Direct Frequency Comb Spectroscopy of Trapped Ions

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Direct frequency comb spectroscopy of trapped ions is demonstrated for the first time. It is shown that the $4s\,^2S_{1/2}$–$4p\,^2P_{3/2}$ transition in calcium ions can be excited directly with a frequency comb laser that is up-converted to 393 nm. Detection of the transition is performed using a shelving scheme to suppress the background signal from nonresonant comb modes. The measured transition frequency of $f = 761\,905\,012.7(0.5)$ MHz presents an improvement in accuracy of more than 2 orders of magnitude.

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Optical frequency comb lasers provide a phase coherent link between radio frequency sources and optical frequencies [1,2]. As a result optical frequencies can be counted, which has made spectroscopy and optical clocks possible with an extremely high accuracy on the order of 10^{-16}–10^{-17} [3,4]. In most experiments a continuous wave (cw) laser is used as a probe of an atomic or molecular transition, which is then calibrated against a frequency comb (see, e.g., [5] for an experiment on atoms, [6] for references to measurements on tightly confined ions, and [7,8] for measurements on ions in the weak binding limit).

However, frequency combs can also be used for direct excitation, without the need of a cw laser. This is possible because the pulsed output of a comb laser (as seen in the time domain) is equivalent to many equidistant narrow modes in the frequency domain. Direct frequency comb spectroscopy has been demonstrated in beam experiments [9,10], atomic vapor cells [11], and cold neutral atoms in magneto-optical traps [12,13], but not yet on cold ions in an ion trap.

Ion traps provide the opportunity to simultaneously trap different species. By laser cooling one type of ion, the other ions in the trap can be sympathetically cooled [14,15]. A system to trap and cool one ion species can then be used without major modifications to trap and cool other types of atomic and molecular ions. Frequency combs offer a wide spectrum of frequencies through coherent broadening in nonlinear optical fibers [16] and doubling in nonlinear crystals or higher harmonic generation in gas jets [17,18]. The combination of direct frequency comb spectroscopy and ion trapping thus provides the possibility to perform spectroscopy on various ionic transitions in a single measurement system.

In this Letter we demonstrate for the first time direct frequency comb spectroscopy of ions in a trap. It is shown that this technique can be applied using an up-converted frequency comb at 394 nm, without amplification of the comb pulses. Furthermore, we combine it with a shelving scheme [19] to suppress background signal from nonresonant comb modes, resulting in a good signal-to-noise ratio despite the low power per comb mode. Calcium ions are used for this experiment because a more accurate calibration of the $4s\,^2S_{1/2}$–$4p\,^2P_{3/2}$ state is of interest for the search for a change of α over time spans of many billion years [20]. Apart from this application, trapping and laser cooling of the calcium ion has been widely studied [21–23], in particular, for atomic clocks [24,25] and quantum computation [26].

The spectroscopy is performed in a linear Paul trap. This trap consists of four linear electrodes at a distance $r_0 = 4$ mm to the trap axis. To two diagonally facing rods an oscillating voltage $V_0 = 60$ V at a frequency $\Omega = 2\pi \times 3.3$ MHz is applied, corresponding to a stability parameter $q = 0.04$. The end caps are formed by two ring electrodes at a voltage $V = 10$ V. Further details on the trap are described in [7]. The ion trap is mounted in a vacuum chamber, evacuated to a pressure of 3×10^{-9} mbar. Calcium ions are produced by a two-step ionization process: Evaporated atoms from an oven are first excited at 422 nm to the $4p\,^1P_1$ state by a frequency-doubled cw Ti:sapphire laser (Coherent 899), and subsequently ionized by part of the doubled frequency comb spectrum ($\lambda <$ 391 nm). The comb is also used for the spectroscopy on the ions (see below). The total system is schematically depicted in Fig. 1.

In order to reduce the Doppler effect on the single-photon spectroscopy transition, laser cooling is applied on the $4s\,^2S_{1/2}$–$4p\,^2P_{1/2}$ transition using a 397 nm diode laser (Toptica DL100). The relevant energy levels are shown in Fig. 2. The cooling laser is set at a red-detuning $\Delta f \approx 10$ MHz from resonance, referenced to a wave meter (Atos model LM-007). The wave meter is regularly calibrated by scanning the cooling laser over the transition, and the locking point is set relative to the resonance. During the measurements the cooling range is locked within the relative accuracy of the wave meter of ±3 MHz.

