

Precision measurement of the $2^3S_1 \rightarrow 2^3P_2$ interval in positronium using phase-variation Ramsey spectroscopy

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The $2^3S_1 \rightarrow 2^3P_2$ interval in positronium (Ps) has been measured using a phase-variation separated oscillatory fields method. The experiment was performed in a low-magnetic-field region using a beam of 2^3S_1 atoms generated in a Xe gas cell via a charge exchange reaction. The Ps beam passed through two spatially separated microwave field regions whose relative phase was varied. The resonance frequency was obtained from the frequency dependence of the phase of the resulting interference signal, which was scanned over a range of less than 10 MHz. We obtained a value of $8626.82 \pm 0.48_{\text{stat}} \pm 0.05_{\text{sys}}$ MHz, in good agreement with the theoretical value of 8626.78 ± 0.08 MHz calculated using $O(m_e\alpha^6)$ QED theory.

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I. INTRODUCTION

The theory of quantum electrodynamics (QED) is one of the most accurate and precise theoretical frameworks in existence [1] and has been tested to extreme precision (part per trillion) in electron $g - 2$ measurements [2]. Indeed, at this level of precision, uncertainties in the value of the fine-structure constant α as well as hadronic and electroweak contributions must also be taken into account. Bound-state QED calculations are somewhat more complex as several additional parameters must also be included (see [3] for a detailed discussion), but high-precision calculations for simple atomic systems are still possible and may be tested in experiments (e.g., [4]). In the specific case of positronium (Ps), the electron-positron bound state [5], the sensitivity to physical constants is relaxed, recoil effects are enhanced, hadronic contributions are suppressed [6], and, at the current level of precision available in both theory and experiment, weak force interactions are negligible [7]. Thus, precision spectroscopy of Ps is an ideal way to test bound-state QED theory and may also offer a route to investigate possible effects of particles or forces not currently included in the Standard Model of particle physics [8]. However, such tests are only meaningful if experimental and theoretical precision are comparable. Unfortunately this is not yet true for any energy interval in Ps, with experimental results typically more than an order of magnitude less precise than the corresponding theory [9]. QED corrections of Ps energy levels have been completed up to $O(m_e\alpha^6)$ [10], along with some higher-order terms [11,12], and we also note the corrections given in [13,14]. For $n = 2$ fine-structure intervals the calculations have achieved uncertainties of

80 kHz; the experiment we report here closes the gap on this discrepancy, achieving a precision only approximately six times larger than this, i.e., 490 kHz.

Measurements of Ps $n = 2$ fine-structure intervals have been conducted since the work of Mills and co-workers [15], who discovered that a small amount of Ps can be produced in $n = 2$ excited states following positron bombardment of certain target materials [16]. Subsequent measurements were conducted [17,18], all using essentially the same methodology, that is, Ps atoms were produced inside a waveguide or cavity, and $2^3S_1 \rightarrow 2^3P_J$ transitions were driven (where $J = 0, 1, 2$ is the total angular momentum quantum number) using appropriately tuned microwave radiation (approximately 8.6–18.5 GHz). The detection method was a coincidence between the Lyman- α ($\lambda = 243$ nm) photon emitted from the radiative decay of the 2^3P_J level and an annihilation gamma-ray photon emitted from the subsequent 1^3S_1 and 1^1S_0 annihilation decay [19]. This method was complicated by several factors related to the properties of Ps produced in this way [20–22], namely, (i) the velocity (approximately 100 km s^{-1}) of the Ps atoms led to significant transit time broadening, (ii) the low Ps production efficiencies resulted in poor statistics, and (iii) the equal distribution of $n = 2$ sublevels generated a relatively large Lyman- α background from the fluorescence decay of $2P_J$ states unrelated to the microwave-induced signal.

More recent experimental investigations of the Ps fine-structure intervals [23,24] have used a different methodology; instead of relying on production of excited states from collisions with solid targets, ground-state atoms were optically excited to 2^3S_1 levels using a Stark-mixing technique [25]. The atoms then passed through grids to enter waveguides tuned to drive $2^3S_1 \rightarrow 2^3P_J$ transitions. The signal was obtained via measurements of the time-dependent annihilation radiation signal, obtained using single-shot lifetime spectroscopy [26] and fast gamma-ray detectors [27]. This method was able to achieve sub MHz precision, but also revealed some problems related to systematic shifts and line-

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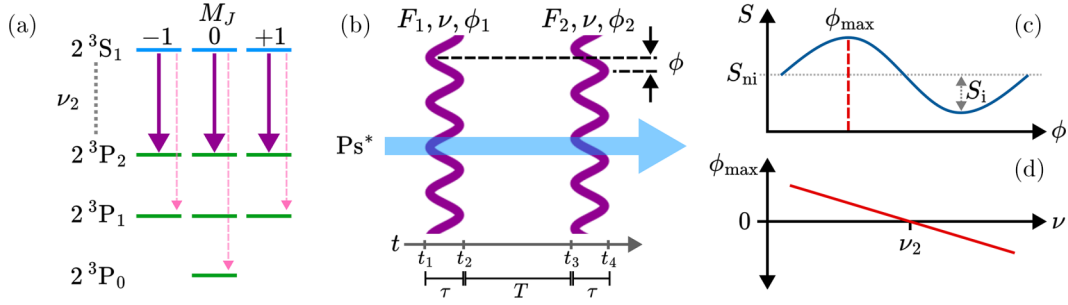


FIG. 1. Phase-variation separated oscillatory field method applied to $n = 2$ positronium fine-structure intervals. (a) Diagram of the relevant magnetic sublevels M_J of the ν_2 transition (thick arrows) and off-resonant channels (thin dashed arrows). The P states decay rapidly via fluorescence to the ground state (not shown). (b) The Ps^* beam is directed through two spatially separated microwave fields that drive the $2^3S_1 \rightarrow 2^3P_2$ transition while the relative phase ϕ is scanned. (c) Sinusoidal interference pattern in the measured Ps^* signal S_B from which the phase at maximum $\phi_{\max}$ is extracted. (d) Linear dependence of $\phi_{\max}$ on the driving frequency ν , with the resonance frequency ν_R extracted using the condition $\phi_{\max} = 0$.

shape distortions due to frequency-dependent variations of the microwave power and reflections that ultimately limited the overall precision of the extracted resonance frequencies [28].

