Lifetime measurement of the metastable $3d {}^{2}D_{5/2}$ state in the ${}^{40}Ca^{+}$ ion using the shelving technique on a few-ion string

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We present a measurement of the lifetime of the metastable $3d^2D_{5/2}$ state in the ⁴⁰Ca⁺ ion, using the so-called shelving technique on a string of five Doppler laser-cooled ions in a linear Paul trap. A detailed account of the data analysis is given, and systematic effects due to unwanted excitation processes and collisions with background gas atoms are discussed and estimated. From a total of 6805 shelving events, we obtain a lifetime τ =1149±14(stat.)±4(sys.)ms, a result which is in agreement with the most recent measurements.

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I. INTRODUCTION

The metastable $3d^2D_{5/2}$ state in ${}^{40}Ca^+$ is interesting for such diverse areas of physics as atomic structure calculations, optical frequency standards, quantum information, and astronomy. For atomic structure calculations it is an important test case for the study of valence-core interactions and core-polarization effects [1]. The long lifetime of the ${}^{2}D_{5/2}$ state implies a sub-Hz natural linewidth of the 729 nm electric quadrupole transition to the ${}^{2}S_{1/2}$ ground state, thus making this transition an attractive candidate for an optical frequency standard [2,3]. In addition, its long lifetime makes the ${}^{2}D_{5/2}$ state a suitable choice for one of the two states in a quantum bit in connection with quantum computation [4]. Finally, in astronomy, the ${}^{2}D_{5/2}$ state has been used in a study of the β pictoris disk [5], and it is also commonly used in the study of Seyfert 1 galaxies and T Tauri stars [6]. As a consequence, the natural lifetime of the ${}^{2}D_{5/2}$ state has attracted much attention in recent years, but unfortunately the results of the many measurements [3,7–14] and theoretical calculations [1,6,15–19] of the lifetime are scattered over a rather broad range (see Fig. 1 in Ref. [7] for an overview). Among the experimental results, the lifetime found by Barton *et al.* [7], using the so-called shelving technique on a single trapped and laser-cooled ⁴⁰Ca⁺ ion, has the smallest error bars, with an estimated lifetime of τ =1168±7 ms.

In this paper we present a measurement of the lifetime of the $3d {}^{2}D_{5/2}$ state, using the same shelving technique but on a string of five ions. The measurement results in a lifetime of τ =1149±14(stat.)±4(sys.)ms.

The experimental setup and the experimental procedure are described in Sec. II. In Sec. III, we give a detailed account of the data analysis, including a description of the maximum likelihood method used for the statistical data analysis and a discussion of systematic errors with emphasis on radiation and collision effects. Finally, in Sec. IV, the estimated lifetime based on the measurements is given and discussed.

II. EXPERIMENTAL SETUP

A sketch of our experimental setup is shown in Fig. 1. The linear Paul trap used in the experiments is situated in a stainless steel ultrahigh-vacuum chamber. The trap consists of four cylindrical gold-coated stainless steel rods arranged in a quadrupole configuration, where two diagonally opposite rods are separated by 7.00 mm. The rods are 8.00 mm in diameter, and each rod is sectioned into three parts, where the center piece is 5.40 mm long, and the two end pieces are 20.00 mm long. By applying a rf voltage to two diagonally opposite electrode rods and applying the same voltage with opposite phase to the other two electrode rods, we obtain an effectively harmonic radially confining potential. In the experiments reported here, the peak-peak amplitude of the rf voltage is 600 V and the frequency is 3.894 MHz, which results in a radial trap frequency of $\omega_r \approx 2\pi \times 550$ kHz. Axial confinement is provided by a 580 mV dc voltage on all eight end electrodes, yielding an axial trap frequency ω_{z} $\approx 2\pi \times 50$ kHz. By adding additional small dc voltages to the individual electrodes, we can carefully center ions in the trap. At the center of the trap a collimated atomic Ca beam is crossed by a photoionizing laser beam, and ⁴⁰Ca⁺ ions are produced by an isotope-selective resonance-enhanced twophoton ionization process [20,21] and loaded into the trap. The Ca atomic beam originates from a calcium sample contained in an oven. The Ca atoms effuse out of a hole in the oven, and by a number of skimmers a collimated atomic beam is produced. An oven shutter enables us to fully block the atomic beam. In the present experiments the oven was heated to 420°C, under which conditions the chamber pressure was measured by an ion gauge [27] to be 6.0 $\times 10^{-11}$ Torr. After having loaded five ions and forced them onto a string by adjusting the trap parameters and applying Doppler laser cooling as described below, the oven temperature was reduced, and the oven shutter was closed. During a 1 h measuring session, the pressure dropped to about 3.6 $\times 10^{-11}$ Torr. The ions are Doppler laser cooled on the $4s {}^{2}S_{1/2}$ - $4p {}^{2}P_{1/2}$ transition with typically 15 mW of 397 nm light from a frequency-doubled Ti:sapphire laser. From the $4p \,{}^2P_{1/2}$ state, the ions will not always decay back to the $4s {}^{2}S_{1/2}$ state but sometimes decay by a dipole-allowed tran-

