Two-photon laser excitation of trapped $^{232}\text{Th}^+$ ions via the 402 nm resonance line

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Experiments on one- and two-photon laser excitation of $^{232}\text{Th}^+$ ions in a radiofrequency ion trap are reported. As the first excitation step, the strongest resonance line at 402 nm from the $(6d^77s)J=3/2$ ground state to the $(6d7s7p)J=5/2$ state at 24874 cm$^{-1}$ is driven by radiation from an extended cavity diode laser. Spontaneous decay of the intermediate state populates a number of low-lying metastable states, thus limiting the excited state population and fluorescence signal obtainable with continuous laser excitation. We study the collisional quenching efficiency of helium, argon, and nitrogen buffer gases, and the effect of repumping laser excitation from the three lowest-lying metastable levels. The experimental results are compared with a four-level rate equation model, that allows us to deduce quenching rates for these buffer gases. Using laser radiation at 399 nm for the second step, we demonstrate two-photon excitation to the state at 49960 cm$^{-1}$, among the highest-lying classified levels of Th$^+$. This is of interest as a test case for the search for higher-lying levels in the range above 55000 cm$^{-1}$ which can resonantly enhance the excitation of the $^{229}\text{Th}^+$ nuclear resonance through an inverse two-photon electronic bridge process.

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I. INTRODUCTION

It has been inferred from $\gamma$-spectroscopy of $^{229}\text{Th}$ that this nucleus possesses an isomeric state at an energy of only a few eV above the ground state, establishing the lowest excitation energy that is known in nuclear physics. The most recent experimental value for the $^{229}\text{Th}$ isomer energy is 7.8(5) 0.5 eV [1, 2]. This system has stimulated a number of proposals for studies of the effects of atomic electrons on the nuclear transition (see [3, 4] and references therein). These can be expected to be especially pronounced here because of the matching of the nuclear and electronic excitation energies. The radiative decay of the isomeric state can be strongly enhanced in a so-called electronic bridge process where the nucleus excites the electron shell and a photon is finally emitted in an electronic transition. Vice versa, in an inverse electronic bridge process, laser excitation of the nucleus can be more efficient by making use of an electronic excitation that will resonantly couple to the nuclear moments.

Since the nuclear transition frequency in $^{229}\text{Th}$ is accessible by frequency upconversion of narrow-bandwidth laser sources, we have proposed a two-photon inverse electronic bridge process in singly ionized $^{229}\text{Th}$ [5].

The electronic energy level system of Th$^+$ is very complex and is well known only up to an excitation energy of about 7 eV. The classified energy levels belong to the lowest 15 configurations of the three valence electrons. More than 400 energy levels have been identified [2], and the wavelengths of about 14000 lines are tabulated [10]. Recent relativistic Hartree-Fock calculations indicate an exponential increase of the energy level density towards the ionization energy of 11.9 eV [11].

While the high density of electronic energy levels in Th$^+$ increases the probability for a strong resonance enhancement of electronic bridge processes leading to excitation of the $^{229}\text{Th}$ nucleus, it also poses an experimental problem: Laser excitation of an ensemble of atoms from the ground state to a definite excited state is often inefficient for a multi-level system such as Th$^+$ because spontaneous decay leads to the accumulation of population in metastable levels that are decoupled from the laser. If the number of metastable levels is not too high, additional repumper lasers may be applied for reexcitation from each of those states. Otherwise, atoms in metastable states can be returned to the ground state by inelastic quenching collisions with a buffer gas. The latter approach has already been utilized for laser spectroscopy of Th$^+$ ions: In order to determine nuclear charge radii of the isotopes $^{227}\text{Th}$ to $^{230}\text{Th}$ and $^{232}\text{Th}$, isotope shifts and hyperfine splittings have been recorded in one- and two-photon laser excitation to levels at 17122 cm$^{-1}$ and 34544 cm$^{-1}$ using Th$^+$ ions in a radiofrequency trap in the presence of helium and hydrogen buffer gases [12].