A significant contributor to these problems stems from the fact that the natural width of $2^3S_1 \rightarrow 2^3P_J$ transitions is 50 MHz, due to the 3.19 ns fluorescence lifetime of the $2P$ levels [29]. In practice, widths of approximately 100 MHz are obtained owing to power or transit time broadening effects. This means that measuring line shapes using standard Rabi spectroscopy requires scanning the microwave frequency over a large range, on the order of 1 GHz, which exacerbates problems arising from microwave power stability. Understanding of the dominant systematics present in these types of measurements has improved over recent years [30,31], and refined measurements are expected. Nevertheless, this approach will ultimately be limited by the requirement to scan over frequency ranges defined by the natural linewidth.

One way to mitigate this problem is to use Ramsey's method of separated oscillatory fields (SOFs) [32,33]. Broadly, SOF methods utilize pulses of radiation to prepare and measure the evolution of atomic superposition states over an intermediate field-free evolution time T . In general, SOF line shapes have the form [34]

$$S \propto A(\Delta, T) \cos(2\pi \Delta T + \phi), \quad (1)$$

where A is a phase-independent amplitude, $\Delta = \nu - \nu_0$ is the detuning from resonance frequency ν_0 , and ϕ is the relative phase between the coherent driving fields. Observed as a function of Δ , the width (proportional to $1/2T$) of the central fringe can be much narrower than the natural linewidth, increasing the precision with which the central frequency can be measured (see, e.g., [35]). This is potentially advantageous for Ps fine-structure measurements, as it means the inherently large frequency ranges required can be reduced. However, in the standard SOF method, an interference signal is obtained as a function of frequency from two line shapes with different relative phase offsets (0 and π) and so is sensitive to both the frequency and phase response of the apparatus. Moreover, even with a narrower central fringe, it remains desirable to obtain line shapes containing multiple fringes, which may still require scanning over frequency ranges that are comparable to the corresponding single-field Rabi measurements.

A variation of the SOF method has been described by Klein *et al.* [36] in which full line shapes are not measured and instead the relative phase between the driving fields is scanned for a small set of discrete frequency detunings close to the resonance frequency. We have recently demonstrated that this phase-variation SOF (PVSOF) technique can be applied to Ps fine-structure measurements [37] in a proof-of-principle determination of the $2^3S_1 \rightarrow 2^3P_2$ interval ν_2 (see Fig. 1). Here we report a more detailed study in which we have reduced the magnetic field and employed a modified waveguide design. We have also performed measurements with microwave propagation in two directions. As we describe below, these changes have made it possible to eliminate or reduce the leading systematic effects present in the previous work: We obtain $\nu_2 = 8626.82 \pm 0.48_{\text{stat}} \pm 0.05_{\text{sys}}$ MHz, in good agreement with QED theory.

II. PVSOF METHOD

Following the notation of [34], the driving fields involved in the PVSOF method, as depicted in Fig. 1(b), can be stated in terms of their amplitude F_i , frequency ν , and phase ϕ_i ,

$$F = \begin{cases} F_1 \cos(2\pi \nu t + \phi_1) & \text{for } t_1 < t < t_2 \\ F_2 \cos(2\pi \nu t + \phi_2) & \text{for } t_3 < t < t_4 \\ 0 & \text{otherwise.} \end{cases} \quad (2)$$

Ideally, the fields are the same except for a relative phase shift $\phi = \phi_2 - \phi_1$. To obtain the desired interference signal that encodes the resonance frequency, ν is fixed and ϕ is scanned between $\pm 1 \pi$ rad while the Ps^* beam intensity is monitored. The resulting ϕ -dependent positronium intensity S can be described by [34]

$$S = S_{\text{ni}}(\nu) + S_i(\nu) \cos[2\pi T(\nu - \nu_0) + \phi], \quad (3)$$

where $S_{\text{ni}}(\nu)$ and $S_i(\nu)$ are frequency-dependent amplitudes of noninterference and interference terms, respectively, and T is the field-free flight time. S is shown schematically in Fig. 1(c): an offset sinusoidal interference pattern with a maximum located at $\phi = \phi_{\max}$. The phase of the interference signal, given by $\phi_{\max}$, is linearly dependent on frequency, resulting in a simple line shape given by a straight line [Fig. 1(d)].

