Lifetime measurement of the metastable $3d^2D_{5/2}$ 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 $^{40}Ca^+$ 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 $\tau = 1149 \pm 14(\text{stat.}) \pm 4(\text{sys.})$ 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 $^2D_{5/2}$ state implies a sub-Hz natural linewidth of the 729 nm electric quadrupole transition to the $^2S_{1/2}$ ground state, thus making this transition an attractive candidate for an optical frequency standard [2, 3]. In addition, its long lifetime makes the $^2D_{5/2}$ state a suitable choice for one of the two states in a quantum bit in connection with quantum computation [4]. Finally, in astronomy, the $^2D_{5/2}$ 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 $^2D_{5/2}$ state has attracted much attention in recent years, but unfortunately the results of the many measurements [3, 7–14] and theoretical calculations [1, 4, 15, 16, 17, 18, 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 $^{40}Ca^+$ ion, has the smallest error bars, with an estimated lifetime of $\tau = 1168 \pm 7$ ms.

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

The experimental setup and the experimental procedure are described in Section II. In Section 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 effects and collision effects. Finally, in Section 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 ultra-high-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 an 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 $\omega_r \approx 2\pi \cdot 550$ kHz. Axial confinement is provided by a 580 mV DC-voltage on all eight end electrodes, yielding an axial trap frequency $\omega_z \approx 2\pi \cdot 50$ 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 $^{40}Ca^+$ ions are produced by an isotope-selective resonance-enhanced two-photon 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 cham-
ber pressure was measured by an ion gauge to be 6.0 \cdot 10^{-11} \text{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 one hour measuring session, the pressure dropped to about 3.6 \cdot 10^{-11} \text{Torr}. The ions are Doppler laser-cooled on the $4s^2S_{1/2} \rightarrow 4p^2P_{1/2}$ 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 $4s^2S_{1/2}$ state but sometimes decay by a dipole-allowed transition to the $3d^2D_{3/2}$ state, from where they are repumped back to the $4p^2P_{1/2}$ 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 (10x 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 CCD-camera, resulting in an all over magnification of 13.5 for the entire imaging system. The CCD-camera has a 50 ms exposure time, and digital images of the ions with 12-bit resolution are recorded to the RAM 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 $3d^2D_{3/2}$ state to the $4p^2P_{1/2}$ state using a diode laser at 850 nm, as shown in Fig. 2. From the $4p^2P_{3/2}$ 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 $2D_{5/2}$ 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 $\tau$.

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. 3a, and our main dataset consists of ~200,000 such images taken in three one hour experimental runs. The details of obtaining the distribution of the shelving periods from these images is described below.

From the images in Fig. 3a, 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 x 13 pixels, corresponding to a region of 9.5 $\mu$m x 9.5 $\mu$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).

\[ \text{IPV} = \sum_{i=1}^{13} \sum_{j=1}^{13} I_{ij} \]

where $I_{ij}$ is the pixel intensity at location $(i,j)$. The lifetime of the $1s^2S_{1/2}$ state before it decays back to the $4s^2S_{1/2}$ state, will in general be $\tau$.

\[ \tau = \frac{1}{\lambda} \]

where $\lambda$ is the decay rate of the $1s^2S_{1/2}$ state. This means that the fluorescence on the $4s^2S_{1/2}$ state will be exponential, with a decay rate of $17.610 \text{ Hz}$. From the $4s^2S_{1/2}$ 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 $4s^2S_{1/2}$ 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.

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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 datapoints 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 datapoints from a single ion is characterized by a rather sharp peak at a low fluorescence level and a Gaussian distribution of datapoints around a level of $\sim 90000$ 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 this Gaussian distribution. The standard deviation of the Gaussian distribution is $\sigma \sim 7500$ IPV, which is mainly set by image-intensifier noise, but also by laser intensity and frequency drifts during the experimental run, and by the finite ion temperature. The peak at the low fluorescence level, or the background level, is due to datapoints originating from cases where the ion is shelved during a whole frame. This background peak is asymmetric with a sharp left edge, since there is essentially no 397 nm light scattered into the ROI's, when the ions are shelved.

FIG. 4: Distribution of datapoints 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 90000 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 80000 IPV.

