).
[5] T. Udem *et al.*, Phys. Rev. Lett. **86**, 4996 (2001).
[6] J. Stenger *et al.*, Opt. Lett. **26**, 1589 (2001).
[7] H. S. Margolis *et al.*, Science **306**, 1355 (2004).
[8] R. J. Rafac *et al.*, Phys. Rev. Lett. **85**, 2462 (2000).
[9] W. M. Itano, J. Res. Natl. Inst. Stand. Technol. **105**, 829 (2000).
[10] P. J. Blythe, S. A. Webster, K. Hosaka, and P. Gill, J. Phys. B **36**, 981 (2003).
[11] M. Eichenseer, A. Y. Nevsky, C. Schwedes, J. von Zanthier, and H. Walther, J. Phys. B **36**, 553 (2003).
[12] A. A. Madej, J. E. Bernard, P. Dubé, L. Marmet, and R. S. Windeler, Phys. Rev. A **70**, 012507 (2004).
[13] S. Weyers, U. Hübner, R. Schröder, C. Tamm, and A. Bauch, Metrologia **38**, 343 (2001).
[14] S. Bize *et al.*, in *Proceedings of the 6th Symposium on Frequency Standards and Metrology*, edited by P. Gill (World Scientific, Singapore, 2002), p. 53.
[15] F. Levi, L. Lorini, D. Calonico, and A. Godone, IEEE Trans. Ultrason. Ferroelectr. Freq. Control **51**, 1216 (2004).
[16] T. P. Heavner *et al.*, in *2004 Conference on Precision Electromagnetic Measurements Digest* (IEEE, Piscataway, NJ, 2004), p. 498.
[17] G. P. Barwood *et al.*, Phys. Rev. Lett. **93**, 133001 (2004).
[18] U. Tanaka *et al.*, J. Phys. B **36**, 545 (2003).
[19] T. Schneider, C. Tamm, and E. Peik, in *Proceedings of the IEEE International Frequency Control Symposium and 17th European Frequency and Time Forum* (IEEE, New York, 2003), p. 72.
[20] W. H. Oskay, W. M. Itano, and J. C. Bergquist, Phys. Rev. Lett. **94**, 163001 (2005).
[21] L. S. Brown and G. Gabrielse, Phys. Rev. A **25**, R2423 (1982).
[22] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University, New York, 1978), Chap. VII, p. 232.
[23] P. Dubé, L. Marmet, A. A. Madej, and J. E. Bernard, in *2004 Conference on Precision Electromagnetic Measurements Digest* (IEEE, Piscataway, NJ, 2004), p. 283.
[24] A. A. Madej, L. Marmet, and J. E. Bernard, Appl. Phys. B **67**, 229 (1998).
[25] J. E. Bernard *et al.*, Phys. Rev. Lett. **82**, 3228 (1999).
[26] G. P. Barwood *et al.*, Opt. Commun. **151**, 50 (1998).
[27] A. A. Madej *et al.*, Metrologia **41**, 152 (2004).
[28] J. E. Bernard, L. Marmet, and A. A. Madej, Opt. Commun. **150**, 170 (1998).
[29] D. J. Wineland and W. M. Itano, Phys. Rev. A **20**, 1521 (1979).
[30] D. J. Wineland, W. M. Itano, and R. S. Van Dyck, Jr., Adv. At. Mol. Phys. **19**, 135 (1983).
[31] D. J. Berkeland *et al.*, J. Appl. Phys. **83**, 5025 (1998).