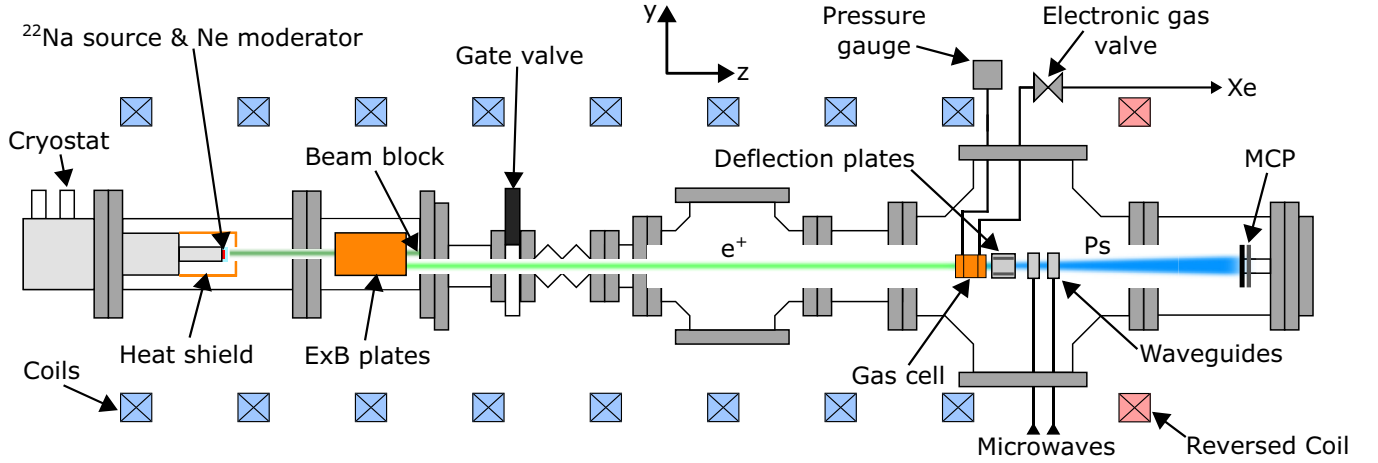


FIG. 2. Schematic representation of the apparatus. A slow monoenergetic positron beam was produced from a ^{22}Na source and a solid neon moderator. The beam energy E_+ was controlled by an applied moderator bias (not shown) and the beam was confined radially by an axial magnetic field generated by a series of coils. The positron beam was deflected off axis by a set of $E \times B$ plates and transported to the Ps production gas cell. The positron and positronium beams were observed directly using a large open-area (90%) microchannel plate (MCP) detector. The green line represents the positron beam, and the blue shaded region represents the diverging positronium beam. The beam emission half angle was 4.3° . The microwave propagation was in the $+x$ and $-x$ directions, i.e., into and out of the page.

The resonance frequency ν_R is determined from the crossing point $\phi_{\max} = 0$, extracted using a simple linear model ($\phi_{\max} = m\nu + c$) via $\nu_R = -c/m$. In practice, $\phi_{\max}$ will be composed of the desired interference phase shift plus additional contributions from various systematic effects.

The main advantages of the PVSOF method over the traditional SOF approach are (i) insensitivity to the frequency response $A(\Delta, T)$ [Eq. (1)] of the experimental setup, (ii) reduced frequency range required to resolve the transition, and (iii) use of a simple line-shape model. More specifically, with current Ps^* beam rates [38] the field-free flight time in a SOF measurement is limited to around a few multiples of the superposition lifetime (approximately 3 ns), but in this case the width of the central fringe of a standard Ramsey measurement would be between 17 and 25 MHz (excluding other broadening mechanisms), offering only a marginal improvement in precision of the resonance frequency.

III. EXPERIMENTAL METHODS

A. Ps^* beam production and detection

The measurements were performed using the apparatus shown schematically in Fig. 2. The methods used have been described in detail elsewhere [37,38]. Briefly, an energy tunable positron beam was generated using a ^{22}Na radioactive source and a solid neon moderator [39]. The positron beam was magnetically guided to a gas cell filled with Xe at a pressure of 0.5 Pa. A beam of Ps atoms was produced via charge exchange $e^+ + \text{Xe} \rightarrow \text{Ps}^* + \text{Xe}^+$, with an energy given by

$$E_{\text{Ps}} = E_+ - E_I + E_B, \quad (4)$$

where E_+ is the mean positron beam energy, E_I is the ionization energy of the Ps production gas (12.13 eV for xenon), and $E_B = 6.8 \text{ eV}/n_{\text{Ps}}^2$ is the binding energy of Ps with principal quantum number n_{Ps} (1.7 eV for $n_{\text{Ps}} = 2$). Both ground-state

Ps and Ps^* atoms are generated using Xe as the target gas [40]. The dependence of the beam energy on the Ps binding energy means that Ps and Ps^* beams will differ in energy by 5.1 eV for a given E_+ . After the gas cell the residual positron beam was deflected using a set of biased parallel plates. The electric field from these plates has a negligible effect on the Ps^* atoms. Using positron beam rates of around 100 ks^{-1} , we generate a Ps^* beam of approximately 2 s^{-1} .

The positron beam was transported into the gas cell using an axial magnetic field of approximately 100 G supplied by a series of coils (see Fig. 2). In the previous PVSOF measurement [37], the last coil was positioned at the entrance aperture of the gas cell and produced a residual magnetic-field gradient along the beam axis and through the waveguides, as depicted in Fig. 3. This caused a shift $\Delta\nu_z$ of the $2^3S_1 \rightarrow 2^3P_2$ transition frequency in each waveguide from the Zeeman effect [19]. The different shifts resulted in a significant contribution to the systematic error on the resonance frequency. For the present study we used an alternative magnetic-field arrangement where an additional coil was positioned downstream and applied with opposing current to null the magnetic field around the waveguides. A comparison of the on-axis magnetic-field profiles for the current and previous setups is shown in Fig. 3. The magnetic fields were measured before and after the experiment using a Hall probe with 1% accuracy. The present configuration resulted in a residual magnetic field (magnitude) of less than 10 G in each waveguide. Consequently, both the Zeeman shift and the discrepancy in shift between the guides were significantly reduced. The total Zeeman shift was determined from the average of the shifts in each waveguide and the systematic uncertainty estimated from the difference, i.e., $\overline{\Delta\nu_z} = -60 \pm 30 \text{ kHz}$, reduced by a factor of 41 relative to the previous configuration.