The spatial mode of the cooling laser is cleaned up in a single mode fiber to reduce background from scattered light. The remaining 0.3 mW is focused to a beam diameter of $w_0 = 0.5$ mm in the trap. Since the excited ions have a

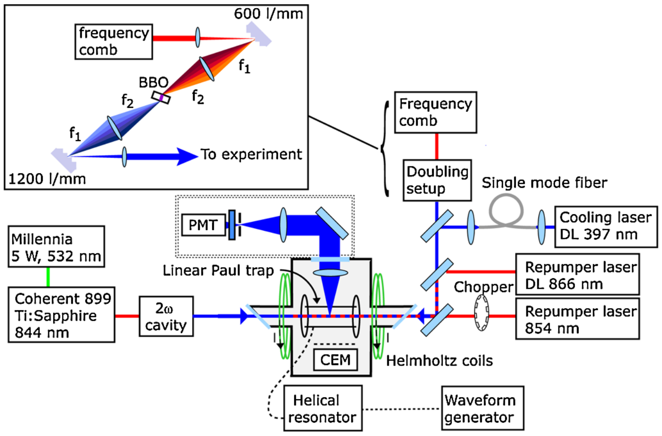

FIG. 1 (color online). Schematic layout of the laser system and linear Paul trap. DL = diode laser, PMT = photo-multiplier tube, 2ω = frequency-doubling setup, CEM = channel electron multiplier. Inset: Setup for chirped doubling of the frequency comb. Lenses are drawn for clarity; in practice only reflective optics are used. The comb spectrum is dispersed on a 600 l/mm grating before being doubled in a beta-barium borate (BBO) crystal. The colors in the doubled spectrum are overlapped using a 1200 l/mm grating. $f_1 = 20$ cm; $f_2 = 10$ cm.

7% chance to decay to the long-lived $3d\,^2D_{3/2}$ state, a repumper diode laser at 866 nm is used ($P = 1$ mW, Toptica DL100). The spectroscopy is performed on a crystallized ion cloud to reduce the Doppler broadening. The center of the trap is imaged onto a pinhole to remove background radiation and scattered light from the electrodes. Fluorescence from the $4s\,^2S_{1/2}$–$4p\,^2P_{1/2}$ transition is then observed using a photomultipler tube (PMT, Philips XP2020Q). From the decay in fluorescence we determined a lifetime for the ions in the trap of $\tau \approx 8$ minutes, which is limited by the vacuum conditions. This lifetime can vary $\sim$10% from scan to scan due to a change in cooling parameters, in particular, due to the free drifting repumper laser. The number of ions is difficult to determine with the current setup, but is estimated to be of the order of a few hundred ions per cloud based on the absence of discretization in the fluorescence signal (even for long measurement times) and the short loading time of <1 s.

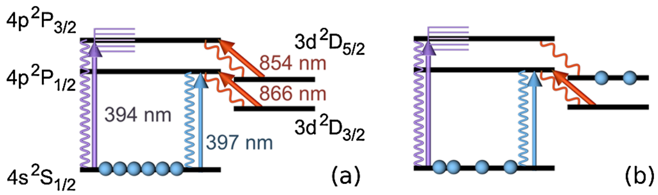

FIG. 2 (color online). Schematic view of the energy levels and the shelving principle. Arrows indicate laser beams; the wavy lines spontaneous fluorescence. The second repumper at 854 nm is periodically blocked using a chopper. If this repumper is present [situation (a)], all ions stay in the cooling cycle. A blocked repumper leads to transfer of the ions into the dark state, and the fluorescence from the cooling laser decreases [situation (b)].

