

Measurement of the $1^3S_1 \rightarrow 2^3S_1$ interval in positronium using field ionization of Rydberg states

Michael W. Heiss^{*,†}, Lucas de Sousa Borges[‡], Artem Golovizin[§], and Paolo Crivelli[§]

Institute for Particle Physics and Astrophysics, ETH Zürich, 8093 Zürich, Switzerland

 (Received 13 July 2024; revised 6 December 2024; accepted 2 January 2025; published 16 January 2025)

We report a 40 parts per 10^9 measurement of the positronium $1^3S_1 \rightarrow 2^3S_1$ interval using pulsed two-photon optical spectroscopy. The transition is detected via field ionization of atoms excited from the $2S$ to the $20P$ Rydberg state. Precise Monte Carlo line-shape simulations allow for the accounting of effects such as Doppler and ac Stark shifts, while an optical heterodyne measurement of the excitation laser pulse is used to correct for laser frequency chirp. A value of $1\,233\,607\,210.5 \pm 49.6$ MHz is obtained. This scheme allows for the measurement of the velocity distribution of positronium atoms to correct for the second-order Doppler effect. This is a major source of systematic uncertainty expected for future measurements of this transition with a cw laser; thus, our technique paves the way toward a new generation of a high-precision determination of this interval in positronium.

DOI: [10.1103/PhysRevA.111.012810](https://doi.org/10.1103/PhysRevA.111.012810)

I. INTRODUCTION

Positronium is the lightest known atom and comprises a structureless pointlike electron and its antiparticle, the positron [1,2]. As such, it is a purely leptonic system and can be described to very high precision by bound-state QED [3–5], without the inherent complications given by the finite size of protonic atoms. Furthermore, being a true onium atom, recoil effects are strongly enhanced and its quantum numbers sum to zero, making it an ideal candidate to test fundamental symmetries like *CPT* invariance [6–8] and for searches of new physics beyond the standard model [4,9–11].

However, positronium is also a very challenging system for precision measurements due to its ephemeral nature. Being a bound state of antiparticles, it tends to self-annihilate quickly, [12,13] and due to its lightness, it exhibits much higher velocities than other atoms at comparable temperatures. Nevertheless, being a precision test bench for QED with many unique features, it represents a particularly interesting system for spectroscopic measurements.

With the advent of high-power narrowband lasers at the required wavelength of 486 nm, optical two-photon spectroscopy of positronium was realized by Chu and Mills measuring the $1^3S_1 \rightarrow 2^3S_1$ transition [14]. This was then improved upon, to be the benchmark QED test in positronium, reaching 12 parts per 10^9 (ppb) using pulsed lasers [15] and a final precision of 3.2 ppb [16–18] using cw lasers.

After nearly two decades without positronium laser experiments, the past ten years have seen a resurgence of precise measurements using lasers in positronium research (for an excellent overview see [19]). However, the 1993 value for the $1^3S_1 \rightarrow 2^3S_1$ transition is still the most precise to date. Significant improvements in our understanding of bound-state QED [20–34] provide strong motivation for a new, more precise determination of this transition.

Here we report a measurement using multiple concurrent detection techniques. This includes an approach to further excite atoms from the $2S$ state to the $20P$ Rydberg state and subsequent field ionisation in a well-defined region of high electric field, allowing for a measurement of the atoms' time of flight and therefore their velocity distribution.

The experiment was conducted in two stages. Data for the first run were acquired without an absolute frequency standard and measurement of the laser chirp. For the second run, a Menlo FC1500-250-WG optical frequency comb and online laser chirp measurements were added to determine the absolute laser frequency accurately (see Sec. II C). Additionally, the target and detector systems were redesigned for the second run, mainly to reduce the background due to backscattered positrons (see Sec. II D).

II. EXPERIMENTAL METHODS

A. Slow positron beam and positronium production

The pulsed slow positron beamline (see Fig. 1) provides less than 10 ns (FWHM) wide bunches of approximately 2×10^4 positrons per second at a repetition rate of 1–10 Hz, which are subsequently reaccelerated to 1–6 keV. Before entering the experimental chamber, they are extracted from the magnetic field and refocused spatially via an electrostatic einzel lens to approximately $\sigma_d = 1.5$ mm beam diameter [35,36].

Positrons are then implanted on a mesoporous silica thin-film target [37], where they can either be backscattered or penetrate the bulk and stop with a mean implantation depth on the order of a few hundred nanometers. A fraction of these

*Contact author: michael.heiss@psi.ch

†Present address: PSI Center for Neutron and Muon Sciences CNM, 5232 Villigen PSI, Switzerland.

‡Present address: Lebedev Physical Institute, 119991 Moscow, Russia.

§Contact author: crivelli@phys.ethz.ch

Published by the American Physical Society under the terms of the Creative Commons Attribution 4.0 International license. Further distribution of this work must maintain attribution to the author(s) and the published article's title, journal citation, and DOI.

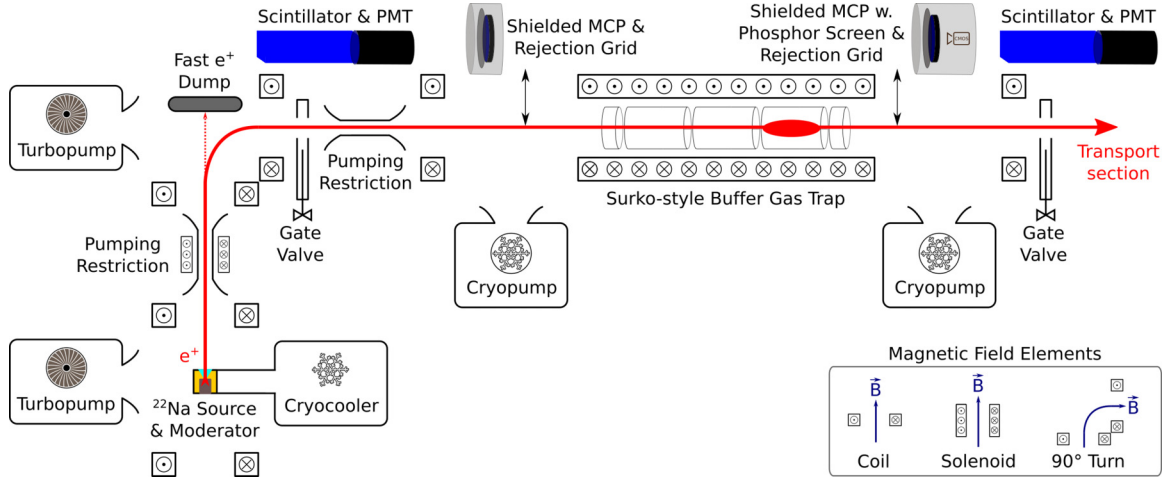


FIG. 1. Schematic overview of the pulsed slow positron beamline at ETH Zurich. Positrons are created in the β^+ decay of the radioactive isotope ^{22}Na and moderated using a solid rare gas moderator to approximately 40 eV. They are then guided through a velocity selector to remove unmoderated positrons from the beam and transported to the buffer gas trap. There they lose energy by inelastic collisions with N_2 gas atoms to be trapped in an electric potential with magnetic radial confinement. In the last stage of the trap, the positron plasma is compressed by a rotating electric field and cooled by collisions with CF_4 gas. The positrons are then extracted in time-compressed bunches and guided to the experimental chamber.

positrons can form positronium by picking up an electron from the bulk material. Positronium rapidly thermalizes and is ejected into the pores with approximately 1 eV [38] kinetic energy. The atoms will then diffuse through the porous network and rapidly cool down due to collisions with the pore walls [39]. This process will only continue as long as the de Broglie wavelength

$$\lambda_{\text{dB}} = \frac{h}{\sqrt{4\pi m_e k_B T}} \approx \sqrt{\frac{0.24 \text{ eV}}{E_{\text{kin}}}} \times 1 \text{ nm} \quad (1)$$

is significantly smaller than the pore size of approximately 4 nm [40]. As positronium approaches room temperature, the de Broglie wavelength becomes comparable to the pore size and the atom is confined quantum mechanically, which implies a significantly smaller diffusion coefficient [41]. Experimental studies showed that the cooling from the classical to the quantum regime is completed within 5 ns and that the mean time for positronium to diffuse out of the sample depends linearly on implantation energy with approximately 3 ns/keV [42].

Due to the quantum nature of positronium in the pores, the minimum energy of positronium cooling down in the network is given not by the thermal limit (approximately 30 meV for room temperature) but by the ground-state energy of the particle confined to the pore [40]. For the simple model of a particle of mass $2m_e$ in an infinite spherical well potential, the ground-state energy is given by [43]

$$E_0 = \frac{h^2}{4m_e d^2} \approx \left(\frac{27.4 \text{ nm}}{d} \right)^2 \times 1 \text{ meV}, \quad (2)$$

which yields $E_0 \simeq 47 \text{ meV}$ for a $d = 4 \text{ nm}$ pore size.

However, positronium emitted from these porous targets is not purely monoenergetic. The positrons have a broad implantation profile and therefore a fraction of positronium can form close to the surface. In this case, the atoms will be emitted

epithermally before they cool down to the ground-state energy of the pore. A distribution of pore sizes or positronium interacting on the target surface might also lead to smaller emission energies than the calculated ground-state limit. In fact, while the exact velocity distribution is unknown, earlier experiments using the same type of target found that it could be well represented by a Maxwell-Boltzmann distribution with $T = 900 \text{ K}$ for a 3 keV implantation energy [42,44]. Similarly, we found excellent agreement with a Maxwell-Boltzmann distribution for 700–550 K at implantation energies of 4–5 keV. The most probable velocity of the distribution roughly corresponds to the velocity predicted by Eq. (2) and it is in good agreement with values found in earlier measurements for implantation energies above 4 keV [40–42].

B. Laser excitation

A schematic overview of the laser system employed to measure the 1S-2S transition is shown in Fig. 2 (more details on the laser system can be found in [36]). Three separate laser beams at different wavelengths (486, 532, and 736 nm) are generated, combined, and used to excite and photoionize positronium. A Spectra Physics Quanta-Ray Lab 190 injection-seeded Nd:YAG allows for the generation of 532 nm (second harmonic) of up to 500 mJ and 355 nm (third harmonic) of up to 250 mJ with pulse lengths on the order of a few nanoseconds.

The excitation to the metastable 2S state is driven by a modified Radiant Dyes pulsed dye amplifier (PDA), which is seeded at approximately 486 nm using a Toptica TA pro 972 nm diode laser and an included second harmonic generation stage, generating up to 1 W with a linewidth on the order of 200 kHz. The dye consists of coumarin 102 [45] along with a stabilizing agent (1,4-diazabicyclo [2.2.2] octane) [46] dissolved in absolute ethanol, which is pumped by the frequency-tripled output of the Nd:YAG laser,

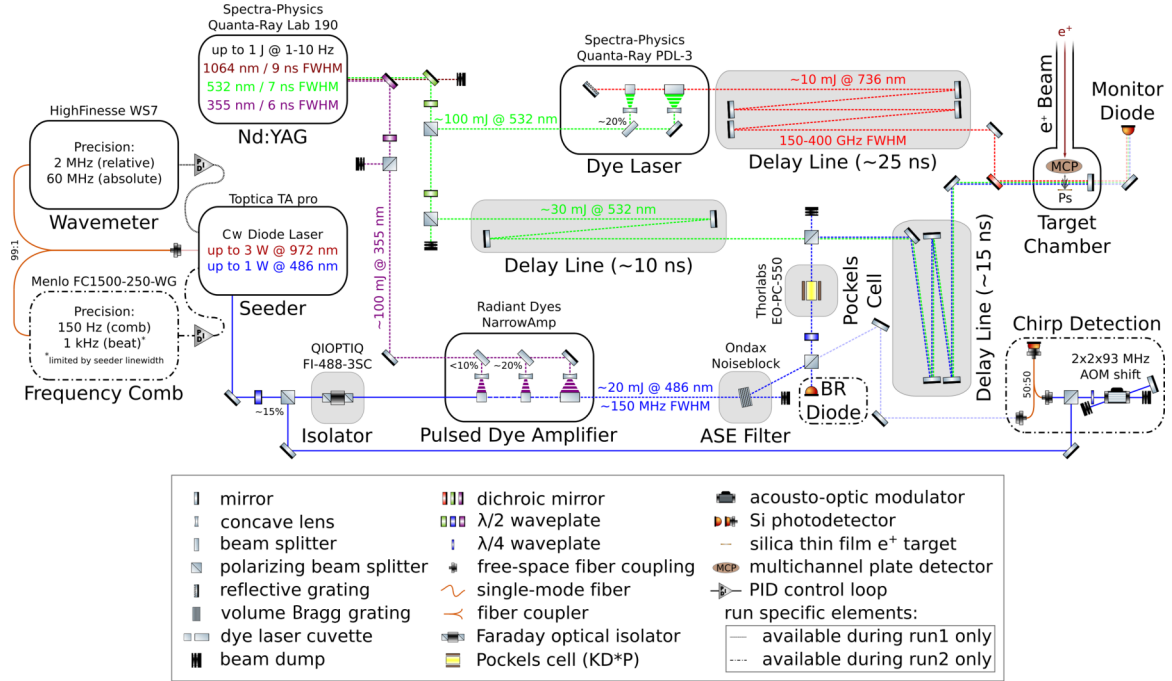


FIG. 2. Schematic overview of the 1S-2S laser excitation system for both runs. Pulsed lasers are denoted by dotted lines and cw lasers by solid lines. Not all elements are shown, e.g., pulse shaping optics and shutters. Positions, orientations, and scales are arbitrary.

which is synchronized to the pulsed positron beam. Using a retroreflecting mirror, this allows for two counterpropagating pulses of up to 20 mJ with a time spread of approximately 6 ns FWHM, centered approximately 3 mm away from the target.

A Pockels cell is used to isolate the PDA from the pulse returning from the retroreflection mirror in the experimental chamber. This also allows us to vary the fraction of the blue pulse transmitted to the chamber by changing the peak-to-peak value of the voltage supplied to its electrodes. By continuously measuring the power transmitted to the experimental chamber, long-term stabilization of the average pulse energy, e.g., to counteract dye degradation, to better than 1% is achieved. The addition of a diode on one of the beam splitters allows us to limit the maximal beam misalignment between the incoming and retroreflected beam axes to be below 1.4 mrad for the beam path length of approximately 5 m.

Since the photoionization cross section is around a factor 3 higher than the excitation cross section, a significant fraction, on the order of a few percent when optimized for efficient excitation, of positronium is ionized in the same laser by a third photon. The freed positrons can be detected either by their annihilation signal in a scintillator [47] or by measuring them directly in a microchannel plate (MCP) placed approximately 4 cm from the target. To guide the positrons from photoionization to the detector, a bias potential on the order of 100 V is applied to the target holder, resulting in an electric field less than approximately 10 V/cm in the laser excitation region.

While direct photoionization in the exciting laser can be used for detection, there is significant broadening and shift due to the ac Stark effect. Furthermore, this does not allow for direct detection of the surviving $2S$ states. Using an additional

laser with photon energies higher than the binding energy 1.7 eV of the $2S$ (or any other excited) state allows for delayed photoionization independent of the $1S$ - $2S$ exciting laser. For this purpose, approximately 30 mJ of the frequency-doubled 532 nm output of the Nd:YAG and a delay line on the order of 10 ns were used. This ionizes any excited-state positronium with a probability close to unity.