The positron beam energy E_+ was measured using a retarding field analyzer (RFA) placed at the position of the

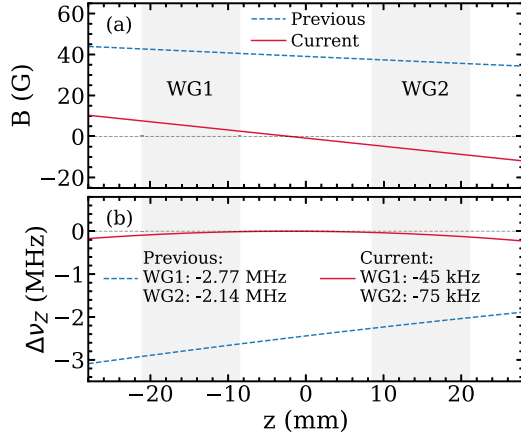


FIG. 3. (a) Estimated magnetic fields in the vicinity of the waveguides for the previous [37] and current experimental arrangements, determined from polynomial fits to Hall probe measurements. (b) Associated Zeeman shifts for the two magnetic-field configurations in (a). The Zeeman shifts averaged over the axial length of the waveguides are listed in the legend for both cases. The shaded regions indicate the interior regions of the two waveguides (WG1 and WG2).

deflection plates (see Fig. 2). The measured value must be adjusted for the different magnetic-field strengths at the position of the RFA and where Ps^* is formed, approximated as the center of the gas cell. This was done by measuring E_+ for different currents applied to the coil ahead of the gas cell (reversed coil switched off) and extrapolating to zero, corresponding to zero magnetic field, to approximate the parallel energy of the positron beam. The results are shown in Fig. 4; we find $E_+(0) = 77.2 \pm 0.1$ eV. Using the measured magnetic-field strength in the center of the gas cell ($B = 67.4 \pm 1$ G), the measured beam energy (77.9 ± 0.1 eV) in the magnetic field used in the PVSOE measurements, and $E_+(0)$, we determine a magnetic-field correction to the positron beam energy of 0.2 eV. Therefore, the mean positron beam energy was $E_+ = 78.1 \pm 0.9$ eV, resulting in a Ps^* beam velocity of $v_{Ps^*} = 3450 \pm 23$ km s $^{-1}$ ($\approx 0.01c$).

The experiment was performed by measuring the Ps^* intensity as the relative phase of the microwave signals was scanned at discrete frequencies. The effects of microwave

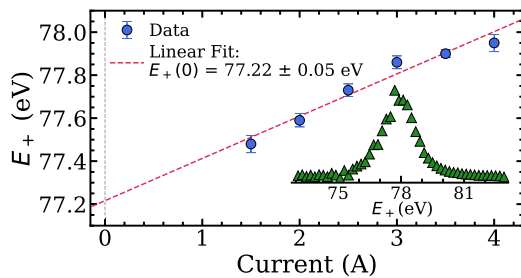


FIG. 4. Positron beam energy E_+ determined with a retarding field analyzer for different currents applied to coil upstream of the gas cell (reversed coil switched off). The energy in zero field [$E_+(0)$] is extrapolated using a linear fit to the data. An example of the measured positron energy distribution for a current of 3 A is shown in the inset.

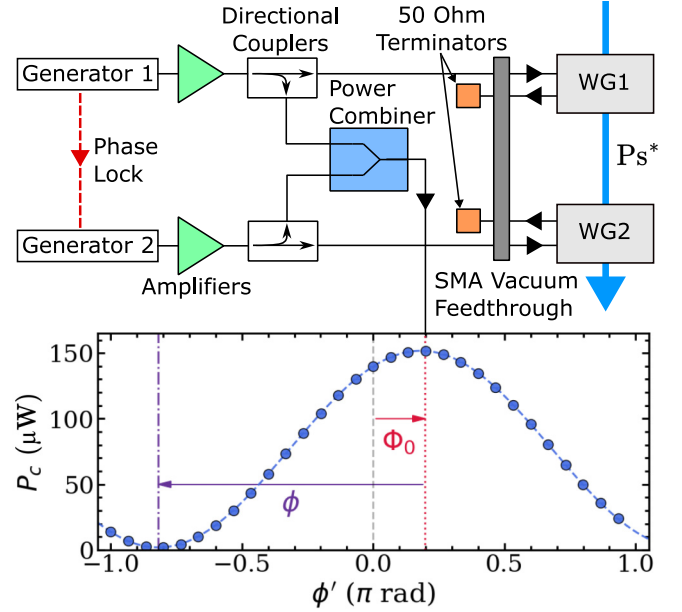


FIG. 5. Schematic of the microwave system showing the phase stabilized generators, amplifiers, directional couplers (−30 dB attenuated outputs), SMA vacuum feedthrough (40 GHz bandwidth), terminations, and waveguides. The outputs of the directional couplers feed into a power combiner and the combined power is monitored by a power sensor (not shown). The data show the combined power P_c as a function of generator 2 phase offset ϕ' , from which the relative phase offset ϕ was set after accounting for the arbitrary phase offset Φ_0 following initialization of the generator settings.

radiation on the Ps^* beam were characterized by the parameter S_B , given by

$$S_B = \frac{S_{\text{off}} - S_{\text{on}}}{S_{\text{off}}}, \quad (5)$$

where S_{on} and S_{off} refer to the count rate measured using the MCP detector with and without microwave radiation applied, respectively. Additionally, the rate was captured with no gas in the cell and used to subtract background and dark counts from these measurements [38].

B. Microwave radiation generation

After leaving the gas cell the Ps^* beam traveled through two WR-112 waveguides (WG1 and WG2), with interior regions separated by 17 mm. Microwave signals in the frequency range 8622–8630 MHz were generated, amplified (approximately 75 mW), and phase controlled [37,41] before being directed to waveguide antennas as indicated in Fig. 5. In the frequency range used the waveguides supported only the TE $_{10}$ mode. The microwave signals were generated using two phase-locked generators, with frequency and relative phase stabilized by 10 MHz and 1 GHz links. However, although the signals were phase locked, changing the generator settings resulted in an arbitrary phase shift of the output signals. To set the phase for each measurement a small fraction of microwave power was extracted from both feeds via directional couplers and summed using a power combiner. The power at

the output of the combiner was recorded as the relative phase of the generator 2 (ϕ') was scanned, providing a sinusoidal response (see Fig. 5), from which the arbitrary phase offset Φ_0 could be identified and subtracted. The relative phase offset ϕ appropriate for the measurement run was then set.