The modes from a frequency comb can be described by the repetition frequency $f_{\rm rep}$ of the pulses and a carrier-envelope offset frequency $f_{\rm ceo}$. The frequency of the nth mode is equal to $f_n = \pm f_{\rm ceo} + n \times f_{\rm rep}$. Both $f_{\rm rep}$ and $f_{\rm ceo}$ are radio frequencies, which are locked to a frequency standard (in our case a Stanford PRS10 Rubidium atomic clock, referenced to the Global Positioning System). The frequency comb laser for this experiment is based on Ti:sapphire. Chirped mirrors are used in the laser for dispersion management, and are chosen such that the output is maximized at the desired wavelength of $\lambda = 788$ nm. This light is frequency doubled in a 3 mm beta-barium borate crystal to obtain the right wavelength range to excite the $4s\,^2S_{1/2}$–$4p\,^2P_{3/2}$ transition. By matching the angular dispersion induced by a grating to the wavelength derivative of the phase-matching angle [27], a wide bandwidth can be phase matched. This method is used (Fig. 1, inset) to obtain a frequency comb in the blue with a FWHM of 13 nm and a power of $P \approx 2$ mW.

The calcium ions are excited by focusing the up-converted comb light in the trap to an elliptical beam with a major axis ($1/e^2$ width) of 0.8 mm, and a minor axis of 0.4 mm. In order to scan over the transition, $f_{\rm rep}$ is varied. A small change in this parameter leads to a frequency scan of the comb near the resonance. Only one comb mode is resonant at the time because a single-photon transition is probed. All other $\approx 10^5$ modes do not contribute to the signal, but do give a background signal due to scattered photons. This signal-to-noise issue is overcome by employing a "shelving" scheme (see, e.g., [19]), depicted schematically in Fig. 2. Ions that are excited to the $4p\,^2P_{3/2}$ state have a 7% chance to decay to the $3d\,^2D_{5/2}$ state which has a lifetime of 1.2 s [28]. Trapped in this state they can no longer contribute to the cooling cycle. Since the fluorescence from the cooling laser is monitored, less signal will be observed in this situation [Fig. 2(b)]. However, if a second repumper laser is used on the $3d\,^2D_{5/2}$–$4p\,^2P_{3/2}$ transition at $\lambda = 854$ nm, ions will be pumped back into the ground state and participate in the cooling cycle [Fig. 2(a)].

The periods with and without the second repumper are alternated using a chopper at 100 Hz, and for each data point the fluorescence counts for both situations are recorded. The fluorescence signal detected at 397 nm will now be unaffected by the presence of the comb laser for the periods where the 854 nm repumper is present ("repumper on" in the upper part of Fig. 3). The situation is different for the periods where the second repumper is blocked. In this case, every time a comb line comes into resonance with the $4s\,^2S_{1/2}$–$4p\,^2P_{3/2}$ transition, ions are pumped into the dark $3d\,^2D_{5/2}$ state, so the measured fluorescence will decrease proportional to the excitation rate. Because of the periodic nature of the frequency comb, this signal is re-

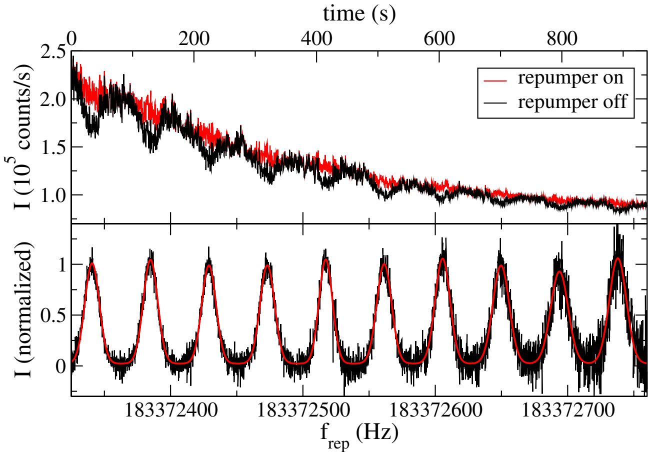

FIG. 3 (color online). Top: Measured fluorescence signal for the periods where the second repumper at 854 nm is on [gray (red) trace] and the periods where the repumper is off (black trace). The comb repetition frequency $f_{\rm rep}$ is scanned against time (upper axis) and frequency (lower axis). Bottom: Normalized fluorescence signal (corrected for decay, thin black trace) and the corresponding fit [thick gray (red) trace].