Here we present experiments on one- and two-photon laser excitation of trapped Th$^+$ ions, aimed at an investigation of the electronic energy level system in the range around 7-8 eV and towards the excitation of the $^{229}\text{Th}$ nuclear resonance by an inverse two-photon electronic laser sources, we have proposed a two-photon inverse electronic bridge process in singly ionized $^{229}\text{Th}$ [5].

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bridge process. In particular, we investigate excitation of the strongest tabulated line of the Th$^+$ emission spectrum at 402 nm which connects the $(6d^27s)J=3/2$ ground state with the $(6d7s7p)J=5/2$ state at 24874 cm$^{-1}$. In the following we label states by their energy in cm$^{-1}$ and their total angular momentum as shown in Fig. 1. Spontaneous decay from the 24874$^{5/2}_J$ state leads back to the ground state with a rather high probability but a number of low-lying metastable states are also populated (see Fig. 1). We measured branching ratios of 11 decay channels after laser excitation in a hollow-cathode discharge. With trapped ions, we study the collisional quenching efficiency of helium, argon, and nitrogen buffer gases, and the effect of repumping laser excitation from the three lowest-lying metastable levels. We show that the experimental results are in good agreement with a simple four-level rate equation model. Using laser radiation at 402 nm and at 399 nm, we demonstrate two-photon excitation to the level 49960$^{5/2}_J$ via the intermediate 24874$^{5/2}_J$ state. The observation of two-photon excitation to this level in $^{232}$Th$^+$ is of interest because it serves as a test case for the search for higher-lying levels which can resonantly enhance the excitation of the $^{229}$Th$^+$ nucleus through an electronic bridge process as pointed out above.

II. EXPERIMENTAL SET UP

The experiment employs a linear radiofrequency (rf) trap of 160 mm total length (see Fig. 2). The trap electrodes are machined from a CuBe alloy and are divided along their length into three sections which are held at different dc potentials. For ion loading, a metallic $^{232}$Th sample is placed between two electrodes near the end of one of the outer sections. Typically a rf trap drive voltage in the range of 0.5 - 1 kV amplitude at a frequency of 2 MHz is used, corresponding to a Mathieu $q$ parameter in the range of 0.2 - 0.4 (for a review see Ref. 13). The end sections are kept at a dc potential of +40 V relative to the central section for axial confinement.

![FIG. 1. Partial level scheme of the thorium ion Th$^+$ showing the main resonance transitions studied in this work and the lowest-lying metastable levels. The hatched area corresponds to a manifold of eleven metastable states which is shown in more detail in the right-hand side of the figure. The level energies are given in cm$^{-1}$ and the subscript denotes the total angular momentum. For the 24874$^{5/2}_J$ level the spontaneous-decay branching fractions are indicated as given in Ref. 12.](image)

![FIG. 2. Schematic of the linear Paul trap used in the experiments (a) and cross section of the trap electrode arrangement, showing the position of the Th sample used for ion loading by N$_2$ laser ablation (b). Dimensions are in millimeters.](image)

The trap is mounted in a stainless-steel ultrahigh-vacuum chamber that reaches a base pressure in the range of $1 \times 10^{-8}$ Pa. For collisional cooling and depopulation of metastable Th$^+$ levels by quenching collisions, either helium, argon or nitrogen at a pressure of up to 0.2 Pa is used as a buffer gas. To produce $^{232}$Th$^+$ ions by laser ablation, a nitrogen laser emitting 4 ns pulses with an energy of $\approx 100 \mu J$ at a wavelength of 337 nm is focussed to a spot size of $100 \mu m \times 150 \mu m$ on a metallic Th target (see Fig. 2 b)). After 5 to 10 ablation pulses at 0.2 Pa helium buffer gas pressure, more than $10^5$ ions are loaded into the trap (for more details see Ref. 17). With argon and nitrogen buffer gases the same number of trapped ions is obtained with 2–5 and 1–2 pulses, respectively. We observe storage times for Th$^+$ in the range of 300–1000 s, limited by the formation of molecular ions in reactions with the background gas.