The waveguides used in the work we describe here differ in construction from those used in previous Rabi measurements [23,24]. In those experiments the waveguides consisted of an open-ended box section with central rectangular windows and two SMA antennas placed either end of the guide. This design can be problematic for phase sensitive measurements due to reflected power from the antenna-waveguide, waveguide-vacuum, and antenna-antenna impedance mismatches that can cause frequency-dependent power and phase variations in the waveguides. Additionally, a significant portion of the microwave power is transmitted through the open ends of the waveguides, which not only reduces the power applied to the Ps^* beam but can also reflect from vacuum chamber walls into the waveguide or into the beam path. For phase-sensitive measurements this may lead to dephasing of the microwaves in the waveguides and/or loss of the already small Ps^* signal.

To address these issues we modified the waveguide design to include closed ends and tuning rods that completely eliminated any waveguide-vacuum impedance mismatch and associated beam and power losses and allowed the antenna-waveguide impedance to be matched via tuning, significantly reducing reflected power from the antenna-waveguide and antenna-antenna impedance differences. A cross-sectional schematic representation of the waveguide showing the position of the antennas, tuning rods, and windows is shown in Fig. 6(a). The internal cross section was $12.6 \times 24.5 \text{ mm}^2$, and the length was 145.5 mm. The waveguide design was simulated in CST Studio Suite [42], wherein the height and position of the antennas and tuning rods were optimized for the frequency range of interest (approximately 8626 MHz), and a reflected power less than -30 dB (less than 0.1%) was obtained. An example of the simulated field profile is shown in Fig. 6(b). Displayed in Fig. 6(c) is a comparison of the measured S_{11} parameters (ratio of transmitted and reflected power) for open-ended and tuned waveguides, demonstrating the improved response. The waveguide design will also be suitable for Rabi spectroscopy, provided the line shape does not extend beyond the edges of the broad minimum as this may introduce line-shape distortions due to the reduction of transmitted power.

Despite the phase stabilization and matching scheme, fixed residual phase offsets were present in the setup due to the components and interconnects between the waveguides and power combiner, where the phase was set. These shifts were determined in a similar manner to our previous study [37]; a Rhode and Schwartz ZNL4 vector network analyser (VNA) was connected across the waveguides and sections of the feed lines, and the (complex) S_{12} parameter was measured carefully as a function of frequency. In this case, S_{12} is the ratio of microwave power exiting and entering the VNA via ports 1 and 2, respectively. The analyzer was calibrated manually (Copper Mountain S2611 Tool) prior to each measurement. The phase shift is given by the argument of the measured S_{12} parameter. From the measurements we isolated the relative phase shift ϕ_μ between the power combiner and the wave-

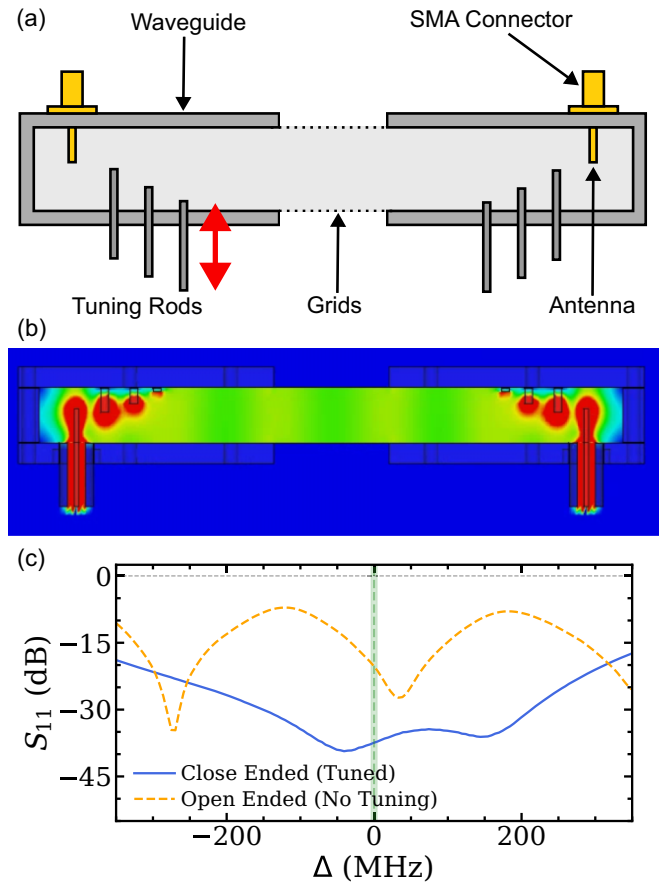


FIG. 6. (a) Schematic of the waveguide design, two of which are used in the experiment, showing three tuning rods, two high-transmission (90%) tungsten grid apertures, SMA connectors, and antennas. (b) Simulated microwave electric-field strength for a frequency of 8626 MHz generated using CST Studio Suite. The color map indicates the time-averaged electric-field strength. (c) Frequency dependence of S_{11} parameters for closed and open-ended waveguides, where the response of the former was adjusted via tuning rods to provide less than -30 dB (less than 0.1%) around ν_2 ($\Delta = 0$). The shaded region indicates the frequency range of the PVSO measurements.

uide SMA antennas. The total measured shifts for $\pm x$ antenna combinations are shown in Fig. 7(a).

An additional frequency-dependent phase shift ϕ_{FF} arises from the fact that during the field-free flight time T , the phase of the traveling-wave microwave signal in WG2 advances. Using the measured ν_{Ps^*} (see Fig. 4), the angular divergence of the beam [38], and the geometry of the experimental arrangement as input, we performed Monte Carlo simulation of 10^7 Ps^* atoms traveling between the waveguides and determined $T = 4.93 \pm 0.02 \text{ ns}$. The number of microwave cycles elapsed during the field-free flight time is $T\nu$, where ν is the driving frequency; therefore, the phase advance of radiation in the second waveguide over the field-free flight time (mapped onto the interval $\pm 1 \pi$ rad) is $\phi_{\text{FF}} = (2T\nu \bmod 1) - 1$ [37]. Figure 7(b) shows the average phase ϕ_{FF} determined from the simulated phase distribution for each of the frequency detunings used in the PVSO measurements.

