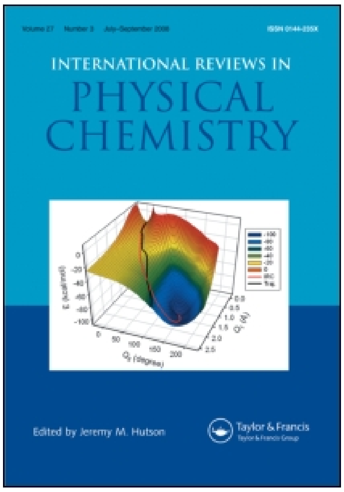

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Two-photon transitions in positronium

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Difficulties caused by hadronic size effects encountered in quantum electrodynamics (QED) calculations of Lamb shifts in the hydrogen atom (H) are missing in positronium (Ps), a purely leptonic system. Precision measurements of the hyperfine structure in Ps thus provide less ambiguous tests of QED. A review of this problem, leading up to present-generation two-photon absorption experiments, is presented. For future investigations of Ps with two-colour lasers, calculations of the 1^3S_1–2^3S_1 and 1^3S_1–3^3S_1 two-photon transition amplitudes and probabilities are carried out. A new feature is the occurrence of a 'destructive interference profile' (DIP) in the $n=3$ pre-resonance region.

1. Background

Positronium is the electron–positron bound state $[e^-e^+]$. A review (Rich 1981) of the experimental aspects of this problem through 1979 provides an early history of Ps research and its relationship to QED. The importance of Ps and muonium (Badertscher *et al.* 1984, Oram *et al.* 1984, Owen 1984) has grown in recent years because of theoretical difficulties encountered in Lamb-shift calculations, attributed to finite-size effects of the proton (Borie 1981, Lundeen and Pipkin 1981, Mohr 1975). Comparison of theory and experiment for H indicates a residual 40 p.p.m. error, which is not easily resolvable and which blocks hope of checking QED beyond first order in the Lamb shift. On the other hand, corrections to second order of the fine-structure splitting in the ground state of Ps have already provided an important test of QED (Lepage 1977, Caswell and Lepage 1978, 1979, Caswell *et al.* 1977).

As in H, the 1S ground state of Ps is composed of a triplet 1^3S_1 and a singlet 1^1S_0. The lifetime of 1^1S_0 Ps is about 125 ps through annihilation primarily into two γ-photons, while 1^3S_1 annihilates primarily into three γs with a lifetime of about 140 ns. These states are split in zero order by $\sim$203·4 GHz, which is about 143 times larger than the hyperfine splitting (hfs) in H (1420·4 MHz). A part of this factor is caused by the e^+/H magnetic moment ratio of 658, reduced by 2^3 because of the increased distance scale. Added to these contributions is a term, $\frac{1}{4}\alpha^4mc^2$ (where mc^2 is the rest-mass energy and α is the fine structure constant) in the 1^3S_1 energy resulting from the zero-order virtual annihilation and re-creation of Ps. The latter term ($\sim$87·6 GHz) accounts for about $\frac{3}{7}$ of the total splitting. On top of the zero-order contributions is a multitude of higher-order radiative corrections, calculated thus far to order α^6mc^2. A chart of these contributions in diagram form is provided in Rich's review (1981).

Two-photon spectroscopy is capable of determining splittings in the excited states of Ps (Fulton and Martin 1954). The principal quantum number spectrum of Ps is equivalent to that of H, except that it is compressed by a factor of two because of the smaller reduced mass. The ionization potential of Ps is 6·8 eV, placing the 'Lyman series' in the near ultraviolet.

The $n=2$ fine structure of Ps is far different from that of H, being similar to that in He with distinct singlet and triplet manifolds. (Compare figures 13 and 14 of Bethe and Salpeter (1957).) Typical splittings between states of different angular momentum J are of the order of 10 GHz. The degeneracy with respect to J, removed in H by the Lamb shift and hfs interaction, is removed by LS coupling in $n>2$ Ps. The $n=3$ fine-structure splittings are smaller than those of $n=2$ by a factor of about $(\frac{2}{3})^3$ (Ferrell 1951). The lifetimes of these states depend on the probabilities of γ-annihilation and ordinary radiation. The latter transitions in Ps are governed by H-atom intensity formulas (Bethe and Salpeter 1957), with appropriate scaling.