For excitation of the $0_{3/2}\rightarrow 24874_{5/2}$ transition (see Fig. 1), a continuous-wave (cw) extended-cavity diode laser (ECDL) with a maximum output power of 7 mW at 402 nm and a linewidth of less than 1 MHz is used. The 24874$^{5/2}_J$ – 49960$^{5/2}_J$ transition is excited by a similar laser system emitting at 399 nm. The metastable 1521$^{5/2}_J$ level is depleted by a frequency-doubled ECDL producing light at a wavelength of 428 nm (see Fig. 1). The output of these lasers is passed to the trap through polarization-maintaining single-mode fibers in order to clean the beam profiles, thus minimizing light scattering off the trap electrodes. Beam diameters in the trap are $\approx 1$ mm. For low-resolution spectroscopy over extended wavelength ranges, a tunable modelocked Ti:Sapphire laser system producing pulses of about 3 ps duration and 90 MHz repetition rate is used. Its output wavelength can be tuned in the range of 700–900 nm and in the corresponding second- and third-harmonic ranges.

As shown in Fig. 3 the fluorescence emission of the trapped $^{232}$Th$^+$ ions is detected with the use of two photomultipliers placed behind a fused-silica collection lens. In order to discriminate between the fluorescence emissions associated with one- and two-step excitations, a combination of spectral filters and a dichroic beamsplitter separates the spectral sensitivity ranges of the photomultipliers.
FIG. 3. Experimental arrangement for laser excitation of trapped Th$. Two photomultipliers (PMT) are used for fluorescence detection. A nitrogen laser is used for loading the trap. SHG (THG) second harmonic generation (third harmonic generation). For further details see text.

### III. SINGLE-WAVELENGTH LASER EXCITATION OF $^{232}$Th$^+$

In an investigation of possible first excitation steps from the ground state, fluorescence signals of $^{232}$Th$^+$ are readily observed by illuminating the trapped ion cloud with output of the picosecond Ti:Sapphire laser. A typical excitation spectrum of electric-dipole transitions around 400 nm is shown in Fig. 4(a). In order to compensate variations in signal strength caused by fluctuations of the number of loaded ions, the fluorescence signal registered at each laser wavelength was normalized to the signal resulting from resonant cw diode-laser excitation of the 402 nm transition. Helium was used as a buffer gas at a pressure of $\approx 0.2$ Pa. The transitions from the ground state displayed in Fig. 4(a) and their relative strengths are in agreement with the data tabulated in Ref. [2] for the investigated scan range.

The spectrum resulting from 402 nm cw laser excitation is shown in Fig. 4(b). While the line widths in Fig. 4(a) are determined by the spectral width of the employed laser, the linewidth in Fig. 4(b) is determined by Doppler broadening. For helium pressures above 0.1 Pa the Doppler width of $\approx 700$ MHz (FWHM) indicates that the trapped ions are collisionally cooled to approximately 300 K for motion along the trap axis. With argon and nitrogen buffer gas, cooling to room temperature is achieved at pressures of $\approx 0.2$ Pa and $\approx 0.01$ Pa, respectively. With these gases at 0.2 Pa pressure, larger fluorescence signals are observed than with helium, because of more efficient collisional quenching of metastable levels (see below). For cw excitation of the 402 nm transition, the strength of the fluorescence signal is strongly affected by population trapping in metastable levels.

For a quantitative overview on the decay channels of the $24874_{3/2}$ level we performed measurements of the fluorescence emission resulting from laser excitation of Th$^+$ ions in a hollow-cathode discharge. The hollow-cathode lamp has a similar construction as described in Refs. [18, 19]. The cathode is a 2.5 cm long copper cylinder with an inner diameter of 6 mm, covered by a thorium foil on the inner wall, and is cooled by liquid nitrogen. The discharge is operated at a current of 40 mA with an inner diameter of 6 mm, covered by a thorium foil on the inner wall, and is cooled by liquid nitrogen. With an inner diameter of 6 mm, covered by a thorium foil on the inner wall, and is cooled by liquid nitrogen. With an inner diameter of 6 mm, covered by a thorium foil on the inner wall, and is cooled by liquid nitrogen.