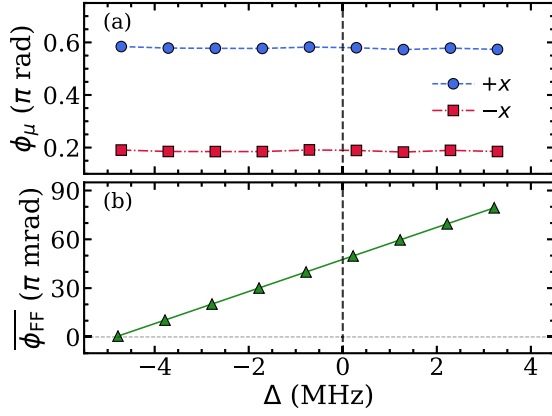


FIG. 7. (a) Measured relative phase shift ϕ_μ between the power combiner and the waveguide SMA antennas for $\pm x$ propagation directions. (b) Field-free phase advance for frequency detunings used in the PVSOF measurements determined via Monte Carlo simulations.

IV. RESULTS

S_B was measured for eight relative phase offsets between $\pm 1 \pi$ rad and for nine frequency detunings spanning from -4.7 to $+3.5$ MHz either side of the ν_2 frequency with microwaves propagating along the $+x$ direction. The measurements were repeated with microwaves propagating from the opposite direction ($-x$), so first-order Doppler shifts could be canceled by averaging the extracted resonance frequencies. Each measurement consisted of recording the MCP hit rate for 10 min with microwaves on and off, along with a short 100 s measurement where no gas was present in the cell, used to subtract noise and dark counts. The sequence was repeated at least 50 times for each relative phase offset, resulting in a total measurement time of around 100 days.

Example measurements of S_B as a function of ϕ for frequencies (8622 and 8629 MHz) close to the expected resonance frequency and for both microwave propagation directions ($\pm x$) are shown in Fig. 8. Similar data were

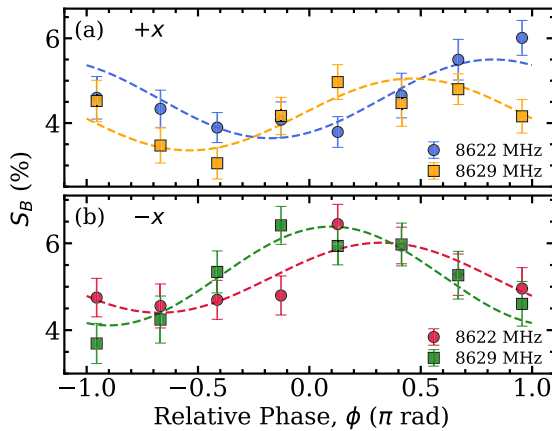


FIG. 8. Measured Ps* signal S_B versus relative phase offset ϕ of the microwave signals for (a) $+x$ and (b) $-x$ microwave propagation directions and frequencies of 8622 and 8629 MHz. The dashed lines are sinusoidal fits to the data and the error bars represent statistical uncertainties.

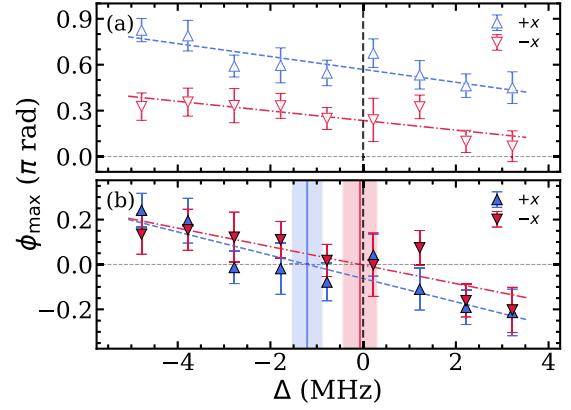


FIG. 9. Modulation phase $\phi_{\max}$ in units of π rad versus frequency detuning Δ with respect to the ν_2 theory value. Data were recorded with microwave propagation along $\pm x$, as indicated, (a) without and (b) with systematic phase shifts subtracted as described in the text. Also shown are linear fits to the datasets. The vertical lines and shaded bands in (b) indicate the zero-crossing points obtained from the fits, yielding $\nu_+ = 8625.57 \pm 0.64$ MHz and $\nu_- = 8626.71 \pm 0.72$ MHz.

obtained for all other frequencies measured in the range 8622–8630 MHz, with similar amplitude (approximately 1%) and vertical offset (approximately 5%). The data exhibit the sinusoidal oscillation characteristic of the PVSOF interference signal. The phase at which S_B is maximal ($\phi_{\max}$) was extracted by fitting a function of the form

$$f(\phi) = a \cos[\pi(\phi - \phi_{\max})] + c, \quad (6)$$

where (a, c) are additional fit parameters corresponding to the modulation amplitude and mean signal. The values of $\phi_{\max}$ obtained in this way are shown in Fig. 9(a) for all frequency detunings Δ . The extracted phase decreases by approximately 0.3π rad over a frequency range of approximately 8 MHz in both cases, but are offset from $\phi_{\max} = 0$ by different amounts due to the systematic phase shifts discussed in Sec. III B. The same results are shown in Fig. 9(b) after applying the ϕ_μ and ϕ_{FF} phase corrections. The data span the $\phi_{\max} = 0$ axis close to $\Delta = 0$. The measured resonance frequencies were extracted using linear fits resulting in $\nu_+ = 8625.57 \pm 0.64$ MHz and $\nu_- = 8626.71 \pm 0.72$ MHz for $+x$ and $-x$ propagation directions, respectively. The average of these two measurements provides a (first-order) Doppler-free resonance frequency $\nu_R = 8626.14 \pm 0.48$ MHz, where the propagated error is statistical only.

