Isotope shifts of the $4s^2 \, ^1S_0 \rightarrow 4s5p \, ^1P_1$ transition and hyperfine splitting of the $4s5p \, ^1P_1$ state in calcium

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Using a technique based on production of ion Coulomb crystals, the isotope shifts of the $4s^2 \, ^1S_0 \rightarrow 4s5p \, ^1P_1$ transition for all naturally occurring isotopes of calcium as well as the hyperfine splitting of the $4s5p \, ^1P_1$ state in $^{44}\text{Ca}$ have been measured. The field shift and specific mass shift coefficients as well as the hyperfine structure constants for $^{43}\text{Ca}$ have been derived from the data.

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I. INTRODUCTION

Isotope shifts and hyperfine splitting of optical transitions provide valuable information about atomic electron configurations and not at least properties of the nuclei. While from isotope shifts, nuclear charge distributions can be deduced (see, e.g., Refs. [1,2]), from hyperfine splittings, nuclear spins, magnetic dipole moments, and electric quadrupole moments can be determined [3].

Although isotope shifts and hyperfine splittings already have been measured for a large number of transitions in neutral Ca (see Refs. [4–6] and references therein) and in singly charged $\text{Ca}^+$ ions [7–9], the $4s^2 \, ^1S_0 \rightarrow 4s5p \, ^1P_1$ transition considered in the present paper has hitherto not been measured. In contrast to previous experiments, the present measurements use ion Coulomb crystals as means to obtain the spectroscopic data.

II. EXPERIMENTAL PROCEDURE

In the experiments, we have used a frequency doubled cw laser system tuned to the $4s^2 \, ^1S_0 \rightarrow 4s5p \, ^1P_1$ transition at a wavelength of $\lambda = 272$ nm. The degree of excitation at a particular wavelength is determined from the ion production rate when excited neutral Ca atoms absorb yet another $\lambda = 272$ nm photon directly from the $4s5p \, ^1P_1$ state or from the metastable $4s3d \, ^1D_0$ state, populated through spontaneous emission as depicted in Fig. 1(a) [10]. As shown in the sketch of the experimental setup in Fig. 2(a), the spectroscopic laser beam at $\lambda = 272$ nm crosses a well-collimated effusive thermal beam of calcium atoms at right angles in the center of a linear Paul trap [11]. This geometry is chosen in order to obtain small Doppler shifts of the transition under study as well as to have a large capture efficiency of the ions produced. Since the atomic beam is derived from an oven containing natural metallic calcium, all the isotopes $^{40}\text{Ca}$ (96.9%), $^{42}\text{Ca}$ (6.47%), $^{43}\text{Ca}$ (0.135%), $^{44}\text{Ca}$ (2.086%), $^{46}\text{Ca}$ (0.004%), and $^{48}\text{Ca}$ (0.187%) are present. The detection of the ions produced within a given exposure period is done by first trapping them independently of the specific isotope, and then converting almost all ions into $^{40}\text{Ca}^+$ through near-resonant electron transfer collisions with atoms in the atomic beam containing 96.9% $^{40}\text{Ca}$ atoms. Finally, the number of trapped ions is counted with a near-100% efficiency by monitoring the fluorescence from the $^{40}\text{Ca}^+$ ions when laser cooled into a Coulomb crystal [12,13]. Below, the key parts of the applied technique are discussed in detail.

A. Isotope and hyperfine selective ion production

The laser system used for the spectroscopy consists of a tunable, single-mode ring cw dye laser operated at 544 nm with an output power of a few hundreds mW which is frequency doubled to 272 nm by a $\beta$-barium borate crystal placed in an external cavity. The output power at the desired $4s^2 \, ^1S_0 \rightarrow 4s5p \, ^1P_1$ transition wavelength is typically about $\sim 10 \, \text{mW}$, and the laser linewidth is below 1 MHz. This linewidth is much smaller than the full width at half maximum (FWHM) Doppler width of $\sim 50 \, \text{MHz}$ due to the transverse velocity spread of the thermal atomic beam originating from an oven at a temperature of $\sim 600 \, \degree \text{C}$. Hence, since the natural linewidth of the $4s^2 \, ^1S_0 \rightarrow 4s5p \, ^1P_1$ transition according to the NIST database [14] is known to be $\Gamma = 2 \, \text{MHz}$ ($> 50\%$ uncertainty), the Doppler effect is the resolution limiting factor in the experiments. With isotope shifts typically of the order of GHz and hyperfine splittings of about $\sim 100 \, \text{MHz}$ of $^{43}\text{Ca}$, not only can one selectively excite individual even isotopes (no nuclear spin), but also the three