In order to obtain a simple analytic description, we approximate the Th$^+$ level system up to the $24874_{3/2}$ level by the four-level system shown in Fig. 5: the 402 nm transition from the ground state [1] to state [3] is driven by Rabi frequency $\Omega_1$, the metastable state [2] is depleted by 428 nm repumping light with Rabi frequency $\Omega_2$, and the manifold of eleven higher-lying metastable states is represented by a single level $|m\rangle$. Here we assume that $|m\rangle$ is depleted only by quenching collisions. The excited state [3] radiatively decays into the states [1], [2] and $|m\rangle$ with rates $\gamma_1$, $\gamma_2$ and $\gamma_m$. Their sum, $\gamma = \gamma_1 + \gamma_2 + \gamma_m$, determines the radiative lifetime of the cathode. A mirror with a central hole for passage of the laser beam collects the fluorescence light from the center of the cathode onto the entrance slit of a grating monochromator. After passage through the monochromator the light is detected with a photomultiplier and recorded differentially with and without laser excitation, in order to separate the laser-induced fluorescence from emission excited by the discharge. The spectral sensitivities of monochromator and photomultiplier are calibrated with a tungsten reference lamp. Since laser stray light would perturb the fluorescence intensity measurement at the wavelength used for excitation, the intensity ratios of the lines at 402 nm, 434 nm and 482 nm were also measured with laser excitation of the $1521_{3/2}-24874_{3/2}$ transition at 428 nm. The wide dynamic range of the detection method allowed us to measure relative intensities of 11 emission lines listed in Ref. [3], complementing a previous study that had reported branching fractions for 6 lines [14]. The two weakest lines at 812 nm and at 1073 nm were not observed. Table I summarizes the results. Based on the observed reproducibility for different discharge conditions, we attribute a relative uncertainty of about 0.1 to the branching fractions for the weak decay channels. The branching fraction for decay on the resonance line 402 nm back to the ground state of 0.92(3) is in good agreement with the value 0.94 from Ref. [14] and higher than the value 0.85 obtained in the analysis in Ref. [20]. Cyclic laser excitation of the 402 nm resonance line in a single Th$^+$ ion can therefore be expected to result in about 15 fluorescence photons before decay into a metastable level occurs.

### IV. EFFECTIVE 4-LEVEL MODEL FOR COLLISIONAL QUENCHING AND REPUMPING

In order to obtain a simple analytic description, we approximate the Th$^+$ level system up to the $24874_{3/2}$ level by the four-level system shown in Fig. 5: the 402 nm transition from the ground state [1] to state [3] is driven by Rabi frequency $\Omega_1$, the metastable state [2] is depleted by 428 nm repumping light with Rabi frequency $\Omega_2$, and the manifold of eleven higher-lying metastable states is represented by a single level $|m\rangle$. Here we assume that $|m\rangle$ is depleted only by quenching collisions. The excited state [3] radiatively decays into the states [1], [2] and $|m\rangle$ with rates $\gamma_1$, $\gamma_2$ and $\gamma_m$. Their sum, $\gamma = \gamma_1 + \gamma_2 + \gamma_m$, determines the radiative lifetime of the
The populations of state (3) as $\tau = \frac{1}{3}$. For our analysis we use the experimental lifetime value $\tau = 23$ ns. We assume that $\gamma_1 = b_1 \gamma$ and $\gamma_2 = \gamma_3 = (1 - b_2) \frac{1}{2}$, and $b = 0.94$ as the branching fraction for decay to the state (1), because the branching fractions for decay to the 1521 s/2 level and for decay to $|m|$ are approximately equal (see Ref. [14] and Table I). The populations of $|2\rangle$ and $|m\rangle$ can decay to the ground state through quenching collisions with buffer gas and the corresponding rates are denoted by $\Gamma_2$ and $\Gamma_m$. Neglecting the light-induced coherence between states $|1\rangle$ and $|2\rangle$, the population distribution among the levels can be described by rate equations for the population probabilities $p_i$ ($i = 1, 2, 3, m$). In the steady-state limit the rate equations of the four-level system shown in Fig. 5 can be expressed as:

\[
\begin{align*}
-\gamma S_1 p_1 + \Gamma_2 p_2 + \gamma_1 p_3 + \gamma S_1 p_3 + \Gamma_m p_m &= 0, \\
-\gamma S_2 p_2 - \Gamma_2 p_2 + \gamma_2 p_3 + \gamma S_2 p_3 &= 0, \\
\gamma S_1 p_1 + \gamma S_2 p_2 - \gamma p_3 - (S_1 + S_2) \gamma p_3 &= 0, \\
\gamma_m p_3 - \Gamma_m p_m &= 0, \\
\end{align*}
\]

(1)

with the normalization condition $\sum p_i = 1$. Here $S_j$ ($j = 1, 2$) are the saturation parameters for the transitions $|j\rangle - |3\rangle$. Assuming thermalization of velocities due to both velocity-changing collisions and interaction with the trap potential, and vanishing detunings from the transitions $|j\rangle - |3\rangle$, we approximate the optical pumping rates as:

\[
\gamma S_j \approx 2 \sqrt{\pi} \frac{\Omega_j^2}{kv},
\]

(2)

where $kv \approx 2\pi \times 360$ MHz is the Doppler width. For linearly polarized laser fields, the effective Rabi frequencies $\Omega_j$ are obtained by averaging over the Zeeman sublevels:

\[
\Omega_j^2 = \frac{(2j_3 + 1)}{3(2J_3 + 1)} \Omega_j^2,
\]

(3)

where $J_j$ is the total angular momentum of the level $|j\rangle$.

Solving the rate equations, the population of state $|3\rangle$ is:

\[
p_3 = \frac{2G_2 G_m S_1 + 2G_m S_1 S_2}{(1 - b)(G_2 + G_m) + 4G_2 G_m S_1 + 6G_m S_1 S_2 - 2G_2 G_m S_2 - (1 - b) G_m S_1 S_2} \cdot (4)
\]

where $G_k = \Gamma_k/\gamma$, $(k = 2, m)$. The observed fluorescence rate is proportional to $p_3$. If both optical excitations $|j\rangle - |3\rangle$ saturate the corresponding transitions, $S_1 \gg (1 + b) G_2/(1 - b)$ and $S_2 \gg (G_2 + G_m)$, the fluorescence rate is limited by the quenching relaxation of the state $|m\rangle$:

\[
p_3 \approx \frac{2G_m}{1 - b} \cdot G_2.
\]

(5)

In the absence of the repumping field ($S_2 = 0$), level $|2\rangle$ is depleted only by quenching collisions. In this case the fluorescence rate is reduced and can be expressed as follows:

\[
p_3 \approx \frac{2G_m}{1 - b} G_2 + \frac{G_m}{1 - b} G_m.
\]

(6)

According to Eq. 5 and Eq. 6, the fluorescence enhancement factor $\gamma$ due to repumping from level $|2\rangle$ obtained in the limit of high 402 nm and 428 nm laser powers is given by $\gamma = 1 + \Gamma_{35}/\Gamma_2$.

V. QUENCHING RATES AND POPULATION OF THE 24874 s/2 LEVEL

Based on the results of the four-level model description and using repumping excitation from the 1521 s/2 level, we determine the collisional quenching rates of this level and of the manifold of the other metastable levels which are populated during continuous excitation of the 402 nm 01/2–24874 s/2 transition. Quenching rate coefficients are determined for helium, argon, and nitrogen buffer gases. In order to find conditions which minimize the population of metastable levels and thus maximize the population of the 24874 s/2 state, we also investigate the effect of additional repumping excitation from the manifold of the levels above the 1521 s/2 level, which are described as the effective limit $|m\rangle$ in the model calculation (see Fig. 5).