V. SYSTEMATIC EFFECTS

In our previous measurement [37] Zeeman and Doppler shifts represented significant systematic errors. As discussed above, we have significantly reduced the Zeeman shift and performed measurements with microwaves propagating along the $\pm x$ directions, eliminating any first-order Doppler shift. The remaining systematic effects related to the present measurement are ac Stark and Bloch-Siegert shifts, caused by the driving fields, the second-order Doppler shift, and quantum interference effects.

A. ac Stark shift

An undesirable effect of the driving fields is the perturbation of the Ps^* energy levels due to virtual transitions to off-resonant levels, i.e., the ac Stark or light shift. To estimate this frequency shift, we need only consider the $2^3P_0(0)$ and $2^3P_1(\pm 1)$ levels [see Fig. 1(a)], as the polarization of the microwave signals in the waveguides allows only $\Delta M_J = 0$ transitions, with $J = 1 \rightarrow 1$, $M_J = 0 \rightarrow 0$ strictly forbidden by electric dipole selection rules. Additionally, while the Ps^* beam is naturally polarized [41] the average population of each of the ± 1 states is equal to $M_J = 0$. The ac Stark shift was estimated via $\Delta \nu_{\text{ac}} \approx \Omega_{\text{off}}^2 / 4\Delta_{\text{off}}$ (see, e.g., [43]), where Ω_{off} and Δ_{off} are the Rabi frequency and detuning of the off-resonant state, respectively. The power input to the waveguides (75 mW) implies the driving field amplitude was approximately $E_0 = 7.2$ V/cm, resulting in Rabi frequencies of 45 and 39 MHz for the $0 \rightarrow 0$ and $1 \rightarrow 1$ components of the ν_2 transition, and 39 and 31 MHz for off-resonant transitions to the 2^3P_1 and 2^3P_0 states. The ac Stark shifts associated with virtual excitation of the off-resonant levels are therefore -26 and -87 kHz. Due to the incoherent nature of this effect, we average the shift over all three states 0 and ± 1 and find $\Delta \nu_{\text{ac}} = -67$ kHz. To account for possible variations in microwave field intensity arising from power variations and coupling of the power into the waveguide, we apply a conservative error of $E_0 = 7.2 \pm 0.5$ V/cm. Along with the variations in the interaction time due to the beam energy spread, this yields an associated shift and error $\Delta \nu_{\text{ac}} = -67 \pm 35$ kHz.

B. Bloch-Siegert shift

The Bloch-Siegert shift [44] is a second-order dispersive shift arising from the off-resonant, counterrotating component of the driving field. This effect is usually ignored (i.e., when using the rotating-wave approximation [45]) but does give rise to a small frequency shift by inducing virtual transitions that modify the system energy levels. The shift is given by $\bar{\Omega}^2 / 4\nu_2$, where $\bar{\Omega}$ is the average on-resonance Rabi frequency. Thus, following the same procedure as for the ac Stark shift, we find an average shift from this effect of $+49$ kHz, to which we assign an error of ± 10 kHz based on the uncertainty in the microwave field amplitude described above.

C. Second-order Doppler shift

Second-order Doppler (SOD) shifts are caused by a time dilation effect and hence cannot be canceled out by performing measurements in different directions. It is often the case that, even in very high precision experiments, these effects are not significant, but because Ps atoms are very light the velocities are high and thus the effects can be rather large [46]. For Ps^* beams generated using the gas cell method, as described here, the effects are much more significant. The SOD shift is given by $\nu\beta^2/2$, where $\beta = v_{\text{Ps}^*}/c$ and is approximately constant (approximately 10 Hz variation) over the small frequency range of the PVSO method. Therefore, using the measured Ps^* beam velocity and averaging over the discrete frequencies, we determine a shift of -571 ± 8 kHz,

TABLE I. Estimated systematic corrections $\Delta \nu$ to the measured frequency and associated uncertainties σ . Note that the shifts and associated corrections have opposite signs.

Effect	$\Delta \nu$ (kHz)	σ (kHz)
Zeeman	+60	30
Second-order Doppler	+571	10
ac Stark	+67	35
Bloch-Seigert	-49	10
QI	+33	20
Total	+682	52

where the quoted uncertainty originates from the spread of Ps^* velocities in the beam.

D. Quantum interference

Whereas virtual excitations of off-resonant states cause the well-known ac Stark shifts, real excitations can shift the line center through multipath quantum interference (QI) effects (see, e.g., [47,48]). An estimate of the QI shift $\Delta \nu_{\text{QI}}$ in the PVSO method can be obtained by considering a small off-resonant perturbation $\mathcal{A}_{\text{off}} \propto \epsilon e^{i(\Delta_{\text{off}}T + \theta)}$ of the general SOF amplitude $\mathcal{A} \propto e^{i\Delta T}$, i.e., $\mathcal{A} = \mathcal{A}_0 + \mathcal{A}_{\text{off}}$. The population of the off-resonant state is $\epsilon \approx \Omega_{\text{off}} / \Delta_{\text{off}} \ll 1$ and the accumulated phase $\theta \approx \Delta_{\text{off}}T$. The QI shift can then be approximated by $C\epsilon \sin(\theta) / 2\pi T$, where, for our case, $C \sim O(0.1)$ accounts for the distribution of field-free flight times and radiative decay of the off-resonant $2P$ level. Contributions from $2^3S_1(0) \rightarrow 2^3P_0(0)$ and $2^3S_1(\pm 1) \rightarrow 2^3P_1(\pm 1)$ transitions were weighted by transition strengths of the respective $M_J = 0$ and ± 1 components of the ν_2 transition to obtain $\Delta \nu_{\text{QI}} \approx -33$ kHz. The uncertainty from the driving field amplitude results in only a few kilohertz variation in $\Delta \nu_{\text{QI}}$. Any additional QI shifts will be reduced relative to the above either by large detunings, e.g., $\Delta_{3S} \sim 10^3 \Delta_{2P}$, or, in the case of interference between off-resonant levels, by multiples of ϵ . To encompass the approximate method of the current estimation and any additional effects, we apply a ± 20 kHz uncertainty to the QI frequency shift, which, while relatively small, is nevertheless likely a conservative estimate. In fact, all of the uncertainties of the systematic effects we describe here are considered to be on the conservative side. While this is not of great significance in the present work, due to the dominant statistical error, in more precise experiments it is expected that detailed evaluation of systematic effects will become critical, including those related to QI effects. Although they are intrinsic to the system being studied, QI shifts can be investigated in varying ways, for example, by varying the field-free time T and looking for some residual signature in the extracted frequency due to the $\sin(\Delta_{\text{off}}T)/T$ dependence.