In order to establish a distribution of the shelving periods, we need to introduce a threshold level to discriminate between fluorescence datapoints corresponding to frames where the ion is fluorescing (above the threshold level) or shelved (below the threshold level). From the distribution of fluorescence datapoints in Fig. 4, it is evident that we can choose a threshold level which can be used to unambiguously 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 datapoints contains some points with a value of the integrated fluorescence between the background level and the fluorescing level. These intermediate datapoints 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 datapoint 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 datapoints 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 re-shelving, 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 Fig. 5a-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 the threshold level, as the example in Fig. 5a 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 (\( n \geq 3 \)) are set to be periods with a duration of \( n - 2 \) frames.

ii) If an ion decays and is quickly re-shelved, we cannot be confident that the signal rises above the threshold level, see Fig. 5b, 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, \( T = 0.1 \cdot (F - B) + B \), where \( F \) is the fluorescing level, and \( B \) is the background level, which means that only the very fastest re-shelving events do not rise above the threshold level. Second, we require that after a decay, which ends a shelving period, there must be twenty consecutive datapoints 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 re-shelving 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 twenty consecutive datapoints 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 \(-1 \pm 1\) ms.

iii) As mentioned, two ions may change place, e.g., due to a weak collision with a background gas atom or molecule. Fig. 5c 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. 5d. Positions are only restored if the value of the fluorescence datapoints 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 dataset. 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 \( \pm 4\) 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 dataset 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 \( T = 0.1 \cdot (F - B) + B \), 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 \( \tau \) of the \( ^2D_{5/2} \) state by assuming an exponential distribution with a decay rate given by the inverse lifetime of the \( ^2D_{5/2} \) state. The histogram is comprised of 6805 shelving events with duration up to more than 11 seconds. 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 \( t_i \leq t < t_{i+1} \), where \( t_i = i \cdot \Delta t \), is

\[
p_i = \int_{t_i}^{t_{i+1}} \frac{1}{\tau} e^{-t/\tau} dt = e^{-t_i/\tau} \left( 1 - e^{-\Delta t/\tau} \right), \tag{1}
\]

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, \( T_{\text{max}} \), the \( p_i \)'s should formally be renormalized by the factor \( [1 - \exp(-T_{\text{max}}/\tau)]^{-1} \). In our case where \( T_{\text{max}} \approx 1 \) hour and \( \tau \approx 1 \) s we can, however, safely neglect this factor. In order to make the maximum likelihood estimate, we
now introduce the likelihood function

\[ L = N! \prod_{i=0}^{\infty} \frac{n_i}{n_i!}, \]  

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 \( \tau \), we find

\[ \tau = \frac{\Delta t}{\ln(\frac{\Delta t}{\tau} + 1)}, \]  

where \( < t > = \sum n_i t_i / N \) is the mean duration of the shelving periods. The variance of the lifetime is

\[ \text{Var}(\tau) = -\left( \frac{\partial^2 \ln L}{\partial \tau^2} \bigg|_{\tau = 0} \right)^{-1} = \frac{\tau^4 (e^{\Delta t/\tau} - 1)^2}{N(\Delta t)^2 e^{\Delta t/\tau}}. \]

Using Eq. (3) and Eq. (4), the lifetime and the statistical uncertainty can be determined solely from \( \Delta t \), \( < t > \), and \( N \), and we find \( \tau = 1154 \pm 14 \text{ ms} \). 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. 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.
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 \( \tau = 1154 \) ms.

C. Radiation, collisions and other potential systematic effects

Apart from the systematic errors concerning the data reduction, already discussed in Section II.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 \(^2D_{5/2}\) state to the \(^2P_{3/2}\) state may deplete the \(^2D_{5/2}\) state by excitation to the \(^2P_{3/2}\) state followed by decay to the \(^2S_{1/2}\) ground state or the \(^2D_{3/2}\) 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 \(^2D_{5/2}-^2P_{3/2}\) 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 beamline and adjusted (by changing the angle of incidence) to 30\% transmission at 866 nm and \( \lesssim 5 \times 10^{-4} \) 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 beamline. The filter, the grating and the diaphragm are shown in Fig. 11. The overall power of the lasers was reduced to \( \sim 18 \) nW and \( \sim 1.7 \) mW at the place of the ions, for the shelving laser and the repumping laser, respectively. The waist size of the beams was 670 \( \mu \)m x 700 \( \mu \)m for the repumping laser and 360 \( \mu \)m x 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 de-shelving from the \(^2D_{5/2}\) state, i.e., the excitation rate from the \(^2D_{5/2}\) state to the \(^2P_{3/2}\) state times \((1-b)\), where \( b = 0.008 \) is the branching ratio for decay from the \(^3P_{3/2}\) state back to the \(^2D_{5/2}\) state 24.