FIG. 1. Simplified energy level diagrams of Ca (a) and Ca$^+$ (b) of relevance to the experiments. The straight arrows indicate laser driving transitions, while the wavy arrow symbolizes spontaneous emission. In (a), the solid line beneath the hatched region indicates the ionization limit.

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Thus reveals the excitation spectrum. The number of produced ions as a function of laser frequency is stable. The hyperfine components of the \(4s \ ^1P_1\) state are populated through spontaneous decay. Counting the number of ions in the multicomponent crystal could principally be determined by imaging the fluorescence from the individual isotopes. This is, however, technically very demanding, since each isotope ion would need its own set of laser frequencies due to isotope shifts of the transitions shown in Fig. 1(b). As an alternative route to quantify the total ion production, we choose to expose the multicomponent crystals similar to the one in Fig. 4(a) to the thermal pressure of \(10^{-10}\) Torr. As sketched in Fig. 2(b), for \(U_{RF} \sim 200\) V, \(\Omega = 2\pi \times 3.9\) MHz and \(U_{EC} = 5\) V, the effective trap depth becomes \(\sim 1\) eV. This ensures that ions produced in the trapping region are efficiently trapped despite the thermal velocities of the neutral atoms.

When ions of a certain calcium isotope, e.g., \(^{40}\text{Ca}^+\), are produced, they can be Doppler laser-cooled by driving the \(4s \rightarrow 4p\) \(D_{3/2} \rightarrow 4p \ P_{1/2}\) transitions by laser light around 397 nm and 866 nm, respectively, as depicted in Fig. 1(b). As the ions are cooled to sufficiently low temperatures (\(\sim 10\) mK), they arrange in a spatial ordered structure, often referred to as an ion Coulomb crystal. In our setup, these ion Coulomb crystals are imaged onto an image intensified Charge-coupled device camera by collecting fluorescence from the Doppler cooled ions. A typical picture of a Coulomb crystal containing \(\sim 10,000\) \(^{40}\text{Ca}^+\) ions is shown in Fig. 3. Here, one clearly observes the elliptical projection of the crystal, which for our trapping potential is spheroidal with the trap axis (\(z\) axis) as the axis of rotational symmetry. Single-component Coulomb crystals in our trap have spatially uniform ion densities when viewed on length scales larger than the typical distance between neighboring ions (see Ref. [15]). The specific density is set by the trapping parameters. Hence, by determining the crystal volumes, e.g., by measuring the main axis of the projected ellipse, we can determine the total number of trapped ions.

Generally, when the frequency of the spectroscopy laser is tuned between the resonances the various isotopes, two or more singly charged calcium isotope ions will be produced and trapped. Such multispecies ion ensembles can be cooled into Coulomb crystals as well, with the lighter isotopes more tightly bound towards the trap axis than the heavier due to the dynamical confinement in the \(xy\) plane [15]. In Fig. 4(a), an image of the fluorescence from laser cooled \(^{40}\text{Ca}^+\) ions in such a crystal is shown. The crystal consists mainly of \(^{40}\text{Ca}^+\) and \(^{44}\text{Ca}^+\) ions, where the nonfluorescing \(^{44}\text{Ca}^+\) ions are cooled only sympathetically through the Coulomb interaction with the directly laser cooled \(^{40}\text{Ca}^+\) ions [16,17]. The number of ions in the multicomponent crystal could principally be determined by imaging the fluorescence from the individual isotopes. This is, however, technically very demanding, since each isotope ion would need its own set of laser frequencies due to isotope shifts of the transitions shown in Fig. 1(b). As an alternative route to quantify the total ion production, we choose to expose the multicomponent crystals similar to the one in Fig. 4(a) to the thermal...
atomic beam of calcium until nearly all the ions (~96.9\%) by near-resonant electron transfer collisions of the type
\[ ^{40}\text{Ca}^+ + ^{40}\text{Ca} \rightarrow ^{40}\text{Ca} + ^{40}\text{Ca}^+ \] (1)