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FIG. 1. Experimental setup; see text for details. M, mirror; DM, dichroic mirror; PBS, polarizing beam splitter; $\lambda/2$, half-wave plate.

sition to the $3d^2D_{3/2}$ state, from where they are repumped back to the $4p \, {}^{2}P_{1/2}$ state using a diode laser at 866 nm (see Fig. 2). The ions are observed by collecting fluorescence light, emitted at 397 nm during the Doppler cooling process, with a Nikon objective lens for MM40/60 measuring microscopes (10× magnification, f-number~1.7) placed about 5 cm above the trap center (outside the vacuum chamber). The collected light is amplified by an image intensifier and imaged onto a charge-coupled device (CCD) camera, resulting in an all over magnification of 13.5 for the entire imaging system [28]. The CCD camera has a 50 ms exposure time, and digital images of the ions with 12-bit resolution are recorded to the random access memory of a personal computer at a frame rate of 17.610 Hz. In order to measure the lifetime of the $3d^2D_{5/2}$ state, during the Doppler cooling process we excite ions in the 3d ${}^{2}D_{3/2}$ state to the 4p ${}^{2}P_{3/2}$ state using a diode laser at 850 nm, as shown in Fig. 2. From the $4p {}^{2}P_{3/2}$ state the ions can spontaneously decay to the $3d^2D_{5/2}$ state. When the ion is in the $3d^2D_{5/2}$ state, the optically active electron of the ion is said to be *shelved*, and the fluorescence on the 397 nm transition is quenched. The time spent by the ion in the $3d^2D_{5/2}$ state before it decays back to the ground state, will in the following be called a shelving period. By continuously applying the two cooling lasers and the shelving laser at 850 nm, we obtain characteristic fluorescence signals like the one shown in Fig. 3.

III. DATA ANALYSIS

A. Data reduction

The lifetime of the ${}^{2}D_{5/2}$ state can easily be estimated from the distribution of the shelving periods, since we expect it to be exponential with a time constant equal to the lifetime τ . The duration of a shelving period can be determined by dividing the number of consecutive frames, where an ion is shelved, by the frame rate of the CCD camera. Our raw data are digital images of five ions, as shown in Fig. 3(a), and our main data set consists of $\sim 200\ 000$ such images taken in three 1 h experimental runs. The details of obtaining the distribution of the shelving periods from these images are described below.

From the images in Fig. 3(a), it is evident that the ions are spatially well resolved, and that a region of interest (ROI) around each ion can be defined. The ROI is 13×13 pixels, corresponding to a region of 9.5 μ m × 9.5 μ m in the trap region. In order to establish a fluorescence data point which reflects the real ion fluorescence rate within a given image frame, we simply integrate the pixel values within the ROI. This is a valid measure, since the image intensifier and the CCD chip have a linear response to the fluorescence collected by the objective lens. In the following the ion fluorescence will be given in integrated pixel values (IPV).



FIG. 2. Relevant levels and transitions in ${}^{40}\text{Ca}^+$. Doppler laser cooling is performed with lasers at 397 nm and 866 nm. A laser at 850 nm excites the ion from the $3d \,{}^2D_{3/2}$ state to the $4p \,{}^2P_{3/2}$ state, from where it can decay to the $3d \,{}^2D_{5/2}$ state. The dashed line indicates the electric quadrupole transition by which the ion can decay from the ${}^2D_{5/2}$ state to the ground state.



FIG. 3. (a) A sequence of CCD images including a shelving event for the central ion. The white square indicates the region of interest (ROI) within which the fluorescence is integrated to obtain the signal shown in (b). (b) Fluorescence signal from the central ion for an image sequence containing the nine images above. The data points corresponding to the nine images are indicated by open circles. The dashed line indicates the threshold level discussed in the text.

As shown in Fig. 4, the distribution of the fluorescence data points from a single ion is characterized by a rather sharp peak at a low fluorescence level and a Gaussian distribution of data points around a level of ~90 000 IPV, originating from cases where the ion is scattering 397 nm light during a whole frame. In the following we define the fluorescing level as the center of the Gaussian distribution. The standard deviation of the Gaussian distribution is σ ~7500 IPV, which is mainly set by image-intensifier noise, but also by laser intensity and frequency drifts during the experimental run as well as by the finite ion temperature. The peak at the low fluorescence level, or the background level, is due to data points originating from cases where the ion is shelved during a whole frame.