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

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

\[
R_{12} = \frac{2J_2 + 1}{2J_1 + 1} \frac{\pi^2 c^3}{\hbar^2 \omega_L^4} A_{21} I g(\omega_L - \omega_{12}),
\]

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, \( A_{21} = 7.7 \cdot 10^6 \) s\(^{-1}\) the Einstein coefficient for spontaneous decay from the \(^2P_{3/2}\) state to the \(^2D_{5/2}\) state, \( I \) the intensity of the incoming radiation, and \( g(\omega_L - \omega_{12}) \) a normalized Lorentz-distribution. Assuming a flat background spectrum of the diodelasers, i.e., the intensity per frequency interval \( \Delta I/\Delta \omega_L \) is constant, we can integrate Eq. (5) over frequency \( \omega_L \) and find an excitation rate of

\[
R = \frac{2J_2 + 1}{2J_1 + 1} \frac{\pi^2 c^2}{\hbar^2 \omega_{12}^4} A_{21} \frac{\Delta I}{\Delta \omega_L}.
\]

Using a diffraction grating we have measured \( \Delta I/\Delta \omega_L \lesssim 0.19 \) nW/(mm\(^2\)·GHz) near 854 nm at the power used in the experiment, and we then find \( R = 0.77 \) s\(^{-1}\). Multiplying this rate by \( 1 - b \) and the transmission of \( 5 \times 10^{-4} \) of the long-pass filter, we find a de-shelving rate of \( 3.6 \cdot 10^{-4} \) 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 $^2D_{3/2}$ state to the $^2P_{3/2}$ state. From the observed shelving rate, we can then find the excitation rate on the 850 nm $^2D_{3/2}$- $^2P_{3/2}$ transition and compare it to the calculated excitation rate for the 854 nm $^2D_{5/2}$- $^2P_{3/2}$ transition, taking the different linestrengths 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 minutes we observed 12 shelving events, i.e., the observed shelving-rate is $5.8 \cdot 10^{-3} \text{s}^{-1}$. 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 $^2D_{3/2}$- $^2P_{3/2}$ transition: $(3/5b) \cdot 5.8 \cdot 10^{-3} \text{s}^{-1} = 5.1 \cdot 10^{-2} \text{s}^{-1}$. By multiplying this number with the relative linestrength between the $^2D_{3/2}$- $^2P_{3/2}$ transition and the $^2D_{5/2}$- $^2P_{3/2}$ transition of 8.92, we find an estimated value of $0.45 \text{s}^{-1}$ for the excitation rate on the $^2D_{5/2}$- $^2P_{3/2}$ 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 de-shelving rate seems to be reasonable.

Above we considered de-shelving due to the repumping laser. In exactly the same way we could consider de-shelving 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 lifetime measurements at three different power levels of the shelving laser, 18 nW, 193 nW and 2081 nW, yielding lifetimes of $1146 \pm 24 \text{ ms}$, $1160 \pm 29 \text{ ms}$ and $1092 \pm 27 \text{ ms}$, respectively. When using higher power, the laser was detuned from resonance to get a similar shelving rate in all experiments. In Fig. 4 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 dataset. The measurement at 18 nW was in fact performed at the same shelving laser power as the measurements for the main dataset.