have been converted to \(^{40}\text{Ca}^+\) ions, and subsequently we measure the size of the now nearly pure \(^{40}\text{Ca}^+\) crystal. Since the energy difference between the two sides of Eq. (1) is just the isotope shift of the electronic levels, which is much smaller than the thermal energy of the atoms in the beam, no significant energy barrier exists for the process. Furthermore, since the kinetic energy of the produced \(^{40}\text{Ca}^+\) ions is more than an order of magnitude smaller than the trap potential depth, essentially 100\% of the ions produced through Eq. (1) stay trapped. In Fig. 4(b), the two-component crystal presented in Fig. 4(a) has been converted via the electron transfer process into a nearly pure \(^{40}\text{Ca}^+\) crystal.

III. SPECTROSCOPIC RESULTS

A. The 4s\(^5p\) \(^1P_1\) excitation spectrum

Figure 5 shows the relative ion production rate or, equivalently, the relative rate at which calcium atoms are being excited to the \(^1P_1\) state, as a function of the detuning of the spectroscopy laser. These relative rates were obtained from knowledge of the volumes of the created Coulomb crystals, the laser exposure times, and the intensities of the spectroscopy laser. The spectrum contains resonances of all the naturally abundant isotopes, including the one corresponding to \(^{40}\text{Ca}\) which has a natural abundance of only 0.004\%. The results presented in Fig. 5 have been obtained from three partially overlapping frequency scans. The three data series were measured at slightly different oven temperatures: \(T_{\text{oven}} = 612{\degree}\text{C}\) (\(\Delta\)), \(T_{\text{oven}} = 630{\degree}\text{C}\) (\(\blacksquare\)), and \(T_{\text{oven}} = 602{\degree}\text{C}\) (\(\square\)). The relative rates of the \(\Delta\) data and the \(\blacksquare\) data have been normalized, so they share the same fitted maximum value and position at the \(^{40}\text{Ca}\) resonance peak. In the same way the data indicated by \(\blacksquare\) and \(\square\) have been normalized to the three \(^{43}\text{Ca}\) hyperfine peaks.

The temperature was during each experiment kept stable to better than \(\pm 2{\degree}\text{C}\) corresponding to a maximum uncertainty in the atomic density of about \(\pm 7\%\) during the whole data accumulation time of \(\sim 40\) min. Since the time to measure a single resonance is only a very small fraction of this time, any systematic errors in the resonance profiles due to fluctuating oven temperatures can be neglected. The Doppler broadening of the resonances, which only depends slightly on the atomic mass, is best found by fitting the \(^{40}\text{Ca}\) resonance data to a Voigt profile. By doing this one obtains a total FWHM of \(\sim 54\pm 5\) MHz dominated by the Doppler broadening. At the laser intensity which we apply \(\sim 100\) mW/cm\(^2\), we have assumed that neither the \(^{4s^2}\) \(^1S_0\rightarrow 4s5p\) \(^1P_1\) transition nor the following photoionization process is saturated. Consequently, the ion production rate is expected to be proportional to the laser intensity squared. We accounted for fluctuations in the spectroscopic laser intensity during the data accumulation time by using this assumption. That this assumption is rather good is supported by noting that the relative measured resonance peak values in Fig. 5 are in good agreement with the natural abundances of the calcium isotopes, which are \(^{40}\text{Ca}\) (96.9\%), \(^{42}\text{Ca}\) (0.647\%), \(^{43}\text{Ca}\) (0.135\%), \(^{44}\text{Ca}\) (2.086\%), \(^{46}\text{Ca}\) (0.004\%), and \(^{48}\text{Ca}\) (0.187\%).