In order to establish a distribution of the shelving periods, we need to introduce a threshold level to discriminate between fluorescence data points corresponding to frames where the ion is fluorescing (above the threshold level) or shelved (below the threshold level). From the distribution of fluorescence data points in Fig. 4, it is evident that we can choose a threshold level which can be used to unambigu-



FIG. 4. Distribution of fluorescence data points from a single ion, binned in intervals of 500 IPV. The maximum of the narrow background peak near 4000 IPV is not shown but has a value of 8000. From the Gaussian distribution around 90 000 IPV with a width of $\sigma \sim 7500$ IPV, we can define a fluorescing level as the center of this distribution. The inset shows the intermediate points between 0 IPV and 80 000 IPV.

ously distinguish between the background level and the fluorescing level of an ion. The specific choice of threshold level is discussed in the following.

From the inset of Fig. 4, it can be seen that the distribution of fluorescence data points contains some points with a value of the integrated fluorescence between the background level and the fluorescing level. These intermediate data points arise from images where the ion is only fluorescing during a fraction of the exposure time of the CCD chip. This occurs naturally when an ion is shelved or decays to the ground state during the exposure of a single frame. Since a particular choice of threshold level decides whether an intermediate data point is counted as belonging to a shelving period or not, it affects the precise distribution of the shelving periods. Fortunately, the choice of another threshold level on average only adds a constant amount to all the shelving periods, and therefore the decay rate extracted from their distribution is not influenced by the choice of threshold level. This fact allows us to choose a threshold level in a broad range between the background level and the fluorescing level.

Unfortunately, intermediate fluorescence data points also occur in the following three situations: (i) shelving followed by fast decay to the ground state, (ii) decay to the ground state followed by fast reshelving, (iii) a shelved and an unshelved ion change places, e.g., due to a weak collision with a background gas atom or molecule or due to the finite temperature of the ions. Examples of these events, all taking place within one or two camera frames, are shown in Figs. 5(a)-5(c). Hence, before we choose the threshold level to be used for extracting the distribution of shelving periods, we have to consider these three types of events in some detail.

(i) When an ion is shelved at a certain instant of a frame and decays back to the ground state within that same frame or the next, then the signal does not necessarily fall *below*



FIG. 5. Examples of events which are problematic in connection with the data analysis. In all graphs the dashed line indicates the chosen threshold level of \sim 12 500 IPV. (a) Shelving and fast decay; corresponding frames indicated by open squares. (b) Decay and fast reshelving; corresponding frames indicated by open squares. Here the signal does rise above the threshold level, but for an even faster event this may not be the case. (c) A shelved and an unshelved ion change places. (d) The signals in (c) with the positions of the ions restored, i.e., the signals from ion 1 and ion 2 are interchanged after the crossing. At the frame where the two ions change places and the preceding frame, the fluorescence signal from ion 1 and ion 2 are given artificial values of 120 000 IPV and 0 IPV.

the threshold level, as the example in Fig. 5(a) shows. Hence these events may not even be counted as shelving events. In the data analysis we simply account for such events by discarding all periods with a duration of one or two frames from the shelving period distribution. Since the distribution is expected to be exponential, we can subsequently displace the remaining distribution, so that periods originally having a duration of *n* frames ($n \ge 3$) are set to be periods with a duration of n-2 frames.

(ii) If an ion decays and is quickly reshelved, we cannot be confident that the signal rises *above* the threshold level, see Fig. 5(b), and thus two shelving periods can appear as one longer shelving period, which would artificially increase the extracted lifetime. Noting that such events require a *high* shelving rate, it is possible to exclude them on probability grounds. First, we set a low threshold level, T=0.1(F-B)+B, where F is the fluorescing level and B is the background level, which means that only the very fastest reshelving events do not rise above the threshold level. Second, we require that after a decay, which ends a shelving period, there must be 20 consecutive data points above the threshold level; otherwise it is not counted as a shelving period in the data analysis. This requirement is only likely to be fulfilled with a low shelving rate, thus reducing the risk of accepting shelving periods where a quick reshelving event has happened. The probability for an event of decay and quick reshelving, with the signal not rising above the selected threshold level, followed by a decay and 20 consecutive data points above the threshold level, is below 2 permille regardless of the shelving rate. Hence this method gives *at most* a systematic error of -2 ms to the final result, and we will take the systematic error to be -1 ± 1 ms.

(iii) As mentioned, two ions may change place, e.g., due to a weak collision with a background gas atom or molecule. Figure 5(c) shows how a shelved and an unshelved ion changing place, effectively cut one long shelving period into two shorter ones, which artificially shortens the extracted lifetime. Therefore, in such events we restore the position of the ions to obtain a single shelving event, as shown in Fig. 5(d). Positions are only restored if the value of the fluorescence data points for the two ions involved adds up to the fluorescing level F within $\pm 2\sigma$ of this level. We find about 200 such events in our main data set. Since statistically the fluorescence from the two ions does not add up to the fluorescing level within $\pm 2\sigma$ in all events, we estimate a systematic error to the lifetime of +2 ms. True events of one ion shelving and another decaying within the same fraction of a frame will, however, occur, and erroneously be corrected by this procedure. We estimate a systematic error of -10 ms due to the erroneously corrected events. All together the systematic error due to ions switching place is -8 ms, with an estimated uncertainty of ± 4 ms.