Alternatively, the excited-state positronium atoms can further be excited to a Rydberg state, using a modified Spectra Physics Quanta-Ray PDL-3 pulsed dye laser pumped by the second harmonic of the Nd:YAG. The $20P$ state was selected as a compromise between polarizability, fluorescence lifetime, and losses due to collisions with residual gas atoms in our vacuum environment, which was operated at approximately 10^{-8} mbar of residual pressure (see Appendix A). Pulses at 736 nm of energies up to 10 mJ at approximately 7 ns FWHM were produced using Styryl 7 dye [48]. Since the transition $2S \rightarrow 20P$ is a one-photon process, the first-order Doppler shift due to the distribution of the emission angles had to be covered by enlarging the laser bandwidth to values on the order of 300 GHz (FWHM).

The wavelength and bandwidth of the output of the PDL-3 dye laser are regularly measured using a calibrated ASEQ Instruments HR1 spectrometer with 50 GHz resolution and show no significant drift. The drive system for the grating used in the frequency selection of the PDL-3 system allows for changes with a repeatability of better than 5 GHz and frequency scans over a range of many nanometers.

C. Frequency stabilization and measurement

A HighFinesse WS7 wavemeter is used to monitor the output of the Toptica TA pro diode laser used for seeding the

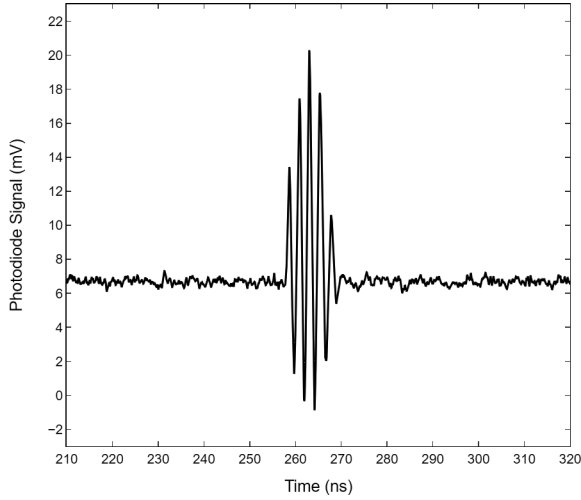


FIG. 3. Typical chirp beatnote oscilloscope waveform taken during run 2.

PDA, with an absolute precision of 60 MHz.¹ For the first run the internal proportional-integral-derivative (PID) control of this device was used to stabilize and scan the frequency of the seed laser.

For the second run, a Menlo FC1500-250-WG optical frequency comb was used as an absolute frequency standard, which was referenced to a precision GPS clock. In addition to measuring the frequency, the beatnote output is used to lock the seed laser to a comb tooth [49]. Not only does this counter possible drift, it also allows us to scan over several several hundred megahertz by changing the repetition rate of the frequency comb.

Frequency chirp [50,51] shifts the output of the pulsed dye amplifier from the frequency of the seed light due to the rapid change in the refractive index of the gain medium [52]. An optical heterodyne technique to measure and correct for this shift [14–16] pulse by pulse was implemented for run 2. Part of the seed light is shifted in frequency using an acousto-optic modulator (AOM) in a second-order double-pass configuration operating at 92.96 MHz and mixed with the output of the PDA using a fiber-optic coupler. The obtained high beatnote frequency at near 370 MHz is needed to precisely measure the frequency chirp of pulses a few nanoseconds wide pulses. The resulting beatnote is then recorded using a fast Thorlabs DET025AFC photodiode and a 1 GHz bandwidth Teledyne LeCroy Waverunner 8104 oscilloscope at a 20 GS/s sampling rate (see Fig. 3).

To extract the instantaneous frequency of the beatnote (which corresponds to the AOM shift plus laser chirp), the signal must first be filtered (see Fig. 4). This is necessary to

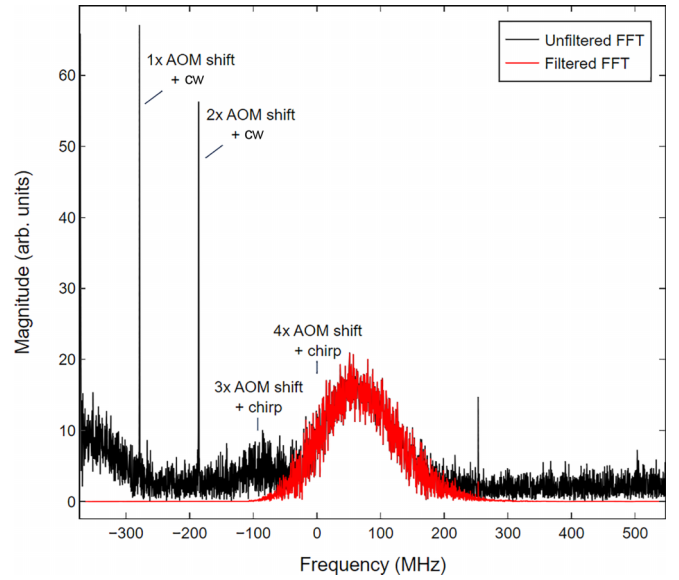


FIG. 4. One-sided fast Fourier transform (FFT) spectrum (after subtraction of total AOM shift) of a typical chirp beatnote taken during run 2 before (black) and after [red (gray)] filtering.

remove high-frequency noise and components related to shifts other than twice the second order of the AOM and to the pulse envelope. To avoid any filter-induced delay, a zero-phase Butterworth bandpass software filter [53,54] is implemented in the analysis. This ensures that the chirp calculated from the filtered signal does indeed correspond to the specific timing of the pulse.

After filtering, a Hilbert transformation [55] is used to extract both the instantaneous envelope and frequency (see Fig. 5). The chirp correction for a specific beatnote is obtained

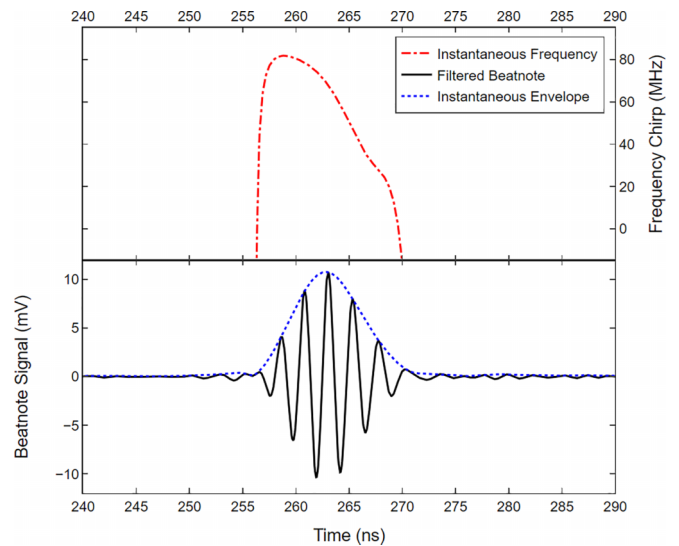


FIG. 5. Filtered beatnote (black solid line), instantaneous envelope (blue dashed line), and frequency (red dash-dotted line), obtained via Hilbert transformation. Note that the instantaneous frequency is only well defined for times with appreciable pulsed laser intensity, which is why it is only shown here for intensities of at least 1% of the peak value.

¹It should be noted that the internal calibration lamp of the device was not functioning at the time of data taking and the device specification states that the absolute error is guaranteed only if the device is frequently calibrated. However, operating the device in conjunction with a frequency comb over several months, we did not measure any shifts above approximately 30 MHz from the stored calibration value.

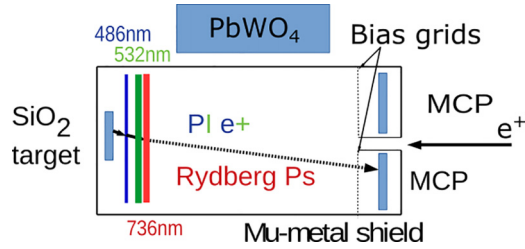


FIG. 6. Sketch of positronium excitation and detection scheme. Positrons from the bunched positron beam are focused onto the silica thin-film target. There they are converted to positronium and emitted into vacuum, which is then laser excited to the $2S$ state by the 486 nm laser and subsequently either ionized by a 532 nm laser or further excited to the $20P$ state using a 736 nm laser. The positrons released either from (direct and/or delayed) photoionization or from field ionization of the Rydberg atoms between the grids and the MCP can be directly detected on the MCP and via their annihilation photons in the PbWO_4 scintillator.

by averaging the instantaneous frequency weighted by the intensity profile. This is done on a pulse-by-pulse basis and each event can then be assigned the chirp corrected frequency.

The calculated value of this correction depends on the specific choice of turn-on and cutoff frequencies. Varying these parameters in our analysis, we found that this introduces a systematic error on the order of 1 MHz in the determination of the chirp corrected frequency.

D. Detection

A schematic overview of the detection can be found in Fig. 6. The implantation of positrons is monitored by the prompt peak in a lead tungstate scintillator and by measuring backscattered positrons in an MCP that is placed approximately 4 cm from the target. Positrons from direct photoionization in the exciting laser as well as from delayed photoionization are guided by an approximately 10 V/cm electric field between the target and the MCP detector assembly.

Positronium atoms in Rydberg states traverse the distance between excitation and detector relatively unperturbed and only ionize in the strong electric field between a grounded grid and the MCP front plate of approximately 4 kV/cm after a time of flight of a few hundred nanoseconds. This allows for the additional measurement of the velocity distribution of positronium atoms, which can be used to measure the second-order Doppler shift. The addition of a position-sensitive detector or parabolic grids to field ionize the atoms in well-defined positions can be used in future experiments to correct this major systematic error on a per-atom basis.

Figure 7 shows the detector and target assembly used during run 1. A matched set of two center-hole MCP plates is used in a chevron configuration, mounted in a custom assembly. A grounded tube through the center axis of the detector allows the positron beam to pass, which results in the active area being an annulus with a 9.14 mm inside diameter and a 40 mm outside diameter. The assembly incorporates two independent bias grids (92% transmission), placed at distances of approximately 3 and 13.5 mm from the front plate,

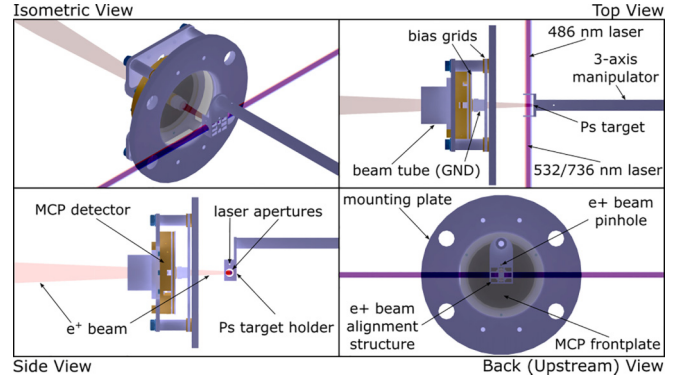


FIG. 7. MCP detector and Ps conversion target assembly for run 1. Most parts of the mounting structure, magnetic shielding, and vacuum chamber are not shown.

respectively. For this measurement both grids were set to the ground potential. The center of the 486 nm laser axis and the center of the grid on which the $20P$ states field ionize are separated by 38.0 ± 1.0 mm. The kinetic energy of positrons implanted on the porous silica thin-film target was 4 keV for this run.

For run 2 the detector geometry was modified to reduce background from backscattered positrons, as well as to reduce losses of approximately 20% through the central aperture (see Fig. 8). To this end, positrons are implanted at a 45° angle of incidence, which necessitates the kinetic energy of the impinging positrons to be increased to achieve the same depth profile as for a 0° angle of incidence. The implantation energy was chosen to be 6 keV, which corresponds to implanting approximately 5 keV perpendicular to the target.

The MCP used two matched plates with 25 mm quality diameter in a chevron configuration, mounted in a custom assembly. A bias grid is mounted at approximately 6 mm from the front plate of the MCP, while a second grid is placed on the mounting structure at a 27.5 mm distance. Both tungsten wire mesh grids, allowing for approximately 92% transmission, were grounded for this measurement. However, due to the grid plane orientation of 45° to the target, an additional loss factor of $1/\sqrt{2}$ per grid is expected on average. The center of the

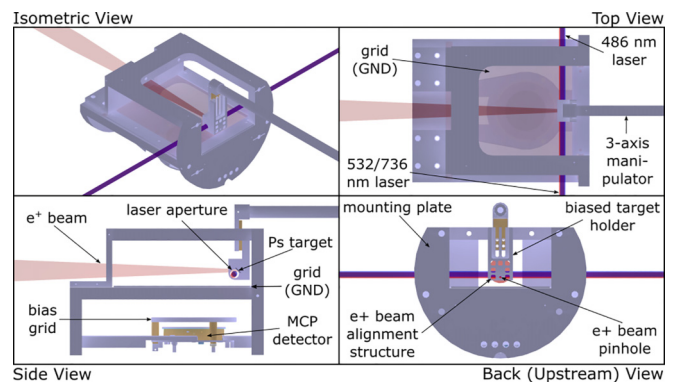


FIG. 8. MCP detector and Ps conversion target assembly for run 2. Most parts of the mounting structure, magnetic shielding, and vacuum chamber are not shown.

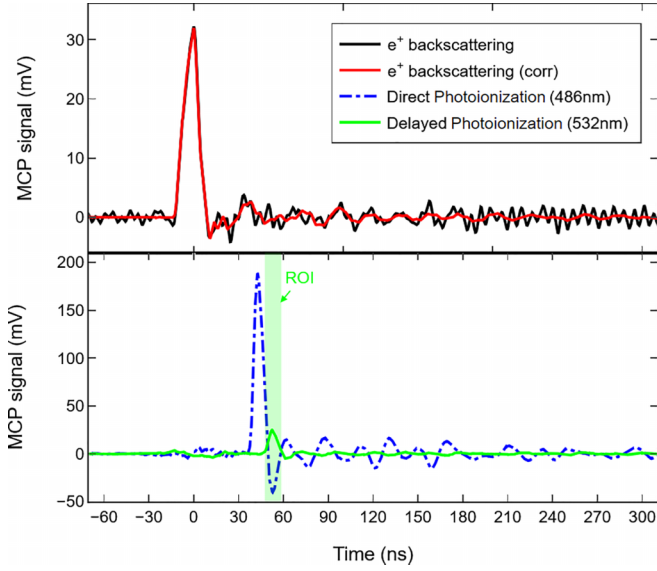


FIG. 9. Averaged MCP waveforms taken during run 1, shown on top for backscattered positrons without laser excitation before (black solid line) and after [red (gray) solid line] HV switching noise correction and on the bottom for direct photoionization (blue dash-dotted line) after subtraction of backscattered positrons and delayed photoionization (green solid line) after subtraction of direct photoionization signals. Also shown on the bottom as a shaded region is the region of interest for the integration of the delayed photoionization signal.

486 nm laser axis and the center of the grid, on which the 20P states field ionize, are separated by 41.8 ± 0.5 mm.

Since most events of interest are due to a single positron and multiple overlapped counts are rare, individual peaks can be counted after the respective backgrounds are subtracted (see Fig. 9) and filtered. Figures 10 and 11 show the time

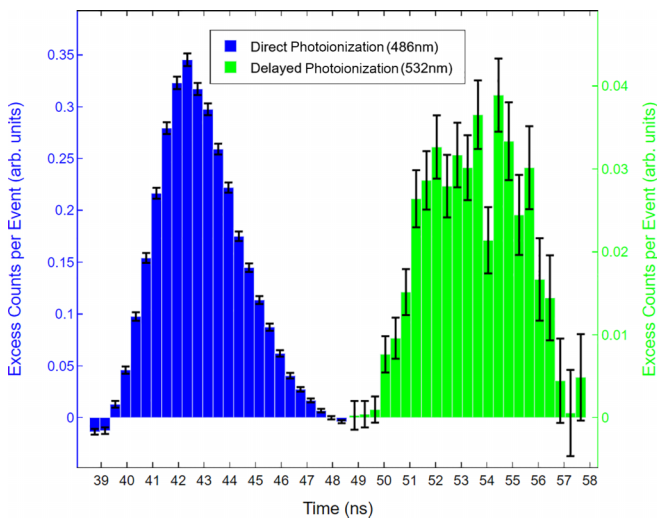


FIG. 10. Histogram of excess MCP counts due to photoionization taken during run 1 [direct photoionization in blue (dark gray) and delayed photoionization in green (light gray)]. The time axis is relative to the implantation of positrons on the porous silica target.