The controlling selection rules for γ-annihilation depend on the charge conjugation operator C (Michel 1952, Wolfenstein and Ravenall 1952). In lowest order, the Ps eigenfunctions $\psi(n,l,s)$ as well as the eigenfunctions $\psi(N\gamma)$ are eigenstates of C with eigenvalues $(-1)^{l+s}$ and $(-1)^N$, respectively. To conserve C in a transition, $(n,l,s)\rightarrow(N\gamma)$, $(-1)^{l+s}$ and $(-1)^N$ must be the same, and momentum conservation requires $N>2$. Thus, even J-states annihilate through the two-γ process, odd J-states through the much slower three-γ process. The lifetimes for annihilation also depend strongly on the spatial overlap of e^- and e^+ in the Ps eigenfunction, S-states annihilating $\gtrsim 10^3$ times faster than comparable P-states.

2. Introduction

A first series of experiments on the 1^3S_1–2^3S_1 two-photon absorption using two equal frequencies, plus a sequential third photon for ionization detection, has been successfully performed by Chu *et al.* (1984). These experiments set a high standard for multi-photon experiments on atomic and molecular beams or 'sprays' under ultra-high vacuum conditions. The experiments also nicely illustrate inherent interconnections among diverse fields of physics and technology.

In the experiments of Chu *et al.* (1984), 50–100 Ps atoms in a 10^{-8} s burst were thermalized in Al in an ultra-high vacuum system. Counter-propagating pulses of width $\Delta t \approx 10^{-8}$ s from an amplified Xe/Cl pumped dye-laser tuned to 486 nm were employed for the measurements. A third laser pulse ionized the metastable 2^3S_1 Ps, the e^+ being extracted into a microchannel plate single-particle detector. At peak sensitivity, an average of one count is detected for every five laser pulses.

The advantage of two-colour, two-photon (2C2P) experiments is that it is possible in principle to probe regions of the two-photon absorption near intermediate resonances. Sensitivity in the resonance and 'pre-resonance' regions should be orders-of-magnitude greater than in an ordinary two-photon absorption experiment using two equal frequencies (see Section 5). However, Doppler-free absorption, one of the important aspects of one-colour, two-photon experiments, cannot be obtained in a counter-propagating 2C2P absorption experiment, since there is no way to adjust the experimental wavevectors $\mathbf{k}$ so that the sample-averaged $\mathbf{k}_1\cdot\mathbf{v}$ and $\mathbf{k}_2\cdot\mathbf{v}$ cancel (Levenson 1982). For the direct study of the 1S–nS transitions in Ps, this would have to be accomplished with four-photon spectroscopy, though there are a number of three-photon options where the excited states of Ps can be studied under Doppler-free conditions. Barring these higher-generation experiments, one can find other ways of reducing the Doppler broadening (Demtröder 1982). The main disadvantage of the 2C2P technique is the current unavailability of far-infrared lasers or masers, though it is

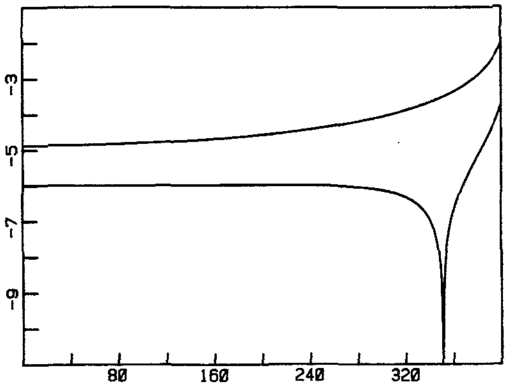

Figure 1. $\mathrm{Log}_{10}\mathscr{F}|S^0_{\mathrm{if}}|^2$ as a function of ν_1 over the range $0{\cdot}6168 \times 10^6$ to $1{\cdot}2168 \times 10^6$ GHz, in units of 1500 GHz. Upper curve, 1^3S_1–2^3S_1; lower curve, 1^3S_1–3^3S_1, showing prominent DIP at $1{\cdot}144 \times 10^6$ GHz. Note that the DIP affects the absorption intensity of 1^3S_1–3^3S_1 over the entire range.

not unreasonable to expect that light sources for these types of experiments will be available in the near future (Demtröder 1982).