The data points in Fig. 6(a) show the relative increase in the fluorescence signal at 402 nm which results from repumping excitation of the 1521 s/2–24874 s/2 transition at 428 nm. Helium was used as a buffer gas at 0.2 Pa pressure. The data were obtained for two settings of 402 nm laser power which differ by more than one order of magnitude. It appears that the fluorescence signal is enhanced by up to a factor of nine at a repumping laser power above 0.5 mW. The enhancement is less pronounced if
FIG. 6. Fluorescence signal of trapped Th$^+$ ions resulting from resonant laser excitation of the 402 nm 0$_3/2$–24874$_5/2$ transition, showing the fluorescence enhancement due to repumping excitation at 428 nm for two settings of 402 nm excitation power (Full and open circles) with helium buffer gas. The data points are normalized to the fluorescence levels observed without 428 nm excitation. The lines correspond to solutions of Eq. 4 using excitation and quenching rate parameters corresponding to the conditions of the experiment (see text). The data points in the inset show the variation of the fluorescence signal with 402 nm laser power observed in the absence of 428 nm excitation. The solid line corresponds to the solution of Eq. 4 using the same parameters as in the main figure.

The inset of Fig. 6 shows that Eq. 4 also accurately describes the observed saturation behaviour of the 402 nm excitation without 428 nm repumping. In this case, population of the 1521$_5/2$ state reduces the effective saturation power for excitation of the 402 nm transition to a few microwatts corresponding to an intensity of $\approx 0.3$ mW/cm$^2$.

The inset of Fig. 6 shows that Eq. 4 also accurately describes the observed saturation behaviour of the 402 nm excitation without 428 nm repumping. In this case, population of the 1521$_5/2$ state reduces the effective saturation power for excitation of the 402 nm transition to a few microwatts corresponding to an intensity of $\approx 0.3$ mW/cm$^2$.

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i.e. two orders of magnitude below the saturation intensity for the two-level system 0$_3/2$–24874$_5/2$. With helium buffer gas, the observed variation of $g$ with pressure points to a linear pressure dependence of the rate $\Gamma_2$ and to a less than proportional variation of $\Gamma_m$ with pressure. At a lower helium pressure of 0.02 Pa, the 428 nm repumping excitation enhances the fluorescence signal by $g \sim 20$.

Using time-separated pulsed 402 nm and 428 nm excitation we obtain a direct measurement of the quenching rate $\Gamma_2$ of the 1521$_5/2$ level. The 1521$_5/2$ level was populated via the 24874$_5/2$ state during a 2 ms pulse of the ECDL at 402 nm. After a variable time delay, the remaining population of the 1521$_5/2$ level is determined by applying a pulse from the 428 nm ECDL and recording the time-integrated fluorescence signal at 402 nm. A similar method was used in Refs. [21, 22]. We observe an exponential decay of the fluorescence signal as a function of the time delay between the 402 nm and 428 nm excitation and a linear dependence of the decay rate on He pressure of $63(3) \times 10^{-4} \text{Pa}^{-1}$. For a pressure of 0.2 Pa, this results in $\Gamma_2 = 13(2) \text{s}^{-1}$, in agreement with the value derived above with Eq. 4 from the data for continuous excitation.