FIG. 6. Histogram over the 6805 shelving events obtained after data reduction. Note that the number of shelving events is on a logarithmic scale. The error bars are the square root of the number of shelving events. The solid line is the maximum likelihood estimate of τ =1154 ms.

During data taking it happened that the ions heated up, so the ion string became unstable. Such events are clearly visible on the images of the ions and were cut out of the data set before performing the data reduction process described above. Likewise, periods where the lasers were adjusted or unstable are not considered in the further data analysis.

After the data reduction process described above and using a threshold level of T=0.1(F-B)+B, we extract a distribution of the shelving periods for each ion, binned in time intervals of $\Delta t=56.786$ ms, which is the inverse of the frame rate. The counts in equivalent bins for all the ions in the three experimental runs are then added to obtain a single distribution, from which a decay rate can be determined. This distribution is shown in a histogram in Fig. 6, with the bins shifted such that the histogram has its origin at time zero.

B. Statistical analysis

From the histogram in Fig. 6, we can infer the lifetime τ of the ${}^{2}D_{5/2}$ state by assuming an exponential distribution with a decay rate given by the inverse lifetime of the ${}^{2}D_{5/2}$ state. The histogram comprises 6805 shelving events with duration up to more than 11 s. Since, at large times, there are only a small number of events in the distribution, a least-squares-fitting method is inappropriate, and hence we employ a maximum likelihood estimate instead.

The probability p_i of falling into column *i* in the histogram, i.e., having a shelving period of duration *t*, which fulfills $t_i \le t < t_{i+1}$, where $t_i = i\Delta t$, is

$$p_i = \int_{t_i}^{t_{i+1}} \frac{1}{\tau} e^{-t/\tau} dt = e^{-t_i/\tau} (1 - e^{-\Delta t/\tau}).$$
(1)

Mathematically, the p_i 's define a proper probability distribution, since $\sum_{i=0}^{\infty} p_i = 1$. The sum starts at i=0, corresponding to the origin of the distribution in the histogram. Since the sum extends to infinity, we must, in principle, be able to measure infinitely long shelving periods. In the case of real experiments, where one is only able to measure periods up to a finite duration, T_{max} , the p_i 's should formally be renormalized by the factor $[1 - \exp(-T_{max}/\tau)]^{-1}$. In our case where $T_{max} \sim 1$ h and $\tau \sim 1$ s we can, however, safely neglect this factor. In order to make the maximum likelihood estimate, we now introduce the likelihood function

$$L = N ! \prod_{i=0}^{\infty} \frac{p_i^{n_i}}{n_i !},$$
 (2)

where n_i is the number of shelving events in the *i*th column of the histogram, and $N = \sum_{i=0}^{\infty} n_i$ is the total number of shelving events. By maximizing *L* (or rather ln *L*) with respect to τ , we find

$$\tau = \frac{\Delta t}{\ln\left(\frac{\Delta t}{\langle t \rangle} + 1\right)},\tag{3}$$

where $\langle t \rangle = \sum n_i t_i / N$ is the mean duration of the shelving periods. The variance of the lifetime is [22]

$$\operatorname{Var}(\tau) = -\left(\begin{array}{c} \left. \frac{\partial^2 \ln L}{\partial \tau^2} \right|_{\partial \ln L/\partial \tau = 0} \right)^{-1}$$
$$= \frac{\tau^4 (e^{\Delta t/\tau} - 1)^2}{N(\Delta t)^2 e^{\Delta t/\tau}}$$
$$= \frac{\tau^2}{N} \left(1 + \frac{1}{12} \left(\frac{\Delta t}{\tau} \right)^2 + O\left[\left(\frac{\Delta t}{\tau} \right)^4 \right] \right). \tag{4}$$

Using Eqs. (3) and (4), the lifetime and the statisitical uncertainty can be determined solely from Δt , $\langle t \rangle$, and N, and we find τ =1154±14 ms. The exponential distribution based on the maximum likelihood estimate is plotted as a solid line on top of the histogram in Fig. 6.

As a check of the efficiency and validity of our data reduction process, we have performed a test of goodness of fit. To find the goodness of fit we employ the Kolmogorov test, which is based on the empirical distribution function (EDF). A general overview of EDF statistics can be found in Ref. [23], which also gives tables of significance levels appropriate for cases like ours, where the lifetime is estimated from the data set. We find from our data a value for the Kolmogorov test of 0.44, clearly below the 10 % significance level value of 0.995, thus showing that the fit is good. We note for completeness that our data set is binned, whereas the values in Ref. [23] are for continuous data. However, since we have more than 100 channels this is not expected to play any significant role.

C. Radiation, collisions, and other potential systematic effects

Apart from the systematic errors concerning the data reduction, already discussed in Sec. III A, there are a few other relevant systematic errors, which will be discussed in this section.