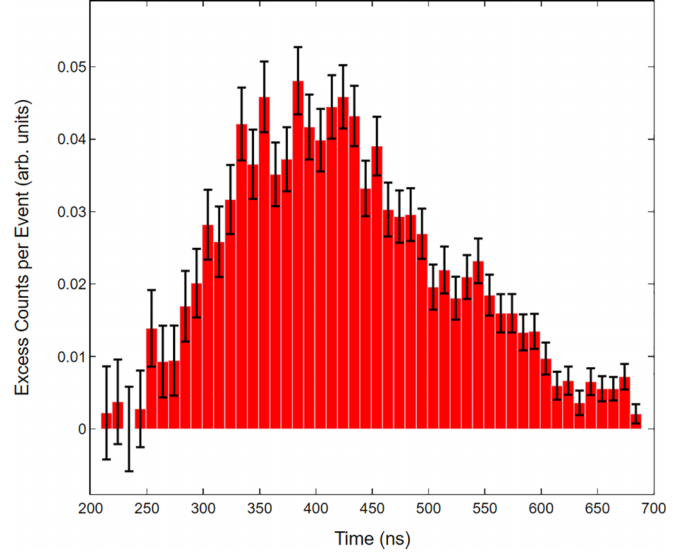


FIG. 11. Histogram of excess MCP counts due to Rydberg field ionization taken during run 1. The time axis is relative to the implantation of positrons on the porous silica target.

spectra of excess counts for photoionization and field ionization for the data set of run 1.

III. RESULTS AND DISCUSSION

A. Results of run 1

Figure 12 shows the sum-normalized measured data points taken during run 1. The results for direct photoionization and field ionization were extracted by directly counting events (peaks above threshold), while for delayed photoionization the average MCP signal was integrated in the region of interest (see Fig. 9). Due to the relatively short time delay of approximately 10 ns between direct and delayed photoionization, reliably identifying peaks was severely impeded by ringing associated with both ion feedback and imperfect impedance matching of the MCP. The frequency shown corresponds to the value set via PID control on the wavemeter and the systematic error is omitted in the graph.

The process of extracting the transition frequency from these results proceeds in three steps. The line shape calculated by a detailed Monte Carlo simulation (see Appendix B 2) is fitted simultaneously to all normalized data points with the only free parameter, aside from the amplitude scaling, being a common offset from zero laser detuning. This allows us to establish a correspondence of measured to simulated frequencies for this specific set of parameters.

To achieve the best signal-to-noise ratio for the time-of-flight spectrum, a subset of frequency points around the peak of the transition is chosen to build the histogram. However, due to the Doppler shift, the exact shape of the time-of-flight spectrum is unique for each frequency, since certain velocity components are favored for certain offsets. Therefore, the frequency correspondence established in step 1 of the fitting process allows for building the matching histogram from simulation. This histogram is then fitted with a χ distribution as outlined in Appendix B 3 for each set of parameters available

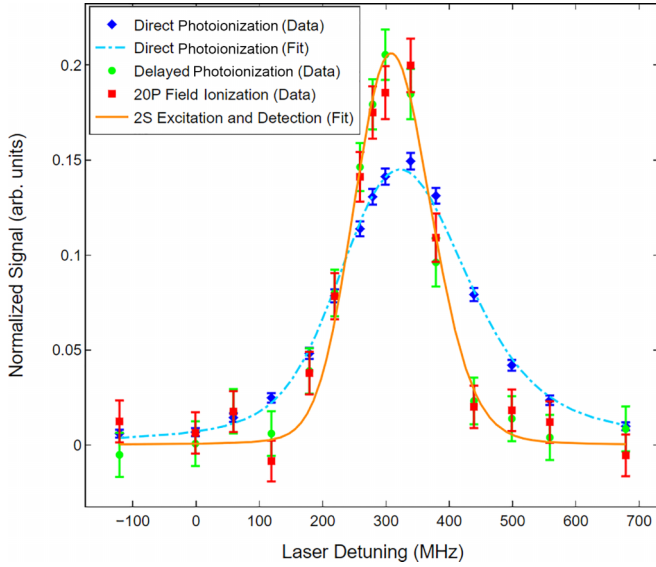


FIG. 12. Positronium direct photoionization (blue diamonds) and 2S excitation measured via delayed photoionization (green circles) and field ionization (red squares) as a function of laser detuning for data taken during run 1. Note that the laser detuning is given as set on the wavemeter and the systematic error is not shown. Furthermore, the chirp was not measured for this data set and is therefore not corrected here. The data are sum normalized and the best fits for all simulated parameter sets for run 1 are shown (light blue dash-dotted line for direct photoionization and orange solid line for 2S excitation).

(see Fig. 30). Note that the simulated time-of-flight distribution assumes a Maxwell-Boltzmann distribution for the initial positronium velocity and the data show excellent agreement. However, as mentioned above, it should be reiterated that there is no reason to expect positronium to be intrinsically thermal at these energies.

Finally, the third step in the fitting procedure entails repeating the process of step 1, additionally fitting the normalized time-of-flight spectrum obtained in the second step. The only free parameter in this additional fitting step is the overall amplitude. Figure 13 shows the fitted function of the best parameter set for the respective time-of-flight (TOF) spectrum. This combined fitting procedure allows for generating a single χ^2 value, which is used to find the best fit for the complete set of parameters simulated.

Aside from determining the best-fitting set of parameters, this method allows for the extraction of an estimate for the systematic error as well. For each individual fit a χ^2 test determines the quality of fit [56] to the simulated line shape and time-of-flight spectrum (see Fig. 14). The reduced χ^2 parameter

$$\chi_r^2 = \frac{\chi^2}{\mathcal{D}} = \frac{1}{\mathcal{D}} \sum_i \frac{(O_i - F_i)^2}{\sigma_i^2} \quad (3)$$

is computed, where $\mathcal{D}$ denotes the degree of freedom and O_i and F_i correspond to the i th observed and fit values, respectively. A cutoff on χ_r^2 for a p value of 0.32 then corresponds to selecting all simulated zero-detuning frequency values that fit the data set with a confidence level of 68%, which we will

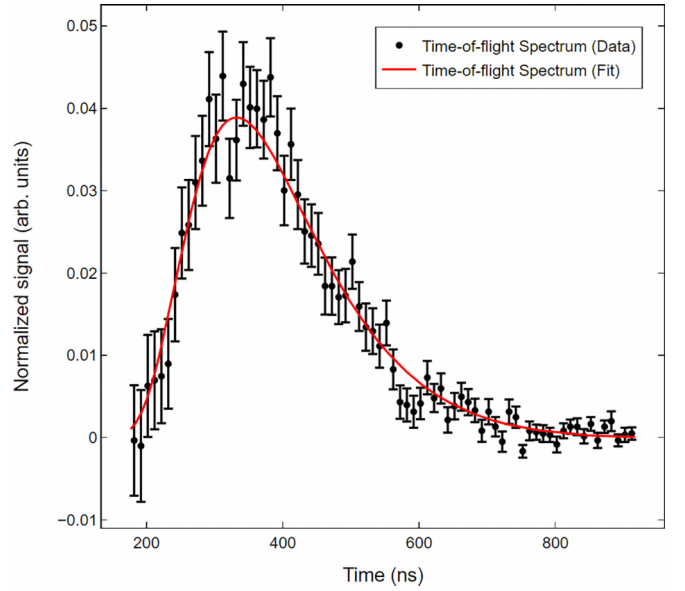


FIG. 13. Normalized time-of-flight spectrum relative to the timing of the 20P excitation to field ionization of the Rydberg atoms on the MCP and the corresponding best fit for all simulated parameter sets for run 1.

use as an estimator for the systematic error. However, since the true variance σ_i^2 for each data point is not known *a priori*, this method can lead to underestimating the systematic error, due to partly unaccounted variance of the data set or an effect that was not accounted for in the simulation. Therefore, in the case of $\min(\chi_r^2) > 1$, the data set is corrected by multiplying an

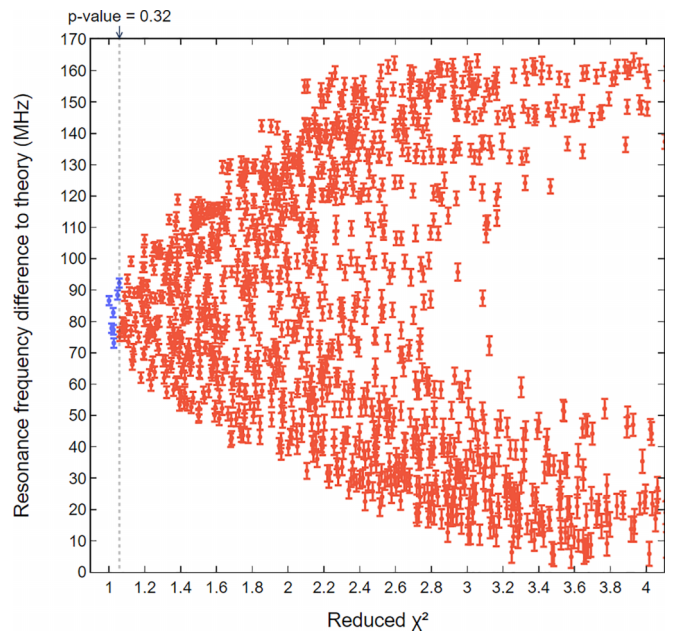


FIG. 14. Plot of reduced χ^2 values for the fits of the data set of run 1 to simulated line shapes and TOF spectra. The cutoff for a p value of 0.32 is shown as a dotted line. Fits below correspond to being within a 68% confidence interval and are taken into account for the estimation of the systematic error.

TABLE I. Sources and magnitude of statistical and systematic errors present in the result for run 1.

Magnitude (MHz)	Description
1.4	data fitting error
0.9	simulation fitting error
9.6	systematic fitting error
15.0	chirp estimation error
60.0	absolute frequency reference error
62.6	quadrature sum

overall error scaling factor and repeating the fitting procedure such that $\min(\chi_r^2) = 1$.

Correcting for the chirp in the result is necessary, since our measurements showed frequency chirp of approximately 60 MHz (see the discussion of run 2 results below) for this laser system operated in a regime similar to that in run 1. The frequencies were therefore corrected by $\Delta\nu_c = 60 \pm 15$ MHz, where the error was conservatively estimated by varying operational parameters within reasonable limits, while measuring the respective laser chirp.

The final result for the resonance frequency in terms of laser detuning obtained during run 1 reads $616\,803\,638 \text{ MHz} \pm 63 \text{ MHz}$, with the respective sources of error given in Table I. This corresponds to a transition frequency of $1\,233\,607\,275 \text{ MHz} \pm 125 \text{ MHz}$ or, equivalently, this result differs from theory by $53 \text{ MHz} \pm 125 \text{ MHz} \pm 0.6 \text{ MHz}$, where 0.6 MHz corresponds to the theoretical uncertainty in the $1S$ - $2S$ interval at $m\alpha^6$.

B. Sources of systematic error and respective magnitudes

To ascertain the relative impact of different sources on the systematic error estimate of run 1, a set of additional simulations was produced, varying only in individual parameters, that is, in the case of misalignment of the incoming and retroreflected laser beam, both angles in the XY and XZ plane were scanned. The systematic error corresponding to the respective parameters was then estimated analogously to the method described above.

Figure 15 shows the respective reduced χ^2 values for scans of the individual parameters. The extracted systematic errors can be found in Table II. Note that this method is limited in scope, since individual errors are in general not uncorrelated. A full scan of the parameter space (see Fig. 14) is necessary to extract a reliable estimate on the overall error. Furthermore, the estimation includes statistical errors due to the

TABLE II. Sources of systematic fitting error for run 1.

Magnitude (MHz)	Parameter
7.7	reflection misalignment
2.9	laser position (relative to target)
2.6	positronium emission time width
1.9	positronium mean velocity
1.9	laser beam waist size
1.7	laser pulse energy
1.5	positronium emission time mean
0.6	MCP position (relative to laser)

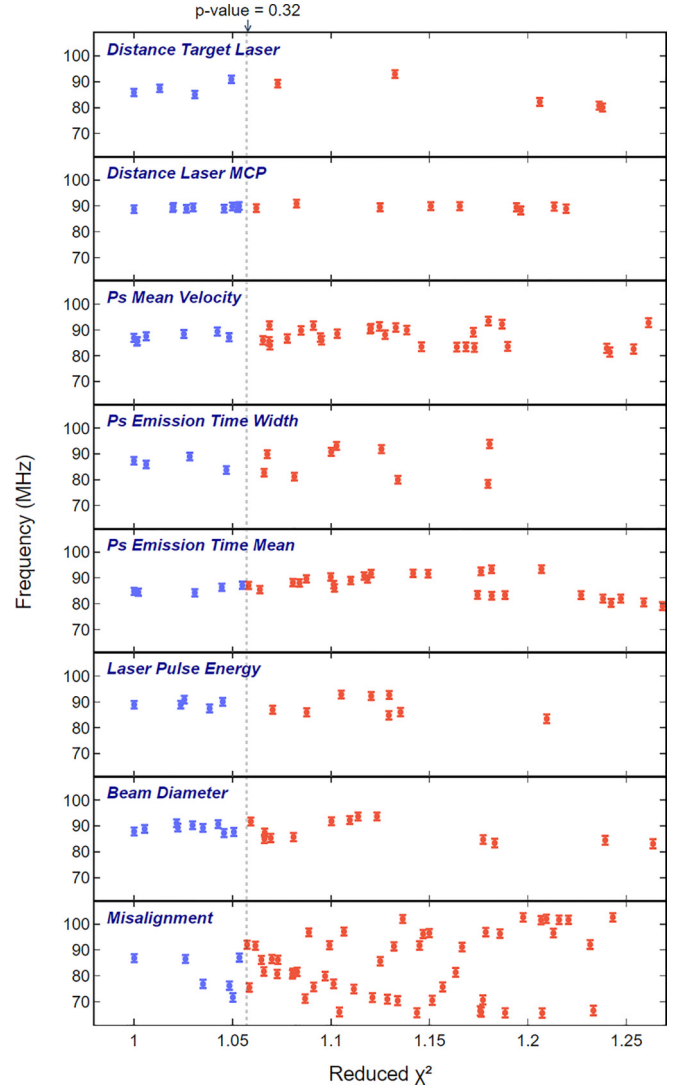


FIG. 15. Plot of reduced χ^2 values for varying individual simulation parameters of run 1. The cutoffs for a p value of 0.32 are shown as dotted lines. Fits below correspond to being within a 68% confidence interval and are taken into account for the estimation of the magnitude of the parameters' influence on the systematic error.

fitting procedure of the simulation output and will therefore be overestimated, especially for smaller contributions. However, these results allow us to compare the relative impact of the parameter uncertainties on the systematic error.

The most significant contribution to the systematic error stems from the residual first-order Doppler shift, which is directly proportional to the misalignment of the incoming and retroreflected beam. Since it also scales linearly with positronium velocity, it is also partly responsible for the contribution from the timing and velocity profile of positronium emission.