B. Isotope shifts

Before deriving the isotope shifts from data like the ones presented in Fig. 5, the uncertainty of the individual data points has to be estimated and taken into account. The uncertainty is essentially due to three effects. First, due to intensity fluctuations of the laser intensity there will be a fluctuation in the number of ions produced. Since for neighboring data points around a resonance this intensity fluctuation is maximally a few percent, the expected square
dependence on the intensity of the ion production leads to an estimated uncertainty of ~5%. Second, in determination of the Coulomb crystal volumes, both systematic and random uncertainties due to the measurements of the main axis of the elliptical projections of the crystals occur. Both these errors are of about ~5%, but since the systematic errors are equal for points symmetrically positioned around a resonance, it will have a small effect on the determination of the resonance frequencies. Hence, in our analysis, we have only accounted for the random errors of 5%. Finally, due to the finite number of ions produced within one measurement, we have included an uncertainty of the square root of the estimated number of ions. If all these uncertainties are accounted for in a weighted least-squares Gaussian fit, the uncertainty on the resonance position becomes lower than 2 MHz.

A more critical error arises when we compare similar scans. Here we find that the measured resonance peak positions are associated with much larger uncertainties than the ones from the Gaussian fits. This additional error originates from local frequency drift of the spectroscopy laser during a whole scan which typically lasts about 40 min. From a series of scans, we have found that this laser drift error leads to a rms uncertainty in the resonance frequencies of about 9 MHz. This last error source is the dominant one for the estimated errors of the isotope shifts given in Table I. In this table, the isotope shift for $^{43}$Ca is found as the center of gravity of the three hyperfine components of $^{43}$Ca which will be discussed in Sec. III C. In addition to these statistical errors, there is also a systematic uncertainty of ±1% arising from the calibration of the spectroscopy laser frequency scan to an optical spectrum analyzer with a known free-spectral range.

For completeness, we have estimated that we might have introduced an unimportant error of a few hundred kHz due to the fact that we have determined the resonance frequencies from single Gaussian fits instead as from a more realistic multipeak Voigt profile fit.

The isotope shift for a given transition is usually described as a sum of the mass and the field shift in the following way [1]:

$$\delta \nu_{\text{RIS}} = M \Delta A - A' \Delta A' + F \delta (r^2 AA')$$

where $M$ is the mass shift coefficient, $A$ and $A'$ denote the atomic masses of the two isotopes, $F$ is the field shift coefficient, and $\delta (r^2 AA')$ is the difference in mean square nuclear charge radii between the isotopes.

The mass shift is usually written as a sum of the normal mass shift (NMS) and the specific mass shift (SMS), which means that we can write the mass shift coefficient as $M = M_{\text{NMS}} + M_{\text{SMS}}$. Here the NMS coefficient is given by the simple expression $M_{\text{NMS}} = \nu_0 m_i/m_e$, where $\nu_0$ is the transition frequency, $m_e$ is the electron mass, and $m_i$ is the atomic mass unit. The NMS originates from the reduced mass correction for the electron, while the SMS comes from the change in the correlated motion of all the electrons (see, e.g., Ref. [18]). Subtraction of the NMS from the total isotope-shift gives the residual isotope shift (RIS),

$$\delta \nu_{\text{RIS}} = M_{\text{SMS}} (A' - A)/AA' + F \delta (r^2 AA')$$

Rewriting Eq. (3) by multiplication by the factor $AA'/(A' - A)$ leads to

$$A' A \over A' - A \delta \nu_{\text{RIS}} = M_{\text{SMS}} + F \left( A' A \over A' - A \delta (r^2 AA') \right),$$

which shows that $M_{\text{SMS}}$ and $F$ can be determined from a linear fit when the $\delta (r^2 AA')$’s are known. Using values of the $\delta (r^2 AA')$’s for calcium from Ref. [2], in Fig. 6, we have plotted the left-hand side of Eq. (4) using the values of Table II as a function of $[A' A/(A' - A)] \delta (r^2 AA')$ for the fixed value of $A = 40$. The SMS coefficient and field shift coefficient, obtained by weighted linear regression fit to the data points in Fig. 6, are listed in Table II.