1. Radiation

From the level scheme of Fig. 2, it is obvious that any radiation which couples the ${}^{2}D_{5/2}$ state to the ${}^{2}P_{3/2}$ state may deplete the ${}^{2}D_{5/2}$ state by excitation to the ${}^{2}P_{3/2}$ state followed by decay to the ${}^{2}S_{1/2}$ ground state or the ${}^{2}D_{3/2}$ state and result in a measured lifetime shorter than the natural lifetime. As a consequence, the occurrence of such radiation must be considered and, if possible, reduced. Blackbody radiation at the relevant transition wavelength is negligible at room temperature, as also discussed by Barton et al. [7]. Other "thermal" sources such as the ion gauge, roomlight, and computer screens were off during the measuring sessions, except for the screen where we watched the images of the ions. This screen was facing away from the vacuum chamber and is hence not expected to cause any problems. Another class of influencing light sources is the lasers used in the experiment. In particular, the broad background of the emission spectrum of the 866 nm and the 850 nm diode lasers contains 854 nm light resonant with the ${}^{2}D_{5/2}$ - ${}^{2}P_{3/2}$ transition. This radiation source was first recognized by Block et al. [8], and as noted by Barton et al. [7] the discrepancy between their own and many of the earlier measurements is possibly due to this previously unrecognized source of error. To reduce the level of 854 nm light from the diode lasers as much as possible, a long-pass filter was inserted in the 866 nm beam line and adjusted (by changing the angle of incidence) to 30 % transmission at 866 nm and $\leq 5 \times 10^{-4}$ at 854 nm, and a grating (1200 lines/mm) with a spectrally selective diaphragm (0.9 mm diameter, 1080 mm from the grating) was inserted in the 850 nm beam line. The filter, the grating and the diaphragm are shown in Fig. 1. The overall power of the lasers was reduced to ~ 18 nW and ~ 1.7 mW at the place of the ions for the shelving laser and the repumping laser, respectively. The waist size of the beams was 670 μ m \times 700 μ m for the repumping laser and 360 μ m $\times 430 \ \mu m$ for the shelving laser.

In order to estimate the lifetime reduction due to radiation emitted from the diode lasers, we calculate the rate of deshelving from the ${}^{2}D_{5/2}$ state, i.e., the excitation rate from the ${}^{2}D_{5/2}$ state to the ${}^{2}P_{3/2}$ state times (1-b), where b=0.068 is the branching ratio for decay from the ${}^{2}P_{3/2}$ state back to the ${}^{2}D_{5/2}$ state [24].

First we consider deshelving due to the repumping laser, which we split into two contributions, one from the offresonant 866 nm radiation and one from the near-resonant background radiation around 854 nm. The deshelving rate due to the 866 nm radiation was calculated by Barton *et al.* [7] to $I_{866} \times 9.4 \times 10^{-5} \text{ s}^{-1}/(\text{mW mm}^{-2})$, where I_{866} is the intensity of 866 nm radiation. With $I_{866}=2.3 \text{ mW mm}^{-2}$ we find a deshelving rate of $2.2 \times 10^{-4} \text{ s}^{-1}$, yielding a lifetime reduction of 0.3 ms.

In order to calculate the excitation rate from the ${}^{2}D_{5/2}$ state to the ${}^{2}P_{3/2}$ state due to radiation near 854 nm, we first consider the rate at a given frequency ω_{L} , as expressed by Eq. (2) in Ref. [7],

$$R_{12} = \frac{2J_2 + 1}{2J_1 + 1} \frac{\pi^2 c^3}{\hbar \omega_{12}^3} A_{21} \frac{I}{c} g(\omega_L - \omega_{12}), \qquad (5)$$

where $J_1=5/2$ and $J_2=3/2$ are the total angular momenta of the involved levels, $\omega_{12}=2\pi c/854.209$ nm [24] is the transition frequency, $A_{21}=7.7 \times 10^6 \text{ s}^{-1}$ [7] is the Einstein coefficient for spontaneous decay from the ${}^2P_{3/2}$ state to the ${}^2D_{5/2}$ state, *I* is the intensity of the incoming radiation, and $g(\omega_L - \omega_{12})$ is a normalized Lorentz distribution. Assuming a flat background spectrum of the diode lasers, i.e., the intensity per frequency interval $\Delta I / \Delta \omega_L$ is constant, we can integrate Eq. (5) over frequency ω_L and find an excitation rate of

$$R = \frac{2J_2 + 1}{2J_1 + 1} \frac{\pi^2 c^2}{\hbar \omega_{12}^3} A_{21} \frac{\Delta I}{\Delta \omega_L}.$$
 (6)

Using a diffraction grating we have measured $\Delta I / \Delta \omega_L \lesssim 0.19 \text{ nW}/(\text{mm}^2 \text{ GHz})$ near 854 nm at the power used in the experiment, and we then find $R = 0.77 \text{ s}^{-1}$. Multiplying this rate by 1-b and the transmission of 5×10^{-4} of the long-pass filter, we find a deshelving rate of $3.6 \times 10^{-4} \text{ s}^{-1}$, yielding a lifetime reduction of 0.5 ms.