Due to the short pulse length (relative to the transit time), the excitation laser preferentially probes a subset of velocities given by its spatial and temporal properties. This results in the second-order Doppler shift contributing to the systematic error present in those parameters, as well as in parameters related to the emission profile. To a lesser degree, the ac Stark shift similarly leads to systematic errors in parameters

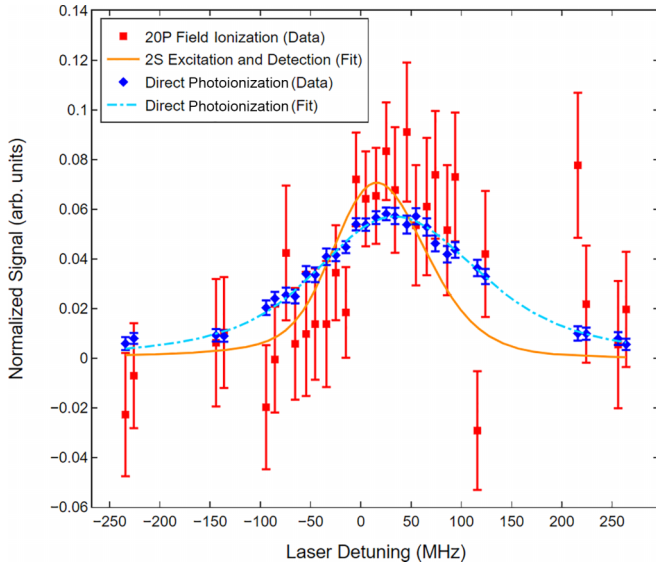


FIG. 16. Positronium direct photoionization (blue diamonds) and $2S$ excitation measured via field ionization (red squares) as a function of laser detuning for data taken during run 2. The data are sum normalized and the best fits for all simulated parameter sets for run 2 are shown (light blue dash-dotted line for direct photoionization and orange solid line for $2S$ excitation).

related to the spatial and temporal intensity profile seen by the positronium atoms, mainly due to uncertainties on the precise beam profile and pulse energy.

C. Results of run 2

Figures 16 and 17 show the data set gathered during run 2 after chirp correction and rebinning, in addition to the best

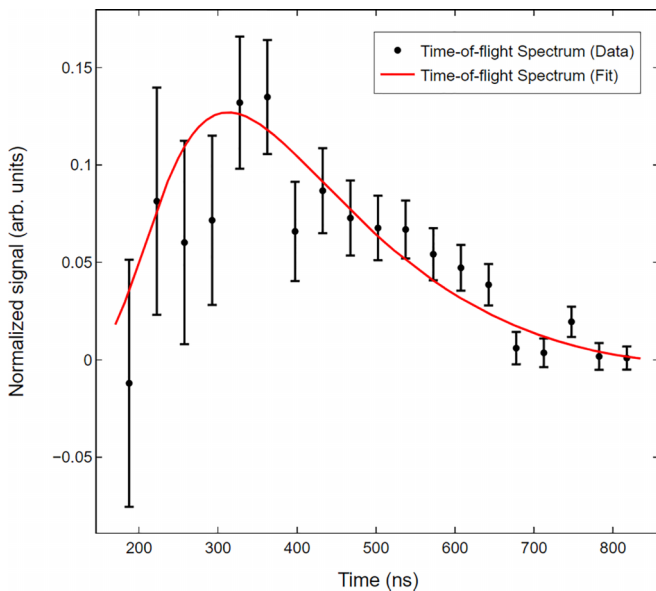


FIG. 17. Normalized time-of-flight spectrum relative to the timing of the $20P$ excitation to field ionization of the Rydberg atoms on the MCP and the corresponding best fit for all simulated parameter sets for run 2.

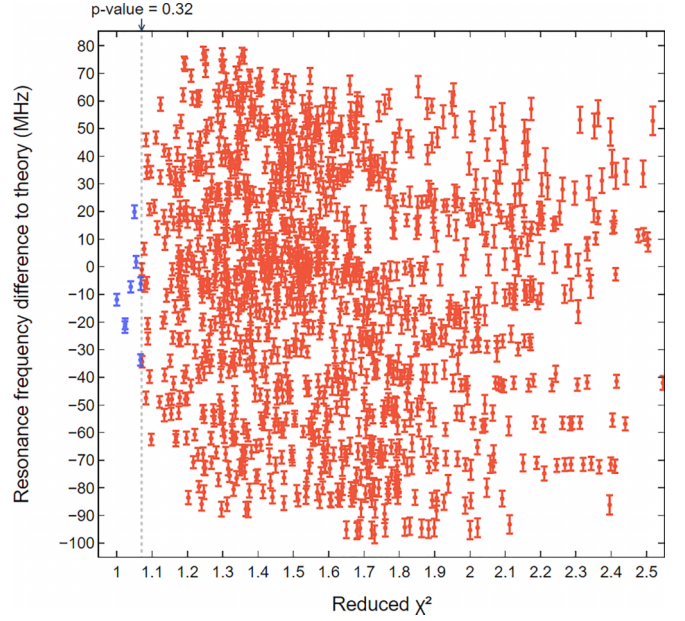


FIG. 18. Plot of reduced χ^2 values for the fits of the data set of run 2 to simulated line shapes and TOF spectra. The cutoff for a p value of 0.32 is shown as a dotted line. Fits below correspond to being within a 68% confidence interval and are taken into account for the estimation of the systematic error.

fit determined by χ^2 minimization analogous to run 1. Unfortunately, the statistical error is significantly larger in this data set. First, the supplied positron rate is approximately a factor 2 smaller than for run 1, due to the decay of the sodium source. Furthermore, the solid angle acceptance of the MCP for field ionization is approximately a factor 2 smaller, in addition to higher losses of the grids due to the shallower angle of incidence. Finally, we found that the quantum efficiency of the detector for photons from positron decay was significantly higher in this arrangement, most likely due to the increased path length at an angle of 45° . This further decreased the signal-to-noise ratio for this data set.

The estimation of the systematic error proceeds analogously to run 1 (see Fig. 18). However, due to larger errors in the data points, the line shape and time-of-flight spectrum cannot be sampled as precisely and do not have the same impact on the quality-of-fit parameter. Therefore, the error estimate is correspondingly higher than in the case of run 1. The final result for the resonance frequency in terms of laser detuning obtained reads $616\,803\,599.2 \text{ MHz} \pm 26.9 \text{ MHz}$, with the respective sources of error given in Table III. This corresponds to a transition frequency of $1\,233\,607\,198.4 \text{ MHz} \pm 53.8 \text{ MHz}$ or equivalently, this result differs from theory by $-23.8 \text{ MHz} \pm 53.8 \text{ MHz} \pm 0.6 \text{ MHz}$.

In summary, the addition of a frequency comb (see Sec. II C) as well as a pulse-by-pulse determination of frequency chirp allowed us to significantly reduce the main systematic errors present in run 1. This resulted in increased precision, even in a situation with a significant reduction in signal-to-noise ratio.

TABLE III. Sources and magnitude of statistical and systematic errors present in the result for run 2.

Magnitude (MHz)	Description
2.1	data fitting error
0.8	simulation fitting error
26.8	systematic fitting error
1.0	chirp correction error
0.2	absolute frequency reference error
26.9	quadrature sum

D. Combined result and summary

Assuming uncorrelated measurements, both results can be combined using the maximum-likelihood estimator for the mean [56] given by

$$\bar{\mu} = \frac{\sum \frac{x_i}{\sigma_i^2}}{\sum \frac{1}{\sigma_i^2}}, \quad (4)$$

where the uncertainty of the combined value is given by

$$\sigma_{\bar{\mu}} = \sqrt{\frac{1}{\sum \frac{1}{\sigma_i^2}}}. \quad (5)$$

The weighted average for the resonance frequency in terms of laser detuning then yields $616\,803\,605.2 \text{ MHz} \pm 24.8 \text{ MHz}$, which corresponds to a transition frequency of $1\,233\,607\,210.5 \text{ MHz} \pm 49.6 \text{ MHz}$ or, equivalently, this result differs from theory by $-11.7 \text{ MHz} \pm 49.6 \text{ MHz} \pm 0.6 \text{ MHz}$. Figure 19 shows the result presented here in the context of the most recent QED theory value and previous experimental values.

IV. CONCLUSION

As outlined in the Introduction, positronium represents an ideal system to probe for new physics beyond the standard model. Spectroscopic precision measurements allows one to stringently test bound-state quantum electrodynamics,

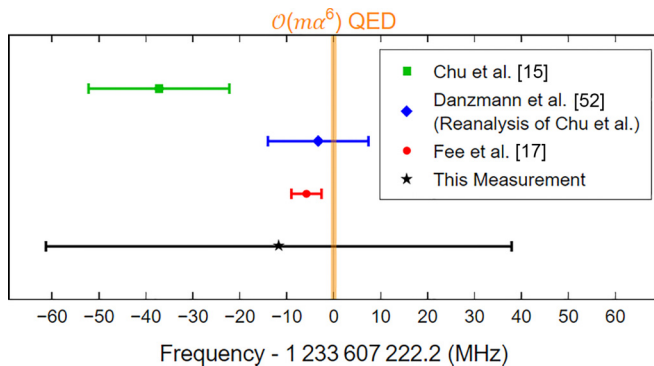


FIG. 19. Summary of $1S$ - $2S$ experimental results and most recent QED theory value and uncertainties. The data set of Chu *et al.* [15] (green square) [15] was reanalyzed by Danzmann *et al.* (blue diamond) [51]. The currently most precise experimental value was measured by Fee *et al.* [17] (red circle). The shaded orange (gray) band corresponds to the theoretical QED prediction at $O(m\alpha^6)$ [57] including an error of 0.6 MHz.

without the complications presented by the finite-size effect of protonic atoms. In particular, the advent of pulsed slow positron beams has led to many advancements in this field [58].

Over the past few decades, measurements in positronium have been a driver for many theoretical developments and vice versa. However, the currently most precise measurement, which is the determination of the $1^3S_1 \rightarrow 2^3S_1$ transition by Fee *et al.* [16] at a level of 2.6 ppb, is still almost an order of magnitude less precise than the most recent calculations. Our results at 40 ppb are not yet competitive with the best determination. However, our technique combined with cw laser excitation [47] will result in an improvement of at least an order of magnitude compared to the current state of the art (see details in Appendix C). This will allow us to check QED calculations up to the current order $m\alpha^6$ and motivate further developments towards a full calculation of order $m\alpha^7$. Moreover, the recent demonstration of positronium laser cooling [59,60] gives great prospects for a new generation of high-precision spectroscopy with this unique atomic system.

ACKNOWLEDGMENTS

We are indebted to A. Antognini, K. Kirch, and F. Merkt for their continuous and essential support of this work. We acknowledge D. Cooke and G. Wichmann for their substantial contributions to the development of the apparatus, which provided the basis for these results. We are grateful to A. Soter, D. Yost, and B. Radics for their very useful comments and discussions. This work was supported by the ERC consolidator Grant No. 818053-Mu-MASS and the Swiss National Science Foundation under Grant No. 166286.

APPENDIX A: RYDBERG STATE SELECTION

The lifetime of excited states with $n > 1$ is limited both by annihilation and radiative decay such that

$$\tau_{n^{(2S+1)}L_J}^a = (\Gamma_{n^{(2S+1)}L_J}^a + \Gamma_{n^{(2S+1)}L_J}^r)^{-1}, \quad (A1)$$

where Γ^a is the decay rate due to annihilation and Γ^r is the radiative decay rate. The annihilation cross section crucially depends on the overlap of the wave functions of the positron and the electron. Therefore, the lifetime of S states ($L = 0$) scales with n^3 [61]. For the same reason, annihilations are highly suppressed for states with $L > 0$. The shortest annihilation lifetime of such a state [62] is

$$\tau_{2^3P_2}^a = 99.57 \times 10^{-6} \text{ s}, \quad (A2)$$

which is still two orders of magnitude higher than

$$\tau_{2^3S_1}^a = 2^3 \times 142.05 \times 10^{-9} \text{ s} = 1.136 \times 10^{-6} \text{ s} \quad (A3)$$

for the equivalent S state. Annihilation lifetimes of P states scale with $n^5/(n^2 - 1)$ [62], which for large n becomes approximately n^3 , analogously to the S states. The radiative decay rate is given by the sum of the Einstein coefficients of spontaneous decay to all lower-lying states [63] such that

$$\begin{aligned} \Gamma_{n^{(2S+1)}L_J}^r &= \sum A_{n'L' \rightarrow nL} \\ &= \sum \frac{16\pi\alpha(E_{n'L' \rightarrow nL})^3}{\hbar^3 c^2} |\langle n'L' | r | nL \rangle|^2, \end{aligned} \quad (A4)$$

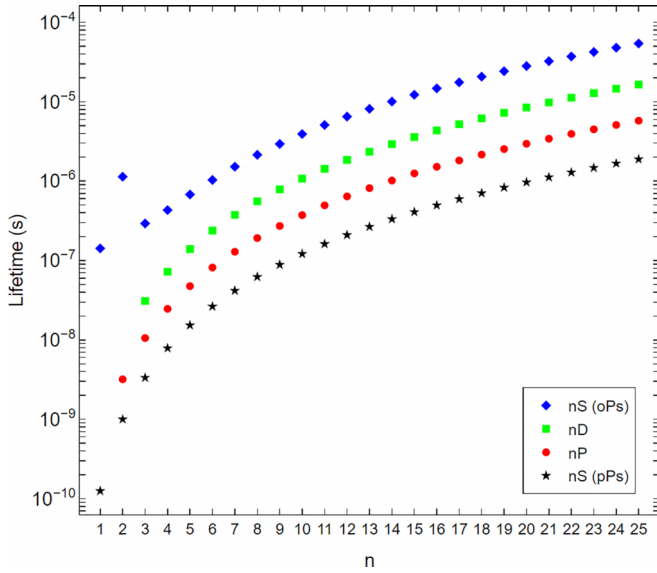


FIG. 20. Lifetime for positronium states with $n < 26$ including annihilation (for $n < 3$) and radiative decay. Numerical values for radiative lifetimes were taken from [64] and scaled by a factor 2 to account for the reduced mass.

where $E_{n'L' \rightarrow nL}$ is the transition energy and $\langle n'L' | r | nL \rangle$ the transition matrix element.

Figure 20 shows the lifetime for S ($L = 0$), P ($L = 1$), and D ($L = 2$) states. For S states with $n > 1$, the lifetime of p -Ps is dominated by annihilation due to it decaying predominantly to two photons, while o -Ps is mainly governed by radiative decay. However, an important exception is o -Ps in the $2S$ state, which is radiatively metastable. In fact, due to the small fine-structure splitting, the decay rate to $2P$ is minuscule and the main contribution is the electric dipole transition directly to $1S$, by the simultaneous emission of two photons [65]. For P and D states the total spin does not play a significant role, since the radiative decay rates are many orders of magnitude larger than the respective annihilation decay rates.

A competing loss mechanism for detecting Rydberg states are collisions on background gas atoms. Assuming the positronium atom is lost upon collision with a background gas atom, the probability for it to reach the MCP is

$$P_{\text{col}}(l) = e^{-l/\lambda}, \quad (\text{A5})$$

where l is the length traveled by positronium and λ is the mean free path²

$$\lambda = \frac{k_B T}{p \sigma_{\text{col}}}, \quad (\text{A6})$$

with k_B the Boltzmann constant, $T \approx 300$ K the temperature, $p \approx 10^{-8}$ mbar the pressure of the background gas, and σ_{col} the collision cross section.