VI. DISCUSSION AND CONCLUSIONS

A summary of the systematic corrections applied to the measured ν_2 transitions frequency, as discussed above, is shown in Table I. Including these corrections, our final experimental result is $\nu_2^{\text{expt}} = 8626.82 \pm 0.48_{\text{stat}} \pm 0.05_{\text{sys}}$ MHz.

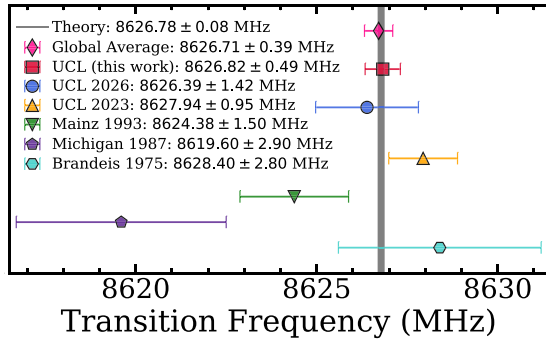


FIG. 10. Comparison of $O(m\alpha^6)$ QED calculation (thick vertical line) with the present and previously measured values for the ν_2 transition frequency from Mills *et al.* [15], Hatamian *et al.* [17], Hagen *et al.* [18], and Cassidy and co-workers [24,37]. Statistical and systematic uncertainties have been combined in quadrature where appropriate. Also shown is the global weighted average of all measured values, including the present value.

This result represents the most precise Ps fine-structure interval measured to date and is in good agreement with the $O(m\alpha^6)$ QED theory result of $\nu_2^{\text{theory}} = 8626.78 \pm 0.08$ [13,14,49]. The extensive theory work leading to this result includes calculations from many authors, going back to [50], as detailed in [9]. The current measurement is shown alongside all previous experimental results and the theoretical value in Fig. 10. Also shown in this figure is the global weighted average of all measurements, which, with an overall uncertainty of 390 kHz, is only marginally more precise than the measurement presented here.

While the current experimental precision obtained here is statistically limited, the systematic uncertainties have been reduced by a factor of 20 over our previous study [37], indicating that further progress can be obtained with some experimental improvements. Despite the reduced magnetic fields used here, the field variation over the spectroscopy region remains a significant systematic uncertainty. Hence, complete elimination of the magnetic guiding field is desirable for future experiments and could be achieved by encasing the spectroscopy region in a mu-metal shield and/or by extracting the positron beam from the magnetic field [51] and focusing it into the gas cell with an electrostatic lens.

Real (QI) and virtual (ac Stark) excitations of off-resonant $2P$ levels induced by the driving field also result in significant contributions to the systematic uncertainty. In future experiments these effects can be both more precisely characterized, via increased knowledge of the driving field amplitude, using, e.g., an atomic sensor, and/or minimized, by increasing the field-free time T relative to the field interaction time τ through larger waveguide separation or smaller microwave field regions. Additionally, hyper-Ramsey sequences [52], where the temporal length, phase, or frequency of the second driving field is modified to account for systematic frequency shifts, could be implemented.

To overcome the statistical limitations, a larger signal-to-noise ratio (SNR) is required. The most straightforward route to achieve this is increasing the positron beam intensity. In the experiments described here, the positron beam was generated from a ^{22}Na source with an activity approximately equal to 200 MBq and after deflection and collimation resulted in an intensity of approximately 100 ks^{-1} at the gas cell. The maximum commercially available activity for this type of radioactive source is approximately 2 GBq, which would result in at least a factor of 10 more Ps^* atoms in the beam. In principle, the PVSO gas cell, waveguide assembly, and detector could be redesigned to fit into a self-contained experimental chamber that could be deployed at an intense positron beam facility, such as the NEPOMUC reactor facility [53], where even higher intensities could be obtained. Alternatively, trap-based positron beams, operated in a pulsed mode [54], could lead to improvements in the SNR since the MCP can be gated, reducing the background level, although this would incur a loss of beam intensity. Increased Ps^* beam intensities may also allow larger waveguide separations to be used, which is advantageous for reducing field-induced systematic effects, as discussed above.

In the longer term, it may be possible to implement a different SOF variation known as frequency-offset SOF (FOSOF) [34]. This technique is related to the PVSO approach; in the PVSO ϕ is scanned in discrete steps, whereas in the FOSOF it varies continuously in time due to an offset in frequency of the driving fields. The FOSOF method has been used for precision measurements of the hydrogen Lamb shift [55] and helium fine-structure intervals [56,57]. It would be challenging to improve the precision with the FOSOF technique applied to our Ps^* beam apparatus without significant advancements. This is because the low beam intensity means the total measurement time could be more than one year due to the need to (i) measure multiple modulation cycles and (ii) repeat the entire Doppler-free measurement with the offset frequencies switched between the waveguides. Therefore, improving the SNR of Ps^* beams, as discussed above, should be the priority for future studies.

If improved experimental methods can be successfully applied and higher precision obtained, it should become possible to perform measurements with precision equal to or higher than the corresponding theory values. Since, at least for the ν_2 transition described here, this only requires a factor of 6 improvement, this goal appears to be quite achievable in the near future.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

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