As a check of this estimate, we performed an experiment, again with five ions, with the cooling lasers on but without the shelving laser. Even without the shelving laser the ions may be shelved due to radiation from the 866 nm repumping laser, which couples the ${}^{2}D_{3/2}$ state to the ${}^{2}P_{3/2}$ state. From the observed shelving rate, we can then find the excitation rate on the 850 nm ${}^{2}D_{3/2}$ - ${}^{2}P_{3/2}$ transition and compare it to the calculated excitation rate for the 854 nm ${}^{2}D_{5/2}$ - ${}^{2}P_{3/2}$ transition, taking the different line strengths into account. In this experiment the power of the 866 nm laser was 7.3 mW, the waist was as above, the long-pass filter was removed and the oven shutter was open. In about 35 min we observed 12 shelving events, i.e., the observed shelving rate is 5.8 $\times 10^{-3}$ s⁻¹. Taking into account the number of ions, the population of the D state ($\sim 1/3$, since both cooling transitions are saturated) and the branching ratio b, we find the excitation rate on the ${}^{2}D_{3/2} {}^{-2}P_{3/2}$ transition: (3/5b)5.8×10⁻³ s⁻¹=5.1×10⁻² s⁻¹. By multiplying this number with the relative line strength between the ${}^{2}D_{5/2}$ ${}^{-2}P_{3/2}$ transition and the ${}^{2}D_{3/2}{}^{-2}P_{3/2}$ transition of 8.92 [24], we find an estimated value of 0.45 s^{-1} for the excitation rate on the ${}^{2}D_{5/2}$ - ${}^{2}P_{3/2}$ transition, which should be compared to $R=0.77 \text{ s}^{-1}$ calculated above. The two numbers are not expected to be equal but only of the same order of magnitude, since the transition wavelengths are different, and the diode laser background is not necessarily equally strong near 850 nm and 854 nm. Also some of the shelving events may be due to collisions, as discussed below. Nevertheless, the numbers agree within a factor of 2 and our calculated estimate of the excitation rate, and hence the deshelving rate seems to be reasonable.

Above we considered deshelving due to the repumping laser. In exactly the same way we could consider deshelving due to the shelving laser. However, since the intensity of the shelving laser is much lower than for the repumping laser, and the grating and the diaphragm strongly reduce the level of 854 nm light, the excitation rate is expected to be extremely small. To check this we performed additional life-time measurements at three different power levels of the shelving laser, 18 nW, 193 nW, and 2081 nW, yielding life-times of 1146 ± 24 ms, 1160 ± 29 ms, and 1092 ± 27 ms, re-



FIG. 7. Decay rate measurements at three different power levels of the shelving laser. A weighted least-squares linear fit to the measured decay rates yields $1/\tau=0.866(8) \text{ s}^{-1}+\text{P}_{850} \times 0.023(7) \text{ s}^{-1}/\text{nW}$, with P₈₅₀ being the laser power.

spectively. When using higher power, the laser was detuned from resonance to get a similar shelving rate in all experiments. In Fig. 7, the linear fit to the decay rates corresponding to the lifetimes shows that there is a weak dependence of the decay rate (or lifetime) on the 850 nm power. However, with only 18 nW the lifetime is only reduced by 0.5 ms. The results of the two low power measurements and the crossing at zero power are in agreement with the result obtained from our main data set. The measurement at 18 nW was in fact performed at the same shelving laser power as the measurements for the main data set.

All together, we include a systematic error of $+1\pm1$ ms in our final result due to deshelving from the two diode lasers.