²The usual relative velocity correction of $\sqrt{2}$ in the denominator of the mean free path is not included, since background gas atoms appear essentially stationary for positronium.

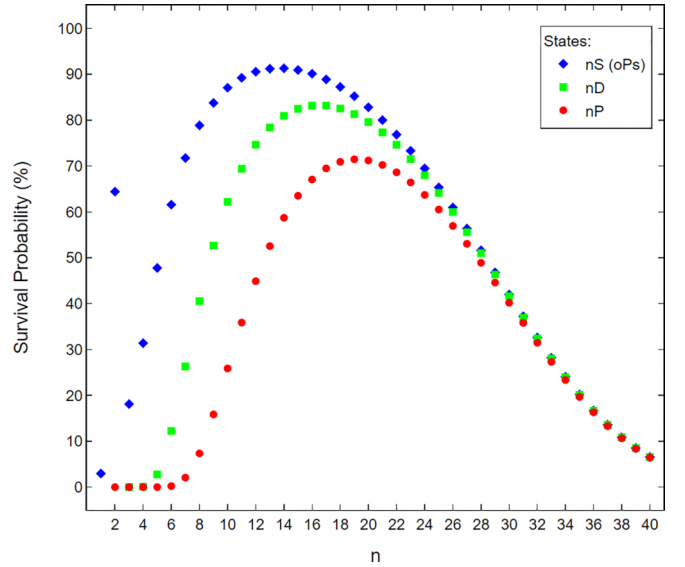


FIG. 21. Survival probability of positronium for different principal quantum numbers in S , P , and D states traveling 5 cm at a velocity of 10^5 m/s in vacuum with a background gas pressure of 10^{-8} mbar.

The cross section σ_{col} can be estimated by assuming elastic collisions of two particle species with different radii such that

$$\sigma_{\text{col}} = \pi(r_{\text{gas}} + r_{\text{Ps}})^2, \quad (\text{A7})$$

where r_{Ps} is the radius of positronium and r_{gas} is the average radius of background gas molecules. The main gas species in the chamber is nitrogen reaching the chamber from the trap, for which the kinetic radius is $r_{\text{N}_2} = 1.8 \times 10^{-10}$ m [66]. For positronium the rms radius

$$r_{\text{rms}} = 2a_0 n \sqrt{\frac{5n^2 - 3L(L+1) + 1}{2}}, \quad (\text{A8})$$

which corresponds to the rms radius of hydrogen [67] scaled with the reduced mass of positronium, is an appropriate approximation. We therefore find

$$\sigma_{\text{col}}^{nP}(n) \approx (3.19 + 2.96n\sqrt{n^2 - 1})^2 \times 10^{-20} \text{ m}^2 \quad (\text{A9})$$

for P states with arbitrary n .

Combining the losses due to collisions with the decay probability yields

$$P^{nP}(l, n) = P_{\text{col}}^{nP}(l, n) e^{-l/v_{\text{Ps}} \tau_{nP}} \quad (\text{A10})$$

for the probability of an atom with velocity v and lifetime τ_{nP} to reach the detector in the same state, after flying a distance of l . Figure 21 shows the survival probability for a pressure of $p = 10^{-8}$ mbar, velocity $v_{\text{Ps}} = 10^5$ m/s, and distance $l = 5$ cm, which correspond to the approximate experimental parameters of both runs. The highest rate is therefore expected for n in the range from 18 to 20.

The final consideration for which specific n to use is the efficiency of field ionization on the detector. The field strengths achieved on the detector assembly are on the order of 2–4 kV/cm. For these field strengths, the probability of ionization has been shown to be close to unity for $n > 19$ [44].

Therefore, the $20P$ state was chosen for the Rydberg detection scheme.

APPENDIX B: MONTE CARLO SIMULATION AND FITTING PROCEDURE

1. Optical Bloch equations

To calculate the probability of exciting ground-state positronium to the $2S$ state, a density matrix approach for a two-level system [68] is used. This is done by solving the set of differential Bloch equations

$$\begin{aligned}\partial_t \rho_{gg}(t) &= -\Omega \text{Im}[\rho_{ge}(t)] - \Gamma_{1S} \rho_{gg}(t), \\ \partial_t \rho_{ge}(t) &= -i\Delta\omega \rho_{ge}(t) + \frac{i\Omega}{2} [\rho_{gg}(t) - \rho_{ee}(t)] \\ &\quad - \frac{\Gamma_i + \Gamma_{1S} + \Gamma_{2S}}{2} \rho_{ge}(t), \\ \partial_t \rho_{ee}(t) &= \Omega \text{Im}[\rho_{ge}(t)] - (\Gamma_i + \Gamma_{2S}) \rho_{ee}(t),\end{aligned}\quad (\text{B1})$$

assuming that all positronium atoms are initially in the ground state. Equations (B1) can be integrated numerically by using a suitable algorithm. To arrive at the simulation results presented in this article (see Appendix B3), an adaptive Runge-Kutta method [69] was employed. Here ρ_{gg} represents the state population of the ground state, while ρ_{ee} is the state population of the excited state. The annihilation decay rates read

$$\Gamma_{1S} = \frac{1}{\tau_{1^3S_1}^a} \approx \frac{1}{142 \text{ ns}} \quad (\text{B2})$$

and

$$\Gamma_{2S} = \frac{1}{\tau_{2^3S_1}^a} \approx \frac{1}{1.14 \mu\text{s}}. \quad (\text{B3})$$

The spontaneous decay of the $2S$ states back into the ground state does not need to be included, since the annihilation rate Γ_{2S} is many orders of magnitude larger. Ionization, however, needs to be included in the model, especially for higher power lasers, since the rate

$$\Gamma_i = 2\pi\beta_i I(t) \quad (\text{B4})$$

is directly proportional to the laser intensity $I(t)$. The ionization coefficient β_i is given by its value for hydrogen, taken from Haas *et al.* [68], after multiplying the proper rescaling factor

$$\begin{aligned}\beta_i &= \frac{1}{Z^4} \left(\frac{m_e}{\mu} \right)^3 \times 1.20208 \times 10^{-4} \text{ Hz m}^2/\text{W} \\ &= 9.61664 \times 10^{-4} \text{ Hz m}^2/\text{W},\end{aligned}$$

where $Z = 1$ is the nuclear charge number and $\mu = \frac{m_e}{2}$ is the reduced mass.

The two-photon Rabi frequency

$$\Omega = 2(2\pi\beta_{ge})I(t) \quad (\text{B5})$$

used in Eq. (B1) is proportional to the laser intensity $I(t)$ and a rescaled two-photon transition matrix element [68]

$$\begin{aligned}\beta_{ge} &= \frac{1}{Z^4} \left(\frac{m_e}{\mu} \right)^3 \times 3.68111 \times 10^{-5} \text{ Hz m}^2/\text{W} \\ &= 2.944888 \times 10^{-4} \text{ Hz m}^2/\text{W}.\end{aligned}$$

Finally, the excitation detuning is given by

$$\Delta\nu = 2\nu_L - \nu_0 \left(1 + \frac{\vec{v} \cdot (\vec{e}_i + \vec{e}_r)}{2c} - \frac{v^2}{2c^2} \right) - \Delta\nu_{ac}^e + \Delta\nu_{ac}^g, \quad (\text{B6})$$

where ν_L is the frequency of the laser used for excitation and ν_0 is the unperturbed transition frequency, which is shifted by the relativistic Doppler effect (shown to second order) and the ac Stark shift. The Doppler shift is given by the positronium velocity $\vec{v}$ and the propagation axes of the incoming ($\vec{e}_i$) and reflected ($\vec{e}_r$) photons. In the case of perfectly overlapping retroreflected laser beam profiles, $\vec{e}_i = -\vec{e}_r$ and the first-order term cancels. Experimentally, this can be realized by employing a resonant Fabry-Pérot cavity. Otherwise, there will be some residual first-order Doppler shift, depending on the angle between the counterpropagating wave fronts on the order of

$$\Delta\nu_{d1} \approx \pm 200 \text{ kHz}/\mu\text{rad}. \quad (\text{B7})$$

The ac Stark shifts are given by

$$\Delta\nu_{ac}^{e(g)} = \beta_{ac}^{e(g)} I(t). \quad (\text{B8})$$

Analogous to the ionization coefficient and the transition matrix element, the ac Stark shift coefficients β_{ac}^e and β_{ac}^g are taken from Haas *et al.* [68], after multiplying the rescaling factor to yield

$$\begin{aligned}\beta_{ac}^e &= \frac{1}{Z^4} \left(\frac{m_e}{\mu} \right)^3 \times 1.39927 \times 10^{-4} \text{ Hz m}^2/\text{W} \\ &= 1.119416 \times 10^{-3} \text{ Hz m}^2/\text{W}\end{aligned}\quad (\text{B9})$$

and

$$\begin{aligned}\beta_{ac}^g &= \frac{1}{Z^4} \left(\frac{m_e}{\mu} \right)^3 \times 2.67827 \times 10^{-5} \text{ Hz m}^2/\text{W} \\ &= 2.142616 \times 10^{-4} \text{ Hz m}^2/\text{W}.\end{aligned}\quad (\text{B10})$$

Due to the relatively high velocities of positronium atoms produced with porous silica targets, the atoms interact with the laser only for a very short period of time and the spatial and temporal profiles of the laser beam need to be taken into account. Assuming sufficiently collimated beams with Gaussian spatial profiles, the intensity can be written as

$$I(y, z) = \frac{2P}{\pi w} e^{-2[(y^2+z^2)/w^2]}, \quad (\text{B11})$$

where y and z are the time-dependent coordinates of the positronium atom, with the propagation axis of the laser assumed to be parallel to the x axis. The waist size w corresponds to the $1/e^2$ radius of the laser beam. While the power P is assumed to be constant for a cw laser, for a pulsed laser a nontrivial temporal profile needs to be taken into account. It is given by a combination of the intrinsic Gaussian time profile of the incoming laser pulse

$$P_i(t) = \frac{E_p}{\sqrt{2\pi}\sigma} e^{-(t-t_{\text{off}})^2/2\sigma^2} \quad (\text{B12})$$

and the reflected laser pulse

$$P_r(t) = \frac{E_p}{\sqrt{2\pi}\sigma} e^{-(t+t_{\text{ref}}-t_{\text{off}})^2/2\sigma^2}, \quad (\text{B13})$$

TABLE IV. Experimental variables and typical values used in Monte Carlo simulation (run 1).

Variable name	Typical value	Description
WaistSize	2 mm	laser beam minimum waist radius
PulseEnergy	6.25 mJ	laser pulse energy
PulseFWHM	6.7 ns	FWHM of temporal pulse shape
LaserTimeOffset	28 ns	mean difference of Ps emission to laser time
MisalignmentY	0 mrad	angle between laser wave fronts (XY plane)
MisalignmentZ	2 mrad	angle between laser wave fronts (XZ plane)
PositroniumTemp	700 K	temperature for velocity distribution
DistanceSourceLaserX	150 mm	X-axis target-mirror distance
DistanceSourceLaserY	0 mm	Y-axis target-laser distance
DistanceSourceLaserZ	3 mm	Z-axis target-laser distance
SigmaBeamX	1.5 mm	X-axis spread of Ps emission area
SigmaBeamY	1.5 mm	Y-axis spread of Ps emission area
SigmaEmission	20 ns	Ps emission time width
DistanceMCPLaserX	0 mm	X-axis laser-MCP distance
DistanceMCPLaserY	0 mm	Y-axis laser-MCP distance
DistanceMCPLaserZ	38 mm	Z-axis laser-MCP distance
TargetAngle	0°	target angle relative to positron beam

where E_p is the pulse energy, t_{off} is the timing offset between positronium emission and the peak intensity of the laser pulse, and t_{ref} is the round-trip time of the laser pulse to the mirror and back.

The combination required is the trivial superposition

$$P(t) = P_i(t) + P_r(t) \quad (\text{B14})$$

when used for the calculation of the ionization and Stark shift coefficients, since these are one-photon processes. However, excitation is strictly a two-photon resonant effect. This is taken into account by using the envelope of the two counterpropagating beams, which results in the expression

$$P(t) = 2\sqrt{P_i(t)P_r(t)}. \quad (\text{B15})$$

2. Description of Monte Carlo simulation

A Monte Carlo simulation was developed to accurately reproduce the line shape for a given set of experimental parameters. Due to the slightly different experimental setup and improved measurement system, runs 1 and 2 use different sets of input parameters, which can be found in Tables IV and V.

The effects of the laser chirp are included by modifying the instantaneous frequency according to the average of the chirp measurements taken during run 2. Figure 22 shows the average shift from the laser detuning during the pulse length and the mean Gaussian time profile of the simulated intensity profile. This chirp profile is corrected by the intensity-weighted average chirp and amounts to

$$\overline{\Delta\nu_c} = 56.6 \text{ MHz} \quad (\text{B16})$$

TABLE V. Experimental variables and typical values used in Monte Carlo simulation (run 2).

Variable name	Typical value	Description
WaistMultiplierY	0.85	correction factor for measured beam size
WaistMultiplierZ	0.85	correction factor for measured beam size
PulseEnergy	6.0 mJ	laser pulse energy
PulseFWHM	5.5 ns	FWHM of temporal pulse shape
LaserTimeOffset	45 ns	mean difference of Ps emission to laser time
MisalignmentY	−1.2 mrad	angle between laser wave fronts (XY plane)
MisalignmentZ	0 mrad	angle between laser wave fronts (XZ plane)
PositroniumTemp	550 K	temperature for velocity distribution
DistanceSourceLaserX	150 mm	X-axis target-mirror distance
DistanceSourceLaserY	0 mm	Y-axis target-laser distance
DistanceSourceLaserZ	3 mm	Z-axis target-laser distance
SigmaBeamX	1.5 mm	X-axis spread of Ps creation area
SigmaBeamY	2.0 mm	Y-axis spread of Ps creation area
SigmaEmission	40 ns	Ps emission time width
DistanceMCPLaserX	0 mm	X-axis laser-MCP distance
DistanceMCPLaserY	−32.1 mm	Y-axis laser-MCP distance
DistanceMCPLaserZ	26.8 mm	Z-axis laser-MCP distance
TargetAngle	45°	target angle relative to positron beam

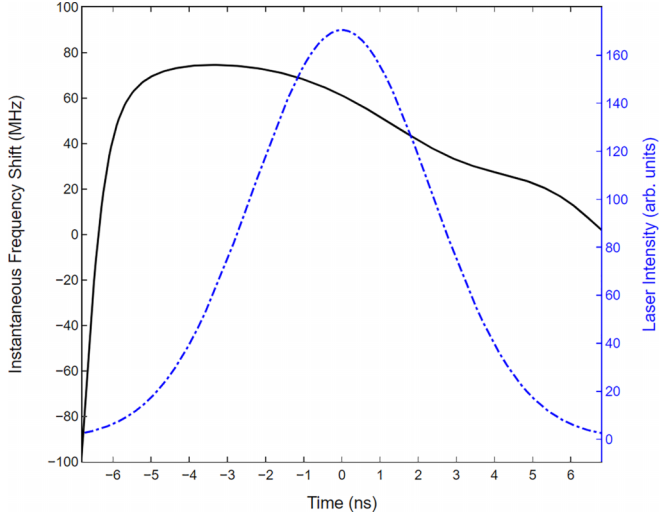


FIG. 22. Average chirp profile (black solid line) as taken during run 2 and simulated laser intensity time profile (blue dash-dotted line) for a time spread of 5.5 ns (FWHM).

for the data shown in Fig. 22. Additionally, for run 2 the simulation is supplied with the spatial laser beam profile taken with a Thorlabs BP209-VIS beam profiler (see Fig. 23). It was found to be a slightly skewed elliptical Gaussian beam with

waist sizes

$$w_{\text{hor}} = (2.91 \pm 0.01) \text{ mm}, \quad (\text{B17})$$

$$w_{\text{ver}} = (2.58 \pm 0.01) \text{ mm}, \quad (\text{B18})$$

where the vertical axis lies parallel and the horizontal axis perpendicular to the target surface. However, due to pointing instability and the averaging nature of the measurement with a rotating slit beam profiler, the true beam diameter is probably slightly lower. This has been taken into account in the simulation by including correction factors for the vertical and horizontal beam sizes (see Table V).