In order to maximize the efficiency of laser excitation to the 24874$_5/2$ level, we investigated extended repumping schemes where in addition to the 1521$_5/2$ level also higher-lying metastable levels are depleted by laser excitation (see Fig. 4). The output wavelength of the pulsed Ti:Sapphire laser (see Sec. II) was tuned to suitable re-pumping transitions for the six lowest metastable levels together with the calculated population probability of the 24874$_5/2$ level. The 1521$_5/2$ level was pumped via the 24874$_5/2$ level and a linear dependence of the decay rate on He pressure $\Gamma_2 = 5.0 \times 10^{-3} \text{s}^{-1}$. For helium buffer gas at 0.2 Pa, a fluorescence enhancement of approximately a factor of three is observed for excitation of the 4113$_3/2$–17122$_3/2$ transition and for a number of other transitions originating from the 4113$_3/2$ level. Excitation from higher-lying metastable levels does not lead to any significant increase in the fluorescence signal. The depletion of the 1860$_3/2$ level increases the fluorescence signal only if there is no repumping excitation from the 1521$_5/2$ level. This can be explained by a collision-induced population transfer between the 1521$_5/2$ and 1860$_3/2$ levels whose energy difference is comparable to the kinetic energy of the buffer gas atoms. With argon or nitrogen buffer gas, repumping from the energy levels above the 1521$_5/2$ level does not result in any significant fluorescence enhancement.

Table II shows the inferred effective quenching rates together with the calculated population probability of the 24874$_5/2$ level under cw laser excitation for the three gases used in our investigations. For helium, additional repumping from the 4113$_3/2$ level yields a maximum pop-
ulation of $3.6 \times 10^{-4}$ in the $24874_{5/2}$ level. For all experimental conditions studied here, population trapping in low-lying metastable levels limits the obtainable population of the $24874_{5/2}$ state. In previous experiments with trapped $\text{Th}^+$ ions, molecular hydrogen and helium buffer gas were compared and hydrogen was found to produce $\approx 100$ times higher fluorescence signal at the same pressure $[13]$. In our experiment, nitrogen shows an even stronger quenching efficiency. From the maximum 402 nm fluorescence signal obtained with nitrogen we deduce that more than 100 photons/s per ion are detected, providing efficient diagnostics of the trapped ions on the timescale expected for the decay of the $^{229}\text{Th}$ isomeric state $[22]$. While nitrogen produces the highest fluorescence rate and most efficient collisional cooling, the noble gases offer the advantage that they can be purified more efficiently using getter materials and cryogenic traps and therefore permit longer storage times for $\text{Th}^+$.

With the use of pulsed optical excitation, even without repumping excitation a significantly higher population in the $24874_{5/2}$ level can be achieved over times short compared to $1/\Gamma_2$ and $1/\Gamma_m$. This could be demonstrated by using an acousto-optical modulator (AOM) to switch on the 402 nm excitation repeatedly with a rise time of approximately $1 \mu$s after dark periods long compared to $1/\Gamma_2$. The resulting initial fluorescence intensity is more than 30 times larger than the steady-state value obtained with 402 nm cw excitation and helium buffer gas. The decay of the fluorescence signal to the level corresponding to cw excitation was dominated by two time constants in the range of a few 100 ns and 1 ms. The longer time constant might reflect the collision-induced population transfer between the various metastable levels (see above). The observed fast time constant can not be directly associated with the spontaneous decay rates to metastable levels because also transit-time and saturation effects and the rise time of the AOM shutter are expected to strongly affect the temporal variation of the fluorescence signal on this time scale.

VI. TWO-PHOTON LASER EXCITATION OF TRAPPED $^{232}\text{Th}^+$ IONS

The level $49960_{7/2}$ shown in Fig. 1 is one of the highest-lying tabulated energy levels that can be excited by an electric dipole transition from the $24874_{5/2}$ state. The radiative lifetime of this level appears to be unknown. Apart from the 399 nm transition to the $24874_{5/2}$ level, there are 17 tabulated decay channels to other levels $[23]$. The energy of the $49960_{7/2}$ state corresponds to 6.2 eV which is close to the range of the expected isomeric excitation energy of $^{229}\text{Th}$.