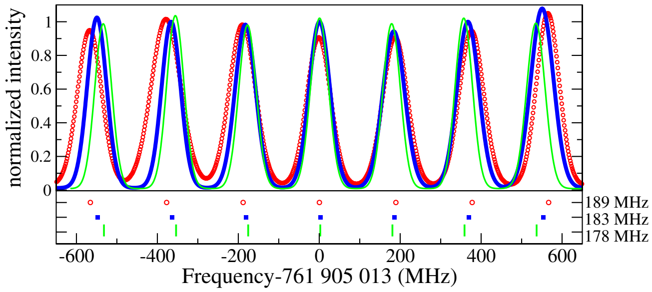

FIG. 4 (color online). Mode number determination: The upper part of the graph shows the fits to the scans at different frequency comb repetition frequencies ($f_{\rm rep}$), multiplied with a mode number n_0 to the approximate optical transition frequency (see text). Three different $f_{\rm rep}$ are shown (frequency uncertainty margins are smaller than the shown data points): 178 MHz (thin green trace), 183 MHz (thick blue trace), and 189 MHz (circles, red trace). The lower part shows the possible transition frequencies corresponding to the upper graph. The overlap of the traces at $f_{\rm trans} = 761\,905\,012.7$ MHz can clearly be seen, and was checked for five different repetition frequencies (only 3 are shown for clarity).

peated for every comb mode that comes into resonance with the probed transition ("repumper off" in the upper part of Fig. 3). The recorded signals for the situations with and without repumper are subtracted and corrected for the loss of calcium ions from the trap, resulting in a typical measurement curve as shown in the lower part of Fig. 3. In order to eliminate residual directionally dependent effects, all measurements are performed in both increasing and decreasing frequency direction. A comb of Gaussians is fitted to the corrected curves, where the width and height of each resonance is varied separately, but with fixed distances as given by the frequency comb spacing. The statistical uncertainty of such a fit is typically 1.8 MHz.

An important issue in frequency comb spectroscopy is the determination of the mode number n_0, usually based on previous measurements. The best known value for the $4s\,^2S_{1/2}$–$4p\,^2P_{3/2}$ transition had long been $\nu = 25\,414.40(15)\ \mathrm{cm}^{-1}$ [29], until a new value was reported of $\nu = 25\,414.4137\ \mathrm{cm}^{-1}$ [30]. Because no uncertainty was known for this measurement, it has been reevaluated recently leading to a best value of $\nu = 25\,414.415(2)\ \mathrm{cm}^{-1}$ [31]. The resulting 1σ accuracy of 60 MHz is insufficient to assign the mode number with confidence. We can, however, determine the mode by changing $f_{\rm rep}$, which is graphically shown in Fig. 4. First an approximate mode number can be deduced from the earlier presented values. Using the selected mode number, one of the peak centers overlaps with the transition frequency, while the others deviate an integer times the repetition rate from this value. After $f_{\rm rep}$ is changed by several MHz, the procedure is repeated. The peak centers of scans with different $f_{\rm rep}$ will overlap at the peak with the correctly assigned mode number, but separate on neighboring peaks (Fig. 4).

We have investigated several systematic effects on the transition frequency. The strongest is due to the always present 397 nm cooling laser on the $4s\,^2S_{1/2}$–$4p\,^2P_{1/2}$ transition. Since its detuning is set at about half the natural linewidth, and the cooling laser couples to the same ground state as the transition that is measured, this laser can cause a significant ac Stark shift. Fluctuations in the cooling laser frequency may lead to a variation in this shift during measurements. However, this does not lead to a systematic effect due to the regular calibration of the detuning. For this average detuning an effective shift is measured, by varying the cooling laser intensity [Fig. 5(a)]. The measured frequency shift is $\Delta f_{\rm trans} = 9.7(1.3)\ \mathrm{kHz}/\mu\mathrm{W} \times P_{\rm cooling}$, where $P_{\rm cooling}$ is the cooling laser power in μW. The corresponding zero crossing is $f_{\rm trans} = 761\,905\,013.06(0.21)$ MHz. In addition, at $P_{\rm cooling} = 200(10)\ \mu$W the measured dependence of the transition frequency on the frequency comb laser power is $\Delta f_{\rm trans} = 0.19(0.24)\ \mathrm{MHz/mW} \times P_{\rm comb}$, with $P_{\rm comb}$ the comb laser power in mW [Fig. 5(b)]. The transition frequency is corrected for the corresponding shift at $P_{\rm comb} = 1.9$ mW of $\Delta f_{\rm trans} = 0.36(0.46)$ MHz. The repumper lasers do not cause a significant light shift, since the 866 nm laser does not couple to either one of the levels involved in the measured transition, and the 854 nm repumper is not present during the shelving intervals. The recoil shift is calculated to be 32 kHz, which is small compared to the measurement accuracy.