For each simulated atom, the primary positronium vertex is created according to an elliptical Gaussian profile of widths SigmaBeamX and SigmaBeamY. The coordinate system is chosen such that the X axis corresponds to the propagation axis of the laser, while the Z axis lies perpendicular to the target. The implantation and emission time profile is approximated by varying the creation time of the atom using an $\mathcal{N}(0, \text{SigmaEmission}^2)$ distribution.

The initial velocity vector is created with a $\cos\theta$ distribution [70] for the direction and a Maxwell-Boltzmann distribution [71] for the magnitude. It therefore reads

$$v^x_i = |v|_i \sqrt{ST_i} \cos(2\pi P_i), \quad (\text{B19})$$

$$v^y_i = |v|_i \sqrt{ST_i} \sin(2\pi P_i), \quad (\text{B20})$$

$$v^z_i = |v|_i \sqrt{1 - ST_i}, \quad (\text{B21})$$

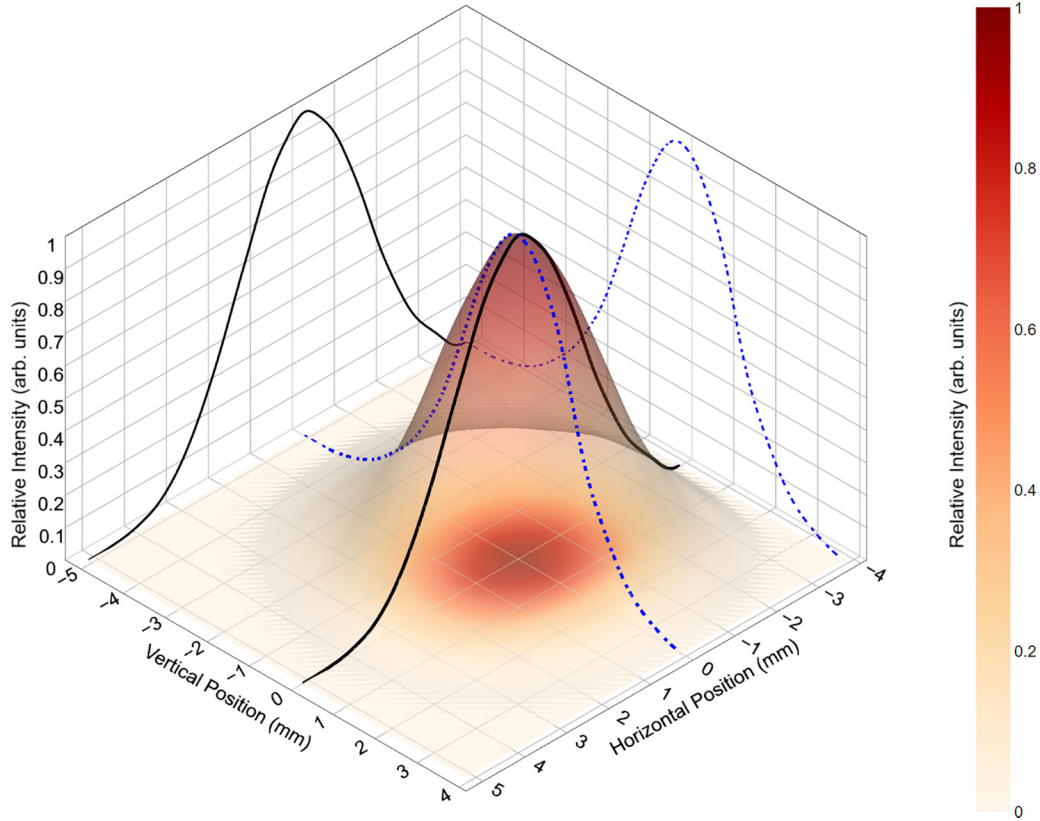


FIG. 23. Three-dimensional surface plot of the spatial laser beam profile taken during run 2, with two-dimensional color space projection on the z plane and two-dimensional contour projections of the beam center for the horizontal (black solid line) and vertical (blue dash-dotted line) planes.

TABLE VI. Output variables of Monte Carlo simulation.

Variable name	Unit	Description
LaserFrequency	MHz	excitation detuning [see Eq. (B6)]
PIProb	%	detection probability for direct PI on the MCP (mean)
Pop1S	%	fraction of ground-state atoms reaching the MCP (mean)
Pop2S	%	fraction of excited-state atoms reaching the MCP (mean)
HitTime	ns	histogram of 2S atoms' arrival time on the MCP
HitTheta	rad	histogram of 2S atoms' angle reaching the MCP
HitPop2S	%	histogram of 2S atoms' fraction reaching the MCP
Velocity	m/s	histogram of 2S atoms' velocity reaching the MCP

where ST_i and P_i are uniformly distributed random variables in (0,1) and

$$|v|_i = \sqrt{\frac{k_B T}{2m_e}} \sqrt{VX_i^2 + VY_i^2 + VZ_i^2}, \quad (\text{B22})$$

where VX_i , VY_i , and VZ_i are random variables with standard normal distribution.

The relativistic Doppler shift (up to second order) for this specific path is then calculated using the velocity vector, MisalignmentY δ_y , and MisalignmentZ δ_z , which represent the misalignment angles with respect to the laser propagation axis along Y and Z. Since $\delta_y \ll 1$ and $\delta_z \ll 1$, it is given simply by

$$\Delta\nu_i^{\text{DS}} = \nu_0 \left(1 + \frac{v_i^y \delta_y + v_i^z \delta_z}{2c} - \frac{|v|_i^2}{2c^2} \right), \quad (\text{B23})$$

where ν_0 is the unperturbed transition frequency.

Since the atoms can only interact with the laser when passing the laser aperture of 6 mm diameter (see Figs. 7 and 8), the state populations in 1S and 2S will only be calculated while they pass this region (discussed below). Otherwise they will be tracked and the populations corrected according to their decay rates. Positronium, which is photoionized, is assumed to be detected regardless of the path, since a small bias voltage on the target transports it towards the MCP. Within reasonable limits for the velocity of the positronium atoms, the pulse energy used for delayed photoionization is sufficiently large such that the ionization rate is close to unity. Likewise, the pulse energy used for the 2S-20P excitation is expected to saturate the transition. Therefore, these effects do not need to be modeled separately in the simulation.

Excited states, which are detected by field ionization, are taken into account only if their path intersects with the active area of the MCP. For these states an additional correction for losses on passing the two grids of

$$\hat{\rho}_i = \rho_i \mathcal{A}^2 (\vec{v}_i \cdot \vec{e}_g)^2 \quad (\text{B24})$$

is taken into account, where ρ_i are the state populations [see Eq. (B1)], $\mathcal{A} = 92\%$ is the open area of the used mesh, and $\vec{e}_g$ is the surface normal vector of the grid.

For each atom, the laser pulse energy and time spread are varied according to a Gaussian distribution, with the standard deviation taken from data. For run 1 the spread was found to be 3.11% for the pulse energy and 4.7% for the time spread, while for run 2 the respective values were measured to be 3.68% and 3.44%.

The evolution of state populations are calculated by numerical integration of the optical Bloch equations [see Eq. (B1)] along the propagation path within the laser aperture. Before each integration step, the laser intensity seen by the atom at that moment [see Eqs. (B14) and (B15)] is calculated according to the spatial laser profile and the current time. Then the intensity-dependent quantities governing the state evolution are determined, which includes the excitation rate (B5), ionization rate (B4), and ac Stark shift (B8). Finally, the excitation detuning (B6) is calculated including the current chirped laser detuning (corrected by the intensity-weighted average chirp) and relativistic Doppler and ac Stark shifts, and the Bloch equations are integrated. This is continued until the atoms leave the region defined by the laser aperture on the target holder.

This process is repeated until the required number of events and laser detuning steps is reached. The simulation saves the results of each individual atom for later analysis. A list of the available output variables can be found in Table VI.

3. Simulation results

In this section we present the results of the simulation in general terms, what the impact is of different effects on the line shape, and the fitting procedures employed. Unless noted otherwise, the data shown correspond to the best fit obtained for the analysis of run 1. Unless otherwise stated, frequency values given in this section usually refer to detuning in the excitation laser, which corresponds to half the value in the transition, since the excitation is a two-photon process.

Since the transition is determined both by direct photoionization in the exciting laser and by delayed ionization, two distinctly different line shapes are measured. Generally, direct photoionization produces a significantly broader line since it effectively limits the probed atoms lifetimes. Furthermore, the profile is generally more skewed, since the process strongly favors higher laser intensities (see also the discussion of the ac Stark shift below).

The natural linewidth of the 1S-2S transition is dominated by the annihilation lifetimes and calculation yields

$$\Delta\omega_n \approx \gamma_{1s} + \gamma_{2s} \approx 2\pi \times 1.3 \text{ MHz}. \quad (\text{B25})$$

However, broadening of the line shape to at least $\Delta\nu \approx 100$ MHz in the transition is evident in all line shapes presented in this work. The main effects responsible for this and other features of the line shape will be explained in the following.

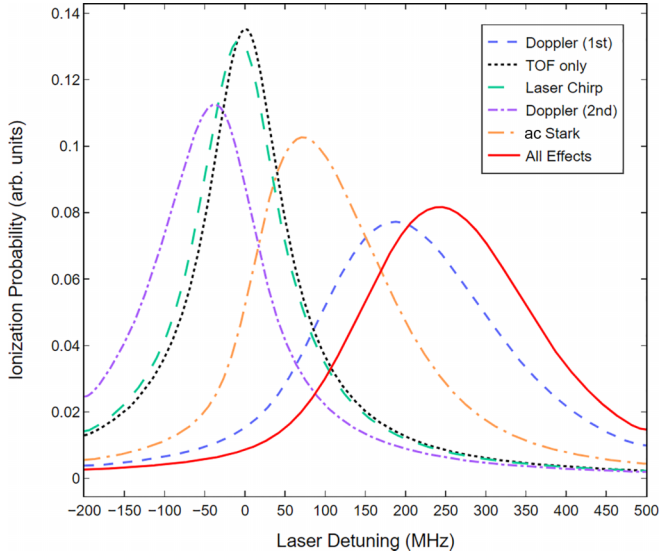


FIG. 24. Impact on the direct photoionization line shape for effects included in the Monte Carlo simulation shown for the parameters found as the best fit to the data acquired during run 1.

A major source of broadening is the limited interaction time of the positronium atoms with the light field, due to either spatial or temporal properties of the laser beam. For Gaussian profiles the time-bandwidth product reads

$$\Delta\nu\Delta t \approx 0.44, \quad (\text{B26})$$

which is a consequence of the uncertainty principle. To give a numerical example, when a stationary atom interacts with a pulsed laser with a Gaussian temporal profile and 5 ns FWHM, this equates to

$$\Delta\nu \approx \frac{0.44}{5 \text{ ns}} = 88 \text{ MHz} \quad (\text{B27})$$

broadening or equivalently to laser bandwidth. If the interaction time is limited by the atom propagating through the laser, this effect is commonly referred to as time-of-flight or transit-time broadening.

Figures 24 and 25 shows the impact of other effects included in the simulation of the photoionization and excitation line shapes. The graphs correspond to the best-fit set of parameters determined for run 1. Run 2 shows analogous behavior unless otherwise noted. Different effects do not simply add up but can have a somewhat complex interaction. Nevertheless, the general effects on the line shape can be identified by studying their impact separately. To this end, the plots show the strictly symmetric line shape, which includes TOF broadening only, in black as a starting point. In addition to the impact of the relevant effects included in the simulation shown separately, the final line shape with all effects combined is plotted.

Laser chirp introduces a slight shift and skew of the line shapes. Notably, it causes a redshift for photoionization and a blueshift for the excitation line, which can be explained by the fact that the chirp is larger for the high-intensity part of the laser pulse (see Fig. 22). Excitation rates generally saturate significantly sooner at higher intensity than photoionization rates, which is why intensity-dependent effects generally affect the line shapes differently.

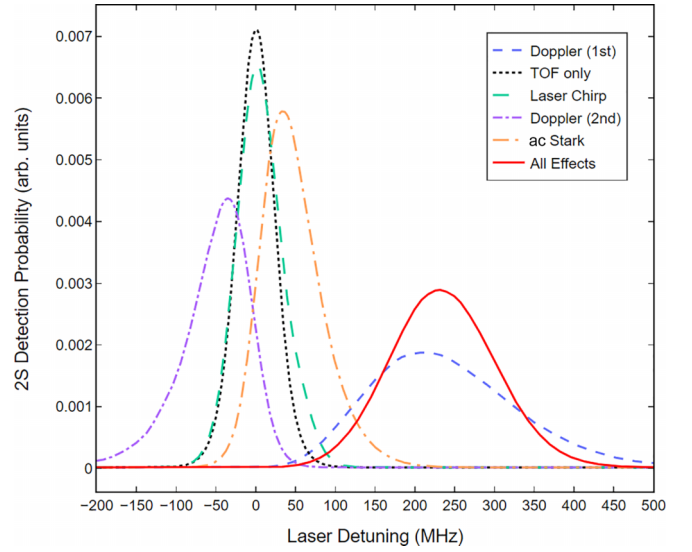


FIG. 25. Impact on the excitation line shape for effects included in the Monte Carlo simulation shown for the parameters found as the best fit to the data acquired during run 1.

The ac Stark effect always blueshifts, broadens, and positively skews the line. Similarly to chirp, the effect is more pronounced in photoionization, since it favors higher laser intensities, which makes it one of the major sources of broadening. The effects from second-order Doppler shift are of similar magnitude but opposite sign. While monoenergetic positronium would lead to a constant shift, the distribution of velocities leads to the broadening and skew of the line.

The impact of the residual first-order Doppler shift is considerably more complex. Generally, misalignment of the laser axis parallel to the target leads to broadening but not shift (see exception below). The reason for this is that the $\cos\theta$ distribution of emission is axially symmetric, so for every blueshifted velocity vector, there is an equally likely redshifted velocity vector. However, this cancellation does not occur for misalignment perpendicular to the target, since all of the possible directions of emitted positronium have at least some velocity component in this direction. This leads to shifts which can have significant magnitude and arbitrary signs, depending on the direction of the misalignment. The resulting shifts for a misalignment of 2 mrad for both signs along both axes can be found in Figs. 26 and 27. The shifts are qualitatively equivalent in both the photoionization and the excitation line shapes. However, the width of broadening in the XY plane is reduced for the excitation line shape, depending on the angular acceptance of atoms undergoing field ionization on the MCP. It is important to note that the symmetry of shifts for misalignments in the XY plane is a consequence not just of the properties of the emission but also of the detection. In fact, in the case of the experimental geometry used for run 2 this symmetry is broken, due to the angle and offset of the MCP relative to the target. This leads to a small but significant shift in addition to the broadening in the excitation line shape, as can be seen in Fig. 28. The reduced broadening due to smaller angular acceptance of the MCP, as described above, is also evident in this plot.