2. Collisions

Another systematic effect which shortens the measured lifetime is collisions with background gas atoms and molecules. There are two relevant types of collisions: finestructure changing (j-mixing) collisions and quenching collisions. In a *j*-mixing collision the internal state can change from the ${}^{2}D_{5/2}$ state to the ${}^{2}D_{3/2}$ state or vice versa. In a quenching collision the internal state changes from the ${}^{2}D_{5/2}$ state to the ${}^{2}S_{1/2}$ ground state. Both types of collisions deplete the ${}^{2}D_{5/2}$ state and hence shorten the measured lifetime. *j*-mixing and quenching rate constants (Γ_i and Γ_o) in the presence of different gases are given in Ref. [25] and references therein. Quite generally *j*-mixing collisions are found to be an order of magnitude stronger than quenching collisions. From a restgas analysis [29], we know that the restgas in our vacuum chamber is mainly composed of H₂ and gas of 28 atomic mass units, i.e., N₂ or CO. In the restgas analysis it was not possible to distinguish between N₂ and CO, since the chamber pressure was so low that the signal from the atomic constituents of these molecules could not be observed. Knoop et al. [25] found the following rate constants in units of cm³ s⁻¹ for collisions with H₂ and N₂: $\Gamma_i(H_2)$ $= (3 \pm 2.2) \times 10^{-10}, \qquad \Gamma_{Q}(H_{2}) = (37 \pm 14) \times 10^{-12}, \qquad \Gamma_{j}(N_{2})$ $=(12.6\pm10)\times10^{-10}$, and $\Gamma_O(N_2)=(170\pm20)\times10^{-12}$. The measurements were performed on a cloud of relatively hot ions, as compared to the laser-cooled ions considered in this paper. As noted in Ref. [25], other measurements of *j*-mixing with H_2 at different collision energies give similar results, so we may expect only a weak energy dependence for the *j*-mixing collisions, and therefore we use the values given in Ref. [25]. On the other hand, higher quenching rates are expected at lower temperatures [25], but to our knowledge there are no measurements of that for Ca⁺. Unfortunately, we are not aware of any similar measurements with CO, and in our estimate of the collision rate below, we therefore assume that the mass 28 restgas is N₂. The relatively large rate constants of N₂ found in Ref. [25] indicate that at least this assumption probably does not lead to a large underestimate of the collision-induced deshelving rate.

Assuming that the values given in Ref. [25] are applicable, we can estimate the collision-induced lifetime reduction. At a pressure of 5×10^{-11} Torr, taking into account the sensitivity to different gases of the ion gauge and using the result of the restgas analysis, we find that the restgas is composed of 54% H₂ and 46% N₂, which yields a total collision-induced deshelving rate of 2.3×10^{-3} s⁻¹, and a systematic error to the lifetime of +3 ms with an estimated uncertainty of ±1 ms.

From the measurement of 12 shelving events in 35 min without the shelving laser on, as described in Sec. III C 1 above, we can obtain an upper limit for the *j*-mixing collision rate if we assume that all the observed shelving events are due to *j*-mixing collisions inducing a transition from the ${}^{2}D_{3/2}$ state to the ${}^{2}D_{5/2}$ state (with rate γ_{35}). Again taking the number of ions and the population of the ${}^{2}D_{3/2}$ state into account, the collision-induced shelving rate is 3.5 $\times 10^{-3}$ s⁻¹. Since the oven shutter was open in that experiment, thus allowing collisions with neutral calcium atoms as well, we expect this number to be larger than under the conditions for the "real" lifetime measurements. The transition rate γ_{53} for the ${}^{2}D_{5/2}$ - ${}^{2}P_{3/2}$ deshelving transition is expected to be given by $\gamma_{53} = 2\gamma_{35}/3$, owing to the principle of detailed balance, so the collision-induced deshelving rate is 2.3 $\times 10^{-3}$ s⁻¹. This is our upper limit for the *j*-mixing collision rate, which should be compared to our estimate above of the total collision-induced deshelving rate, which is dominated by contributions from *j*-mixing collisions. Somewhat fortuitously, the numbers are equal, and hence our calculated estimate seems to be reasonable.

3. Other effects

When observing shelving events from a string of ions, one might consider if there are any correlations in the decay of the individual ions from the ${}^{2}D_{5/2}$ state to the ground state, which could influence the measured lifetime. In the experiments by Block *et al.* [8] indications of correlated decays from the ${}^{2}D_{5/2}$ state were observed, manifested as an overrepresentation of events where several ions decay at the same time. A later detailed experiment by Donald *et al.* [14] showed, however, no such correlations. Apart from sudden bursts of 854 nm radiation, the only reasonable physical mechanism which could lead to correlations is so-called subradiant and superradiant spontaneous emission due to inter-

TABLE I. Overview of estimated systematic errors.

Effect	Systematic error (ms)
Quick reshelving	-1 ± 1
Ions switching place	-8 ± 4
Deshelving, diode lasers	$+1 \pm 1$
Deshelving, collisions	$+3 \pm 1$
Total	-5 ± 4

ference in the spontaneous decay of two or more ions [26]. In the simple case of two ions, superradiant and subradiant spontaneous emission is characterized by a relative change in the normal (single ion) decay rate of the order of $\pm \sin(kR)/kR$ (when $kR \ge 10$), where R is the ion-ion distance, $k=2\pi/\lambda$ with $\lambda=729$ nm in our case [30]. For more ions the effect is of the same order of magnitude. In our case $1/kR \approx 6 \times 10^{-3}$ so just from this argument the effect is small, but not negligible. The interference effect, however, relies on creating and maintaining a superposition state of the form $|\pm\rangle = (|S_1D_2\rangle \pm |D_1S_2\rangle)/\sqrt{2}$, where S and D indicate the internal state, ${}^{2}S_{1/2}$ or ${}^{2}D_{5/2}$, and indices 1 and 2 relate to ion 1 and ion 2. In our experiment such a superposition state can only be created by a random process since the ${}^{2}D_{5/2}$ state is only populated through spontaneous emission, and consequently the relative phase between the states $|S_1D_2\rangle$ and $|D_1S_2\rangle$ is expected to be random. This fact would in itself average out the effect on the lifetime. In addition, if the superposition state is created, it is immediately (as compared to τ) destroyed since, from a quantum mechanical point of view, we are constantly measuring the internal state of the ions. So any superradiant or subradiant effect is in fact expected to be destroyed, and we do not expect any correlation in decays from the ${}^{2}D_{5/2}$ state. We have checked our data for correlated decays, and indeed a statistical analysis shows no evidence of correlations.