The field shift coefficient for the $4s^2 1S_0 \rightarrow 4s5p \ 1P_1$ transition (Table II) is, within the stated error, almost equal to the experimentally determined field shift coefficient for the $4s^2 1S_0 \rightarrow 4s4p \ 1P_1$ transition of $F = -175.8 \pm 1.2$ MHz/fm² reported in Ref. [5]. This can be attributed to the fact that a $p$ electron has negligible overlap with the nucleus compared to

<table>
<thead>
<tr>
<th>Mass (A)</th>
<th>Shift (MHz)</th>
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<tbody>
<tr>
<td>42</td>
<td>967±9</td>
</tr>
<tr>
<td>43</td>
<td>1455±9</td>
</tr>
<tr>
<td>44</td>
<td>1879±14</td>
</tr>
<tr>
<td>46</td>
<td>2746±16</td>
</tr>
<tr>
<td>48</td>
<td>3528±16</td>
</tr>
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</table>
TABLE II. The specific mass shift $M_{\text{SMS}}$ and field shift $F$ coefficients for the $4s^2 \, ^1S_0 \rightarrow 4s5p \, ^3P_1$ transitions of calcium derived from the linear fit presented in Fig. 6. The first stated uncertainty estimate is the one standard deviation obtained from the linear regression to the data of Fig. 6. The systematic error in the isotope shifts due to the frequency scan calibration is included as the second uncertainty estimate. For completeness the NMS coefficient is $M_{\text{SMS}}=604.3 \text{ GHz amu}$.

<table>
<thead>
<tr>
<th>$M_{\text{SMS}}$ (GHz amu)</th>
<th>$F$ (MHz/fm$^2$)</th>
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</thead>
<tbody>
<tr>
<td>243±3±9</td>
<td>179±39±2</td>
</tr>
</tbody>
</table>

an $s$ electron, so the main contribution to the field shifts is expected in both cases to come from the $s$ electrons.

### C. $^{43}$Ca hyperfine splitting

The nuclear spin of $I=7/2$ for $^{43}$Ca leads to three hyperfine levels of the $^1P_1$ state with total spins $F=5/2,7/2,$ and $9/2$, respectively. The hyperfine structure (hfs) constants and isotope shift of $^{43}$Ca are determined by fitting to the normal Casimir formula \[3\]

$$\Delta E_F = \Delta E_{\text{gs}} + \frac{A}{2} C + \frac{B}{4} \frac{3C(C+1)-2I(I+1)J(J+1)}{(2I-1)(2J-1)IJ},$$

(5)

where $C=F(F+1)-I(I+1)-J(J+1)$, $\Delta E_{\text{gs}}$ is the isotope shift of the center of gravity of the hfs, and $A$ and $B$ are the magnetic dipole and electric quadrupole coupling constants, respectively. Several scans across the three hyperfine resonances were made to increase the level of confidence of the $A$ and $B$ constants. The hfs constants derived from these scans are summarized in Table III, while the center of gravity for $^{43}$Ca has been given in Table I. The small value of the $B$ constant indicates that the magnetic dipole coupling has the most prominent contribution to lifting the degeneracy of the $4s5p \, ^3P_1$ level for $^{43}$Ca. Compared with the work of Ref. [5], where the hfs constants for the $4s4p \, ^1P_1$ state in $^{43}$Ca have been measured to be $A=-15.54\pm0.03 \text{ MHz}$ and $B=-3.48\pm0.13 \text{ MHz}$, the $4s5p \, ^3P_1$ state has an opposite sign for the $A$ constant and the $B$ constant is the same order of magnitude or smaller.

### IV. CONCLUSION

With a technique based on determining the number of ions produced, collected, and cooled into Coulomb crystals through resonant two-photon ionization, the isotope shifts of the $4s^2 \, ^1S_0 \rightarrow 4s5p \, ^3P_1$ transition for all naturally occurring isotopes of calcium as well as the hyperfine splitting of the $4s5p \, ^3P_1$ state in $^{43}$Ca have been measured. The field shift and specific mass shift coefficients as well as the hyperfine structure constants for $^{43}$Ca have been derived from the data. Though in the presented experimental scheme, near-resonant charge exchange collisions were used to gain information about the ion number, it is not a requirement for the technique for these to be used. Actually, the technique should be applicable to many atomic species as long as some laser cooled ions are simultaneously trapped and can sympathetically cool the species of interest into a Coulomb crystal [17,19,20]. From the spatial organization of the observable laser cooled species, one can easily deduce the number of the, e.g., nonfluorescing ions of interest.

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