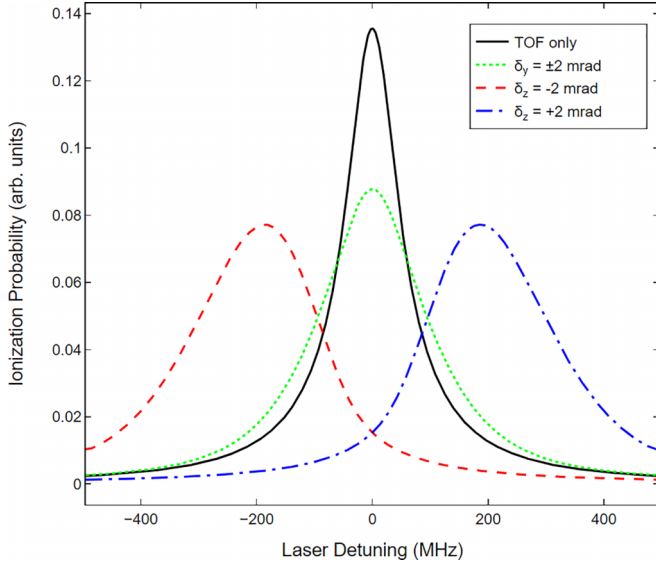


FIG. 26. Impact of the residual first-order Doppler shift for different magnitude and direction of misalignment on the direct photoionization line shape shown for the parameters found as the best fit to the data acquired during run 1.

Ideally, each line would be simulated with very high statistics (greater than 10^5) for a very fine scan of laser detunings (less than 1 MHz) over a wide range (approximately 1 GHz) to directly fit measurement data. However, while this might be feasible for a handful of parameters, it is clearly beyond the scope for several thousand sets of parameters, as used for the data analysis presented in Appendix C. To severely reduce the required amount of computational resources, a fitting procedure was developed to convert simulation results to functional form. This allows for the fitting of data with arbitrary offsets, without further interpolation. While the fits

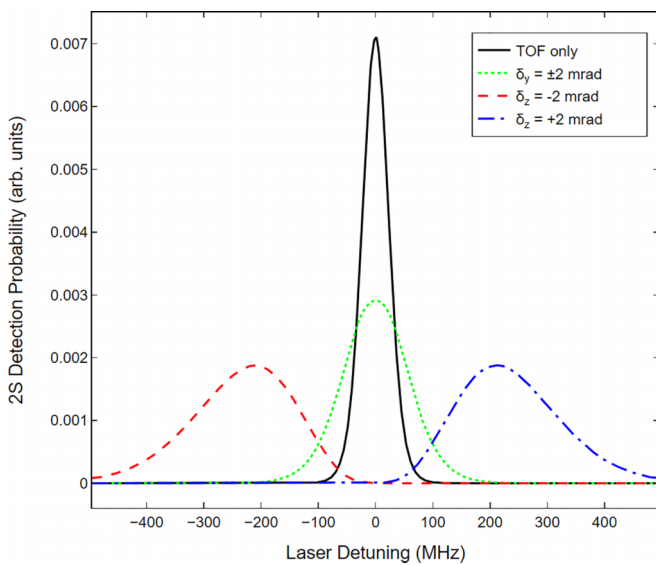


FIG. 27. Impact of the residual first-order Doppler shift for different magnitude and direction of misalignment on the excitation line shape shown for the parameters found as the best fit to the data acquired during run 1.

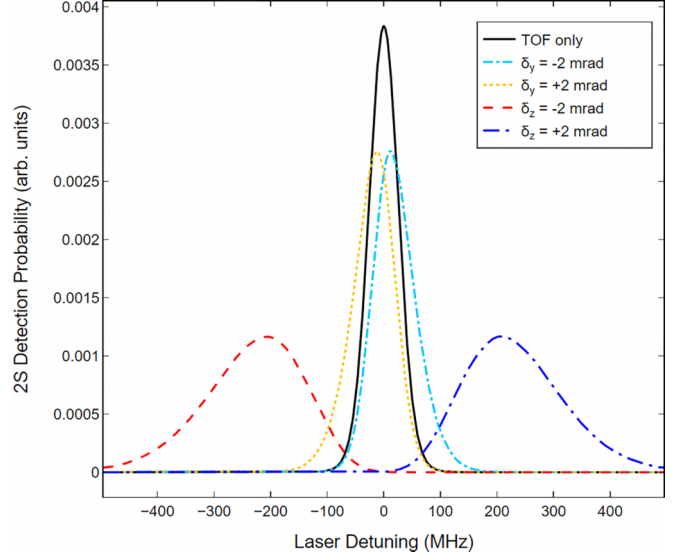


FIG. 28. Impact of the residual first-order Doppler shift for different magnitude and direction of misalignment on the excitation line shape shown for the geometry used during run 2.

give excellent agreement with the simulated line shapes, this introduces an error in the simulated line center, which has to be added to the experimental results.

To accurately model the features of the line shape, an appropriate function is required. While the transition itself would present as a Lorentzian with a width corresponding to the natural linewidth, the effects discussed above change the shape significantly. If the broadening introduced is symmetric and due to a parameter with Gaussian distribution, e.g. for time-of-flight broadening due to a Gaussian spatial profile, the appropriate function to fit would be a Voigt profile, which is given by the convolution of a Lorentzian and a Gaussian profile. However, most effects also introduce skewness to the line shape, which has to be taken into account. Several skewed variations of such profiles exist in the literature; however, most do not capture all relevant features. We found that using an extended approach based on efforts to model infrared absorption peaks [72] yielded excellent results for a wide range of parameters. Based on the Voigt profile

$$V(v, \sigma, \gamma) = \int_{-\infty}^{\infty} G(v', \sigma) L(v - v', \gamma) dv', \quad (\text{B28})$$

where

$$G(v, \sigma) = \frac{e^{-v^2/(2\sigma^2)}}{\sigma\sqrt{2\pi}} \quad (\text{B29})$$

is the Gaussian and

$$L(v, \gamma) = \frac{\gamma}{\pi(\mu^2 + \gamma^2)} \quad (\text{B30})$$

is the Lorentzian distribution, a frequency dependence is included by sigmoidally varying the width parameters such that

$$\sigma(v, \alpha) = \frac{2\sigma_0}{1 + e^{\alpha v}} \quad (\text{B31})$$

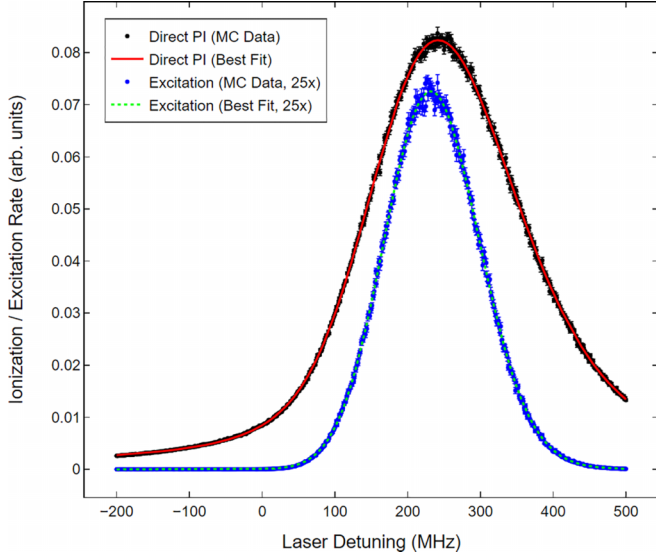


FIG. 29. High-statistics line-shape simulation for direct photoionization (black) and excitation [blue (gray)], including best fits, using doubly skewed Voigt profiles for the most favored parameter set during run 1.

and analogously

$$\gamma(v, \beta) = \frac{2\gamma_0}{1 + e^{\beta v}}, \quad (\text{B32})$$

where α and β are the skewness parameters.

Figure 29 shows the output and corresponding fits of a high-statistics simulation for the best-fit parameter set for run 1. The fits have the form

$$LS(v, v_{\text{loc}}, \sigma_0, \gamma_0, \alpha, \beta, A) = AV((v - v_{\text{loc}}), \sigma(\alpha), \gamma(\beta)), \quad (\text{B33})$$

where v_{loc} is a location parameter that corresponds to the mean value in the limit of no skewness and A is an overall amplitude scaling parameter. The set of parameters of the best fit shown in Fig. 29 of the photoionization line is given by

$$v_{\text{loc}}^{\text{PI}} = 247.98 \pm 0.14 \text{ MHz}, \quad (\text{B34})$$

$$\sigma^{\text{PI}} = 80.0 \pm 0.53 \text{ MHz}, \quad (\text{B35})$$

$$\gamma^{\text{PI}} = 54.78 \pm 0.82 \text{ MHz}, \quad (\text{B36})$$

$$\alpha^{\text{PI}} = -2.564 \times 10^{-3} \pm 5.3 \times 10^{-5}, \quad (\text{B37})$$

$$\beta^{\text{PI}} = -6.2 \times 10^{-5} \pm 1.2 \times 10^{-4}, \quad (\text{B38})$$

$$A^{\text{PI}} = 26.431 \pm 0.066, \quad (\text{B39})$$

while the parameters for the best fit of the excitation line shape read

$$v_{\text{loc}}^{2S} = 232.92 \pm 0.10 \text{ MHz}, \quad (\text{B40})$$

$$\sigma^{2S} = 65.41 \pm 0.22 \text{ MHz}, \quad (\text{B41})$$

$$\gamma^{2S} = 0.07 \pm 0.32 \text{ MHz}, \quad (\text{B42})$$

$$\alpha^{2S} = -6.11 \times 10^{-4} \pm 6.5 \times 10^{-5}, \quad (\text{B43})$$

$$\beta^{2S} = -0.01 \pm 0.10, \quad (\text{B44})$$

$$A^{2S} = 0.47604 \pm 8.7 \times 10^{-4}, \quad (\text{B45})$$

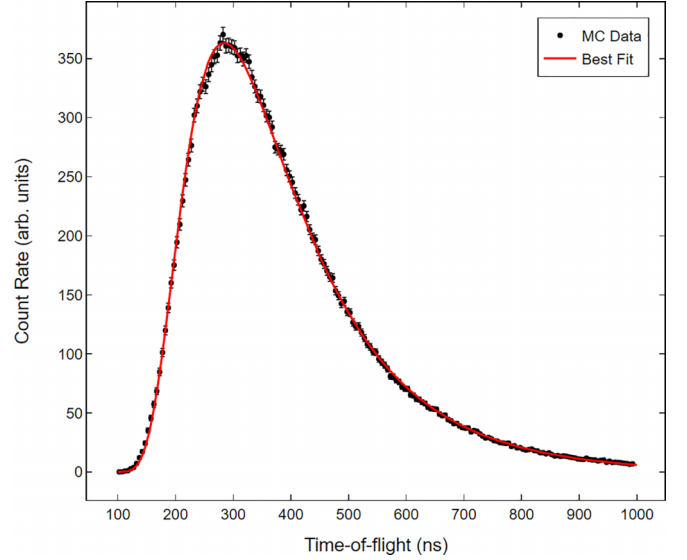


FIG. 30. High-statistics time-of-flight spectrum simulation (black), including best fit (red) using a χ distribution for the most favored parameter set of run 1.

where the error in the location parameter v_{loc} corresponds approximately to the error of the line center (since $\alpha \ll 1$ and $\beta \ll 1$).

In addition to the line shape, the time-of-flight distribution is fitted to allow for direct comparison with measurement. It has been found that a χ distribution

$$\chi(x, k) = \frac{x^{k-1} e^{-x^2/2}}{2^{k/2-1} \Gamma(\frac{k}{2})} \quad (\text{B46})$$

with arbitrary (continuous) degrees of freedom k fits the spectra exceptionally well. Figure 30 shows the TOF spectrum corresponding to the line shapes of Fig. 29 using the function

$$\mathcal{T}(t, l, s, k, B) = B\chi\left(\frac{\frac{1}{t} - l}{s}, k\right), \quad (\text{B47})$$

where the parameter l gives location, s time scaling, and B overall amplitude. The best-fit parameters were found to be

$$l = 5.31 \times 10^{-4} \pm 1.3 \times 10^{-5} \text{ s}^{-1}, \quad (\text{B48})$$

$$s = 1.7231 \times 10^{-3} \pm 4.7 \times 10^{-6} \text{ s}^{-1}, \quad (\text{B49})$$

$$k = 4.00 \pm 0.04, \quad (\text{B50})$$

$$B = 1079.5 \pm 3.0. \quad (\text{B51})$$

Note that the choice of distribution is motivated by the Maxwell-Boltzmann velocity profile, which corresponds to a χ distribution with $k = 3$. However, the parameters do not have a direct physical correspondence since the distribution is a convolution of velocities, excitation, and angular emission probabilities.

Several thousand combinations of parameters within experimental limits were used for the Monte Carlo simulations to cover all possible parameter space for both experimental runs. Each line shape was then fitted according to the description above, which provides a database of functions to fit

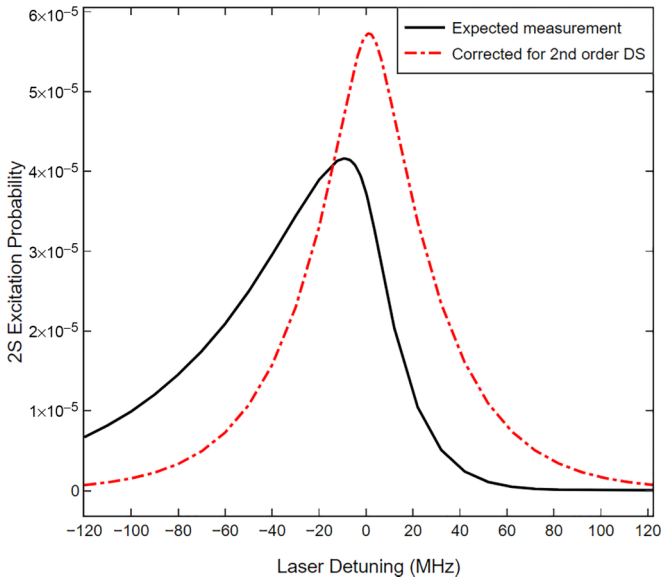


FIG. 31. Predicted line shape for cw excitation at 450 W and 700 K velocity distribution before (black solid line) and after (red dash-dotted line) the subtraction of the second-order Doppler shift.

experimental results, extract the transition frequency, and estimate the systematic errors of the measurement.

APPENDIX C: PROSPECTS FOR A CW MEASUREMENT

To demonstrate how the method presented in this work enables achieving submegahertz uncertainty in a future measurement using a cw laser, we present in Fig. 31 the simulated line shape before and after applying the second-order Doppler shift correction under realistic experimental conditions with a cw source.

The circulating power is 450 W with the laser (310 μm beam waist) positioned 3.5 mm from the positronium formation target. Under these conditions, the ac Stark effect induces a shift of approximately 2 MHz in the atomic transition.

For the runtime estimation, we assume the use of a new standard 1 GBq positron source, a factor 10 times more intense than the source utilized in this study. With a 1 GBq source, about 10^5 positrons per pulse are expected. With our typical 20% positronium conversion efficiency, 50% Rydberg $20P$ excitation probability, and 50% detection efficiency and considering the losses due to atoms decaying from the excitation region to the MCP placed at a distance of 10 cm, we estimate that a 1 MHz determination is possible in 3 days of runtime.

To improve the velocity reconstruction accuracy, a position-sensitive MCP can be employed. Assuming a spatial resolution of 100 μm , a time resolution of $\sigma_t = 10$ ns (accounting for the positron bunch length, positronium diffusion time, and MCP resolution), and a $\sigma_e = 2$ mm initial spatial emission profile, the error in reconstructing the atoms' velocities (around 1%) leads to a systematic uncertainty of approximately 50 kHz estimated using Eq. (B23).