In Ref. [7] mixing of the ${}^{2}D_{5/2}$ state with the ${}^{2}P_{3/2}$ state due to static electric fields was considered and found to be negligible. For our trap we also find this effect to be negligible.

Finally, we note that the read-out time of the camera influences the measured duration of the shelving periods. As for the choice of threshold level, the read-out time has no effect on the measured decay rate and hence on the measured lifetime.

4. The total effect of systematic errors

Above we have identified and evaluated systematic errors originating from the data analysis and from deshelving due to radiation and collisions. An overview of the estimated errors and their uncertainties is given in Table I.

The effects leading to the systematic errors can be modeled by extra decay rates added to the natural decay rate,

$$\frac{1}{\tau_{meas}} = \frac{1}{\tau_{nat}} + \sum_{i} \gamma_i \tag{7}$$

TABLE II. Overview of recent experimental values for the lifetime of the $3d^2D_{5/2}$ state in the ${}^{40}Ca^+$ ion.

Reference	Lifetime (ms)
This work	$1149 \pm 14 \pm 4$
Knoop et al., 2003 [3]	1152 ± 23
Donald et al., 2000 [14]	1177 ± 10
Barton et al., 2000 [7]	1168 ± 7
Block et al., 1999 [8]	1100 ± 18
Lidberg et al., 1999 [9]	1090 ± 50

$$\tau_{nat} \approx \tau_{meas} + \sum_{i} \tau_{meas}^2 \gamma_i,$$
(8)

where τ_{meas} is the measured lifetime as determined from the maximum likelihood estimate, τ_{nat} is the natural lifetime, and the γ_i 's are the extra decay rates, which can attain both positive and negative values in this model. The systematic errors given in the text and Table I correspond to $\tau_{meas}^2 \gamma_i$. Equation (8) shows that the systematic errors should be added linearly, yielding -5 ms, and added to the result of the maximum likelihood estimate, giving a lifetime of 1149 ms. The uncertainties of the systematic errors are independent, and therefore they are added quadratically, yielding an uncertainty of ±4 ms.

IV. RESULT AND CONCLUSION

By correcting the maximum likelihood estimate with -5 ms, as described above, we find that our final result for the lifetime measurement is

$$\tau_{nat} = 1149 \pm 14(\text{stat.}) \pm 4(\text{sys.}) \text{ ms.}$$
 (9)

The largest error is the statistical, but we do have a nonnegligible systematic uncertainty, originating from the correction procedure when ions change places. The associated error, and hence the uncertainty, could be reduced by increasing our signal-to-noise ratio, which would narrow the time window where real events of simultaneous decay and shelving for two different ions could be taken for two ions changing place. The signal-to-noise ratio can be improved by frequency locking the Ti:sapphire laser and power stabilizing the output from the doubling cavity. From Eq. (4) we see that the statistical uncertainty can only be reduced by a longer data acquisition time (increasing N), and not simply by increasing the frame rate, since the second term in the expansion is already negligible in our case.

Our measurement was performed with a string of ions, unlike most other shelving experiments. In all single-ion experiments, one has to consider the fact that the ion may heat up, so the fluorescence level drops significantly, and the ion can appear to be shelved, although it is not. In our experiment with five ions on a string, we can detect and discard all events of this kind since if one ion or several ions heat up, we would see the remaining ions move or heat up as well. Moreover, with a string of ions, the shelved ions are sympathetically cooled by the unshelved ions, so the number of heating events are expected to be reduced using a string of ions, as compared to single-ion experiments. The major drawback of using a string of ions is that ions may change places, which influences the measured lifetime if this is not taken care of in the data analysis, as demonstrated here.

In conclusion, we have measured the lifetime of the metastable $3d {}^{2}D_{5/2}$ state in the ${}^{40}Ca^{+}$ ion using the shelving technique on a string of five ions. Our result agrees roughly at the level of one standard deviation with the already mentioned result obtained by Barton *et al.* [7] and with the value reported in Ref. [3], which together with other recent results are presented in Table II. On the level of two standard deviations, our result agrees with two other measurements where deshelving due to diode lasers was taken into account [8,14] and with the storage-ring measurement by Lidberg *et al.* [9] (see Table II). Furthermore, our result agrees with two theoretical values [16,17]. This newly obtained level of agreement should provide valuable input to future atomic structure calculations and astrononomical studies.

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