Because of stray electric fields, ions can be pushed from the axis towards a higher electric field region. The spectroscopy laser enters the trap on axis, through a 3 mm diameter hole, limiting the maximum deviation from the center at which ions can be probed. We made a conservative estimation of the Stark shift by calculating the maxi-

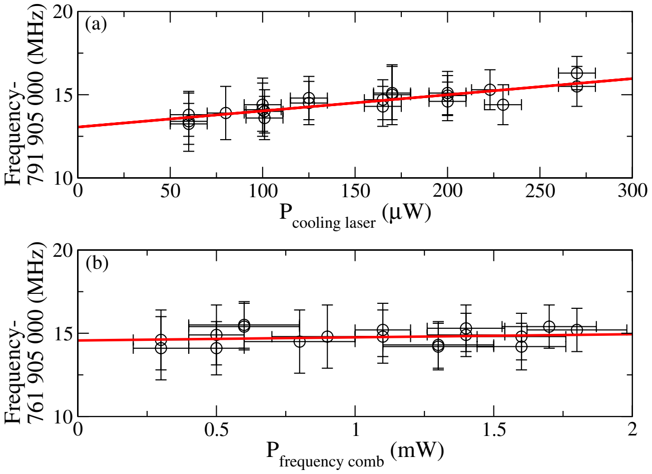

FIG. 5 (color online). (a) Measured data for light shifts induced by the cooling laser at $P_{\mathrm{comb}} = 1.9(0.2)$ mW (circles). (b) Measured data for light shifts induced by the frequency comb laser at $P_{\mathrm{cooling\ laser}} = 200(10)\ \mu$W. The weighted fits to the data are also shown [gray (red) lines].

mum Stark shift at the edge of this region, using the Einstein A coefficients as published in [32]. The calculated shift is only 0.2 kHz, and can thus be neglected for the current measurement. This value is small due to the large energy difference between the $4s$ and $4p$ and the s, p, and d levels that are connected through the Stark interaction, in combination with the low trapping fields that were used.

Since the comb laser beam is linearly polarized, both magnetic substates of the ground state are equally excited. Hence, without optical pumping between the levels no first order Zeeman shift is expected. The relative population of the ground states is expected to be mainly influenced by the lasers involved in the cooling cycle, which are both linearly polarized, so no optical pumping is expected. To experimentally verify this assumption, the Zeeman coefficient was measured by applying external magnetic fields perpendicular and parallel to the propagation directions of the laser beams. On the basis of a previous Zeeman shift determination [7] and magnetic field measurements outside the vacuum chamber, the magnitude of the magnetic field in these directions is estimated to be 40 μT and 20 μT, respectively. These fields correspond to shifts in the transition frequency of $+0.04(0.08)$ MHz and $-0.04(0.08)$ MHz using the measured field dependence, and are thus negligible compared to the measurement accuracy. This leaves the statistical uncertainty due to the comb laser to consider. For a measurement time per data point of 0.1 s, the Allan deviation is 10^{-9}. Since a typical scan consists of about 3000 points measured over 10 minutes, this deviation averages down further to 10^{-11} and does not contribute significantly to the uncertainty budget. Once corrected for the measured shifts, the unperturbed transition frequency of the $4s\,^2S_{1/2}$–$4p\,^2P_{3/2}$ transition in $^{40}\mathrm{Ca}^+$ is found to be $f = 761\,905\,012.7(0.5)$ MHz (1σ uncertainty). This result is consistent with the previous most accurate result of $f = 761\,904\,994(60)$ MHz [31].

In conclusion, direct frequency comb spectroscopy on ions in a linear Paul trap has been demonstrated for the first time, using an up-converted comb laser and shelving detection. The obtained level of accuracy on the $4s\,^2S_{1/2}$–$4p\,^2P_{3/2}$ transition in calcium ions is more than 2 orders of magnitude better than previous calibrations. The applicability of this method extends well beyond the probed ion and transition used for this experiment, if direct frequency comb spectroscopy were used on sympathetically cooled ions in a Paul trap.

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