The second largest contribution to the systematic error is the ac Stark shift, which can be controlled by stabilizing the circulating power in the cavity to within 1%, resulting in an uncertainty of 20 kHz. This can be further cross-checked by measuring at three different power levels and extrapolating to zero power.

The frequency chirp observed in pulsed laser systems will not be present in this experiment, since a cw laser source will be used. The uncertainty associated with the frequency comb, referenced to a GPS as in run 2, is at the kilohertz level. Additionally, as no magnetic fields are used to guide positrons and no electric fields are applied, the Zeeman and dc Stark shifts are expected to contribute negligibly (below 1 kHz).

- [1] S. Mohorovičić, Möglichkeit neuer elemente und ihre bedeutung für die astrophysik, *Astron. Nachr.* **253**, 94 (1934).
- [2] A. E. Ruark, Positronium, *Phys. Rev.* **68**, 278 (1945).
- [3] S. G. Karshenboim, Precision study of positronium: Testing bound state QED theory, *Int. J. Mod. Phys. A* **19**, 3879 (2004).
- [4] G. S. Adkins, D. B. Cassidy, and J. Pérez-Ríos, Precision spectroscopy of positronium: Testing bound-state QED theory and the search for physics beyond the standard model, *Phys. Rep.* **975**, 1 (2022).
- [5] U. D. Jentschura and G. S. Adkins, *Quantum Electrodynamics: Atoms, Lasers and Gravity* (World Scientific, Singapore, 2022).
- [6] V. A. Kostelecký and N. Russell, Data tables for Lorentz and CPT violation, *Rev. Mod. Phys.* **83**, 11 (2011).
- [7] V. A. Kostelecký and A. J. Vargas, Lorentz and CPT tests with hydrogen, antihydrogen, and related systems, *Phys. Rev. D* **92**, 056002 (2015).
- [8] P. Moskal *et al.*, Testing CPT symmetry in ortho-positronium decays with positronium annihilation tomography, *Nat. Commun.* **12**, 5658 (2021).
- [9] M. S. Safronova, D. Budker, D. DeMille, D. F. J. Kimball, A. Derevianko, and C. W. Clark, Search for new physics with atoms and molecules, *Rev. Mod. Phys.* **90**, 025008 (2018).
- [10] C. Frugiuele, J. Pérez-Ríos, and C. Peset, Current and future perspectives of positronium and muonium spectroscopy as dark sectors probe, *Phys. Rev. D* **100**, 015010 (2019).
- [11] C. Vigo, L. Gerchow, B. Radics, M. Raaijmakers, A. Rubbia, and P. Crivelli, New bounds from positronium decays on massless mirror dark photons, *Phys. Rev. Lett.* **124**, 101803 (2020).
- [12] A. H. Al-Ramadhan and D. W. Gidley, New precision measurement of the decay rate of singlet positronium, *Phys. Rev. Lett.* **72**, 1632 (1994).
- [13] Y. Kataoka, S. Asai, and T. Kobayashi, First test of $O(\alpha^2)$ correction of the orthopositronium decay rate, *Phys. Lett. B* **671**, 219 (2009).
- [14] S. Chu and A. P. Mills, Jr., Excitation of the positronium $1^3S_1 \rightarrow 2^3S_1$ two-photon transition, *Phys. Rev. Lett.* **48**, 1333 (1982).
- [15] S. Chu, A. P. Mills, Jr., and J. L. Hall, Measurement of the positronium 1^3S_1 – 2^3S_1 interval by Doppler-free two-photon spectroscopy, *Phys. Rev. Lett.* **52**, 1689 (1984).
- [16] M. S. Fee, K. Danzmann, and S. Chu, Optical heterodyne measurement of pulsed lasers: Toward high-precision pulsed spectroscopy, *Phys. Rev. A* **45**, 4911 (1992).

- [17] M. S. Fee, A. P. Mills, Jr., S. Chu, E. D. Shaw, K. Danzmann, R. J. Chichester, and D. M. Zuckerman, Measurement of the positronium 1^3S_1 – 2^3S_1 interval by continuous-wave two-photon excitation, *Phys. Rev. Lett.* **70**, 1397 (1993).
- [18] M. S. Fee, S. Chu, A. P. Mills, Jr., R. J. Chichester, D. M. Zuckerman, E. D. Shaw, and K. Danzmann, Measurement of the positronium 1^3S_1 – 2^3S_1 interval by continuous-wave two-photon excitation, *Phys. Rev. A* **48**, 192 (1993).
- [19] D. B. Cassidy, Experimental progress in positronium laser physics, *Eur. Phys. J. D* **72**, 53 (2018).
- [20] A. Czarnecki, K. Melnikov, and A. Yelkhovsky, Positronium hyperfine splitting: Analytical value at $\mathcal{O}(m\alpha^6)$, *Phys. Rev. Lett.* **82**, 311 (1999).
- [21] M. Baker, P. Marquard, A. A. Penin, J. Piclum, and M. Steinhauser, Hyperfine splitting in positronium to $\mathcal{O}(\alpha^7 m_e)$: One-photon annihilation contribution, *Phys. Rev. Lett.* **112**, 120407 (2014).
- [22] G. S. Adkins and R. N. Fell, Positronium hyperfine splitting at order $m\alpha^7$: Light-by-light scattering in the two-photon-exchange channel, *Phys. Rev. A* **89**, 052518 (2014).
- [23] M. I. Eides and V. A. Shelyuto, Hard nonlogarithmic corrections of order $m\alpha^7$ to hyperfine splitting in positronium, *Phys. Rev. D* **89**, 111301(R) (2014).
- [24] G. S. Adkins, C. Parsons, M. D. Salinger, R. Wang, and R. N. Fell, Positronium energy levels at order $m\alpha^7$: Light-by-light scattering in the two-photon-annihilation channel, *Phys. Rev. A* **90**, 042502 (2014).
- [25] M. I. Eides and V. A. Shelyuto, Hard three-loop corrections to hyperfine splitting in positronium and muonium, *Phys. Rev. D* **92**, 013010 (2015).
- [26] G. S. Adkins, C. Parsons, M. D. Salinger, and R. Wang, Positronium energy levels at order $m\alpha^7$: Vacuum polarization corrections in the two-photon-annihilation channel, *Phys. Lett. B* **747**, 551 (2015).
- [27] G. S. Adkins, M. Kim, C. Parsons, and R. N. Fell, Three-photon-annihilation contributions to positronium energies at order $m\alpha^7$, *Phys. Rev. Lett.* **115**, 233401 (2015).
- [28] G. S. Adkins, L. M. Tran, and R. Wang, Positronium energy levels at order $m\alpha^7$: Product contributions in the two-photon-annihilation channel, *Phys. Rev. A* **93**, 052511 (2016).
- [29] M. I. Eides and V. A. Shelyuto, Hyperfine splitting in muonium and positronium, *Int. J. Mod. Phys. A* **31**, 1645034 (2016).
- [30] M. I. Eides and V. A. Shelyuto, One more hard three-loop correction to parapositronium energy levels, *Phys. Rev. D* **96**, 011301 (2017).
- [31] G. S. Adkins, J. Gomprecht, Y. Li, and E. Shinn, Recoil corrections to the energy levels of hydrogenic atoms, *Phys. Rev. Lett.* **130**, 023004 (2023).
- [32] M. I. Eides and V. A. Shelyuto, Three-loop corrections to the Lamb shift in muonium and positronium, *Phys. Rev. A* **105**, 012803 (2022).
- [33] M. I. Eides and V. A. Shelyuto, Three-loop corrections to Lamb shift in positronium: Electron factor and polarization, *Phys. Lett. B* **832**, 137247 (2022).
- [34] M. I. Eides and V. A. Shelyuto, Two-loop electron factor contribution to Lamb shift in muonium and positronium, *Phys. Lett. B* **844**, 138087 (2023).
- [35] D. A. Cooke, G. Barandun, S. Vergani, B. Brown, A. Rubbia, and P. Crivelli, Positron extraction to an electromagnetic field free region, *J. Phys. B* **49**, 014001 (2016).
- [36] M. W. Heiss, Precision spectroscopy of positronium using a pulsed slow positron beam, Ph.D. thesis, ETH Zurich, 2021.
- [37] L. Liskay, C. Corbel, P. Perez, P. Desgardin, M.-F. Barthe, T. Ohdaira, R. Suzuki, P. Crivelli, U. Gendotti, A. Rubbia, M. Etienne, and A. Walcarius, Positronium reemission yield from mesostructured silica films, *Appl. Phys. Lett.* **92**, 063114 (2008).
- [38] Y. Nagashima, Y. Morinaka, T. Kurihara, Y. Nagai, T. Hyodo, T. Shidara, and K. Nakahara, Origins of positronium emitted from SiO_2 , *Phys. Rev. B* **58**, 12676 (1998).
- [39] S. Mariazzi, A. Salemi, and R. S. Brusa, Positronium cooling into nanopores and nanochannels by phonon scattering, *Phys. Rev. B* **78**, 085428 (2008).
- [40] P. Crivelli, U. Gendotti, A. Rubbia, L. Liskay, P. Perez, and C. Corbel, Measurement of the orthopositronium confinement energy in mesoporous thin films, *Phys. Rev. A* **81**, 052703 (2010).
- [41] D. B. Cassidy, P. Crivelli, T. H. Hisakado, L. Liskay, V. E. Meline, P. Perez, H. W. K. Tom, and A. P. Mills, Positronium cooling in porous silica measured via Doppler spectroscopy, *Phys. Rev. A* **81**, 012715 (2010).
- [42] A. Deller, B. S. Cooper, T. E. Wall, and D. B. Cassidy, Positronium emission from mesoporous silica studied by laser-enhanced time-of-flight spectroscopy, *New J. Phys.* **17**, 043059 (2015).
- [43] Y. Huang and H. Thomann, Critique and correction of the currently accepted solution of the infinite spherical well in quantum mechanics, *Europhys. Lett.* **115**, 60001 (2016).
- [44] A. M. Alonso, L. Gurung, B. A. D. Sukra, S. D. Hogan, and D. B. Cassidy, State-selective electric-field ionization of Rydberg positronium, *Phys. Rev. A* **98**, 053417 (2018).
- [45] S. A. Tuccio, K. H. Drexhage, and G. A. Reynolds, cw laser emission from coumarin dyes in the blue and green, *Opt. Commun.* **7**, 248 (1973).
- [46] R. von Trebra and T. H. Koch, Dabco stabilization of coumarin dye lasers, *Chem. Phys. Lett.* **93**, 315 (1982).
- [47] D. A. Cooke, P. Crivelli, J. Alnis, A. Antognini, B. Brown, S. Friedreich, A. Gabard, T. W. Haensch, K. Kirch, A. Rubbia, and V. Vrankovic, Observation of positronium annihilation in the $2S$ state: Towards a new measurement of the $1S$ - $2S$ transition frequency, *Hyperfine Interact.* **233**, 67 (2015).
- [48] K. Kato, High-efficiency, high-power difference-frequency generation at 2–4 μm in LiNbO_3 , *IEEE J. Quantum Electron.* **16**, 1017 (1980).
- [49] U. Schünemann, H. Engler, R. Grimm, M. Weidemüller, and M. Zielonkowski, Simple scheme for tunable frequency offset locking of two lasers, *Rev. Sci. Instrum.* **70**, 242 (1999).
- [50] C. Wieman and T. W. Hänsch, Precision measurement of the $1S$ Lamb shift and of the $1S$ - $2S$ isotope shift of hydrogen and deuterium, *Phys. Rev. A* **22**, 192 (1980).
- [51] K. Danzmann, M. S. Fee, and S. Chu, Doppler-free laser spectroscopy of positronium and muonium: Reanalysis of the $1S$ - $2S$ measurements, *Phys. Rev. A* **39**, 6072 (1989).
- [52] I. Reinhard, M. Gabrysch, B. F. von Weikersthal, K. Jungmann, and G. zu Putlitz, Measurement and compensation of frequency chirping in pulsed dye laser amplifiers, *Appl. Phys. B* **63**, 467 (1996).
- [53] A. V. Oppenheim, J. R. Buck, and R. W. Schaffer, *Discrete Time Signal Processing* (Prentice-Hall, Englewood Cliffs, 1998).

- [54] F. Gustafsson, Determining the initial states in forward-backward filtering, *IEEE Trans. Signal Process.* **44**, 988 (1996).
- [55] H. Luo, X. Fang, and B. Ertas, Hilbert transform and its engineering applications, *AIAA J.* **47**, 923 (2009).
- [56] P. R. Bevington and D. K. Robinson, *Data Reduction and Error Analysis for the Physical Sciences*, 3rd ed. (McGraw-Hill, New York, 2003).
- [57] K. Pachucki and S. G. Karshenboim, Complete results for positronium energy levels at order $m\alpha^6$, *Phys. Rev. Lett.* **80**, 2101 (1998).
- [58] J. R. Danielson, D. H. E. Dubin, R. G. Greaves, and C. M. Surko, Plasma and trap-based techniques for science with positrons, *Rev. Mod. Phys.* **87**, 247 (2015).
- [59] L. T. Glöggler *et al.*, Positronium laser cooling via the 1^3S-2^3P transition with a broadband laser pulse, *Phys. Rev. Lett.* **132**, 083402 (2024).
- [60] K. Shu *et al.*, Cooling positronium to ultralow velocities with a chirped laser pulse train, *Nature (London)* **633**, 793 (2024).
- [61] A. Ore and J. L. Powell, Three-photon annihilation of an electron-positron pair, *Phys. Rev.* **75**, 1696 (1949).
- [62] A. Sen and Z. K. Silagadze, Two-photon decay of P-wave positronium: a tutorial, *Can. J. Phys.* **97**, 693 (2019).
- [63] T. F. Gallagher, *Electric Fields* (Cambridge University Press, Cambridge, 1994), pp. 70–102.
- [64] O. Jitrik and C. F. Bunge, Transition probabilities for hydrogen-like atoms, *J. Phys. Chem. Ref. Data* **33**, 1059 (2004).
- [65] M. Göppert-Mayer, Über elementarakte mit zwei quantensprüngen, *Ann. Phys. (Leipzig)* **401**, 273 (1931).
- [66] A. F. Ismail, K. C. Khulbe, and T. Matsuura, *Gas Separation Membranes: Polymeric and Inorganic* (Springer International, Cham, 2015), pp. 37–192.
- [67] R. Shankar and R. Shankar, *Principles of Quantum Mechanics* (Springer, New York, 1994), pp. 353–371.
- [68] M. Haas, U. D. Jentschura, C. H. Keitel, N. Kolachevsky, M. Herrmann, P. Fendel, M. Fischer, T. Udem, R. Holzwarth, T. W. Hänsch, M. O. Scully, and G. S. Agarwal, Two-photon excitation dynamics in bound two-body Coulomb systems including ac Stark shift and ionization, *Phys. Rev. A* **73**, 052501 (2006).
- [69] W. H. Press, *Numerical Recipes in C++: The Art of Scientific Computing* (Cambridge University Press, Cambridge, 2005).
- [70] J. Greenwood, The correct and incorrect generation of a cosine distribution of scattered particles for Monte-Carlo modelling of vacuum systems, *Vacuum* **67**, 217 (2002).
- [71] N. M. A. Mohamed, Efficient algorithm for generating Maxwell random variables, *J. Stat. Phys.* **145**, 1653 (2011).
- [72] A. L. Stancik and E. B. Brauns, A simple asymmetric lineshape for fitting infrared absorption spectra, *Vib. Spectrosc.* **47**, 66 (2008).