In our experiment, trapped $\text{Th}^+$ ions collisionally cooled by buffer gases at 0.2 Pa pressure are continuously excited by 402 nm radiation tuned to the line center of the $0_{3/2}^{+}-24874_{5/2}$ transition and by 428 nm repumping light. A beam of 399 nm light from an ECDL whose frequency is scanned across the $24874_{5/2}^{+}-49960_{7/2}$ transition is overlapped co- or counterpropagating with the 402 nm beam. Excitation to the $49960_{7/2}$ level is detected by monitoring the fluorescence emission in the wavelength range below 320 nm. Figure 4 shows the two-photon excitation spectrum observed for counterpropagating 402 nm and 399 nm excitation beams using helium buffer gas at 0.2 Pa. The fluorescence signal observed in the range 340–650 nm, also shown Fig. 7 indicates the population of the intermediate $24874_{5/2}$ level. The resonant reduction of this fluorescence shows that a substantial fraction of ions ($\approx 20\%$ for counterpropagating beams) is transferred from the $0_{3/2}^{+}-24874_{5/2}$ excitation cycle if the $24874_{5/2}^{+}-49960_{7/2}$ transition is resonantly excited. This shows that also in the case of the complex level-structure of $\text{Th}^+$ efficient two-photon excitation of highly excited states can be achieved.

Generally, one expects that both, stepwise and direct two-photon excitation processes contribute to the population of the $49960_{7/2}$ level. With counterpropagating beams, the linewidth of the two-photon resonance is narrower and the fluorescence signal is approximately 1.5 times higher than with copropagating beams (see Fig. 5). In the copropagating case the sub-Doppler resonance population the $49960_{7/2}$ level is formed predominantly by stepwise two-photon excitation, while in the counterpropagating case an additional contribution of direct two-photon excitation appears. A similar feature was observed in a previous investigation on two-photon excitation between lower-lying energy levels of trapped $\text{Th}^+$ ions $[13]$.

In Figure 5 the experimental data for co- and counterpropagating beams are plotted together with calculated lineshapes based on the model presented in Ref. $[23]$. The homogeneous linewidth of the 402 nm transition was inferred from Doppler-free saturation resonances of the transition at 402 nm. Using nitrogen buffer gas, we here observe a minimum width of 26(2) MHz (FWHM), significantly higher than the natural linewidth of the $24874_{5/2}^{+}$ state of 7 MHz. Apart from smaller contributions from saturation, collisions and transit effects, the dominant broadening mechanism can likely be attributed to a frequency modulation resulting from the driven micromotion of the ions in the trap. For the fitting of the two-photon lineshapes, good agreement with theory was obtained for a width of the $24874_{5/2}^{+}-49960_{7/2}$ resonance which is four times bigger than the width of the $24874_{5/2}^{+}$.
resonance. The resulting linewidths for excitation with co- and counterpropagating laser beams are 95 MHz and 66 MHz, respectively.

Using the pulsed picosecond Ti:Sapphire laser for the second excitation step results in weak fluorescence signals which did not allow us to identify the excitation of higher-lying states. The broad spectrum emitted by this laser excites several resonances from low-lying metastable levels simultaneously.

VII. CONCLUSION

In conclusion, we have demonstrated two-photon excitation of Th\(^{+}\) through the intermediate state at 24874\(\frac{7}{2}\). In order to maximize the population of excited states we investigated collisional quenching of metastable states with different buffer gases and repumping with additional lasers. In continuous excitation with two diode lasers, we have shown the efficient two-photon excitation of a highly excited state in this complex level-structure. This sets the ground for a comprehensive investigation of the electronic level structure of Th\(^{+}\) in the energy range of the 229\(^{+}\)Th isomeric state and for the search for a resonant two-photon electronic bridge excitation of the 229\(^{+}\)Th nucleus over the wide present uncertainty range for the transition energy. For this we plan to use the third harmonic of a pulsed Ti:Sapphire laser with a linewidth in the GHz range in combination with synchronized 402 nm ECDL pulses. A comparison of the fluorescence signals observed with 229\(^{+}\)Th and with 232\(^{+}\)Th shall permit the unambiguous identification of the signature of the unique nuclear structure of 229\(^{+}\)Th.

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