All together, we include a systematic error of $+1 \pm 1 \text{ ms}$ in our final result due to de-shelving 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: fine-structure changing (j-mixing) collisions and quenching collisions. In a j-mixing collision the internal state can change from the $^2D_{5/2}$ state to the $^2D_{3/2}$ state, or vice versa. In a quenching collision the internal state changes from the $^2D_{5/2}$ state to the $^2S_{1/2}$ ground state. Both types of collisions deplete the $^2D_{5/2}$ state and hence shorten the measured lifetime. j-mixing and quenching rate constants $(\Gamma_j$ and $\Gamma_Q$) in the presence of different gases are given in Ref. 24 and references therein. Quite generally j-mixing collisions are found to be an order of magnitude stronger than quenching collisions. From a restgas analysis 24, we know that the restgas in our vacuum chamber is mainly composed of H$_2$ and gas of 28 atomic mass units, i.e., N$_2$ or CO. In the restgas analysis it was not possible to distinguish between N$_2$ and CO, since the chamber pressure was so low that the signal from the atomic constituents of these molecules could not be observed. Knoop 25 found the following rate constants in units of cm$^3$\text{s}^{-1} for collisions with H$_2$ and N$_2$: $\Gamma_j$(H$_2$) = $(3 \pm 2.2) \cdot 10^{-10}$, $\Gamma_j$(N$_2$) = $(37 \pm 14) \cdot 10^{-12}$, $\Gamma_Q$(H$_2$) = $(12.6 \pm 10) \cdot 10^{-10}$ and $\Gamma_Q$(N$_2$) = $(170 \pm 20) \cdot 10^{-12}$. 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...
could lead to correlations is so-called subradiant and super-radiant spontaneous emission due to interference 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 \(kR > 10\), where \(R\) is the ion-ion distance, \(k = 2\pi/\lambda\) with \(\lambda = 729\) nm in our case \[26\]. For more ions the effect is of the same order of magnitude. In our case \(1/kR \approx 6 \cdot 10^{-3}\) 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 \(|\pm\rangle = (|S_i D_2\rangle \pm |D_1 S_2\rangle)/\sqrt{2}\), where \(S\) and \(D\) indicate the internal state, \(2S_{1/2}\) or \(2D_{5/2}\), 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 \(2D_{5/2}\) state is only populated through spontaneous emission, and consequently the relative phase between the states \(|S_i D_2\rangle\) and \(|D_1 S_2\rangle\) 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 \(\tau\)) destroyed since, from a quantum mechanical point of view, we are constantly measuring the internal state of the ions. So any super- or subradiant effect is in fact expected to be destroyed, and we do not expect any correlation in decays from the \(2D_{5/2}\) 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 \(2D_{5/2}\) state with the \(2P_{3/2}\) 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 de-shelving due to radiation and collisions. An overview of the estimated errors and their uncertainties is given in Table II.

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

\[
\frac{1}{\tau_{\text{meas}}} = \frac{1}{\tau_{\text{nat}}} + \sum_i \gamma_i
\]

(7)

or

\[
\tau_{\text{nat}} \approx \tau_{\text{meas}} + \sum_i \tau_{\text{meas}}^2 \gamma_i.
\]

(8)
Table I: Overview of estimated systematic errors.

| Effect                          | Systematic error [ms] |
|--------------------------------|-----------------------|
| Quick re-shelving              | $-1 \pm 1$            |
| Ions switching place           | $-8 \pm 4$            |
| De-shelving, diode lasers      | $+1 \pm 1$            |
| De-shelving, collisions        | $+3 \pm 1$            |
| Total                          | $-5 \pm 4$            |

where $\tau_{\text{meas}}$ is the measured lifetime as determined from the maximum likelihood estimate, $\tau_{\text{nat}}$ is the natural lifetime, and the $\gamma_i$’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 $\tau_{\text{meas}}^2 \gamma_i$. Eq. (9) 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 $\pm 4$ 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

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

The largest error is the statistical, but we do have a non-negligible 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 $3d^2D_{5/2}$ 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], with the value reported in Ref. [3] and with two theoretical papers [16, 17]. On the level of two standard deviations, the result agrees with two other measurements where de-shelving due to diode lasers was taken into account [3, 14] and with the storage-ring measurement by Lidberg et al. [6]. The most recent measured values [6, 7], including our result, are in good agreement and group themselves around a value of about 1160 ms within 1% of that value. This newly obtained level of agreement should provide valuable input to future atomic structure calculations and astronomical studies.

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[30] In Ref. [26] a dipole transition is considered. For an electric quadrupole transition the relative change of the decay rate is of the same order of magnitude.