In order to act as a guide for future multi-photon transitions in Ps, Quattropani and Bassani (1983) outlined some general results expected for the intensities of 2C2P absorption transitions, 1^3S_1–2^3S_1 and 1^3S_1–3^3S_1, as a function of the frequency of one photon. No specific effects of linewidths on the two-photon resonances were included in these calculations. The inclusion of linewidth effects is a straightforward extension of their work and reveals some unexpected features (see figure 1).

3. Gauge optimization

A recent paper by Tung *et al.* (1984), using results of Kelsey and Macek (1976), presented methods by which two-photon emission probabilities in H-like atoms can be calculated analytically. Specifically, the infinite summations over intermediate states can be expressed as repeated parametric differentiations of hypergeometric functions. Except for transitions with small n, these calculations become impractical, and a useful extension to more complex atoms or molecules would seem hopeless. However, for the calculations to be described here, Tung *et al.* found that little computer time is needed to obtain accurate two-photon decay rates for 2S–1S and 3S–1S emission.

As an alternative to the above analytical method, a *gauge-optimized theory* has been introduced (Brown and Robinson 1984). In this theory, a sum over only a few intermediate bound states is required, and the continuum states can be ignored altogether. An extensive amount of two-photon intensity data can thus be obtained quickly and accurately by these methods. For example, a gauge-optimized calculation (Robinson 1982) of the 1s–2s two-photon transition in H was found to give results having better than 0·5% accuracy over the entire laser frequency range, $\frac{1}{2}(E_f - E_i) \leqslant h\nu_1 \leqslant (E_f - E_i)$.

Though there are an infinite number of gauge representations, *gauge* as used here means the use of either $\mathbf{E} \cdot \mathbf{r}$ or $\mathbf{A} \cdot \mathbf{p}$ perturbation operators (Power 1965) in the matter–radiation interaction. The two operators are equivalent providing exact matter eigenfunctions and exact field eigenfunctions are employed. In particular, the use of the semi-classical matter–radiation hamiltonian (Lamb 1952, Yang 1976) is an approximation that destroys the equality of the two gauge forms.

The **E** • **r** and **A** • **p** hamiltonians are related through a unitary gauge transformation employing the specific generating function of Göppert-Mayer (1931). This 'gauge transformation of the first kind' (Pauli 1941) is carried out completely within the Coulomb gauge, $\nabla \cdot \mathbf{A} = 0$. In the work of Brown and Robinson (1984), the equivalence of the hamiltonians, not only for the pure **E** • **r** and **A** • **p** forms, but also for continuous mixtures of these forms, was proved, starting either with the classical lagrangian density (Power 1965) or with the purely quantum-mechanical hamiltonian in second quantization form (Aharonov and Au 1979).

In these velocity-dependent hamiltonians, the gauge transformation shifts momentum between the field and the matter in the interaction operator. It redefines the generalized coordinate system within the framework of ordinary classical canonical transformations (Goldstein 1953). In the **E** • **r** gauge, for example, the velocity dependence of the interaction lies in the field ($\mathbf{E} = -\partial\mathbf{A}/\partial t$), while in the **A** • **p** gauge it resides in the matter ($\mathbf{v} = d\mathbf{r}/dt$). In fact, the intermediate-gauge-form lagrangian density, from which the quantized hamiltonian is derived, can be written as a linear combination of the two extreme forms,

$$L_\xi = (1-\xi)L_0 + \xi L_1 \tag{1}$$

where L_0 refers to **A** • **p**, L_1 to **E** • **r**, and ξ is any real number $0 < \xi < 1$. Such a trivial representation is not possible for the hamiltonians.

The method of gauge optimization is to determine the best gauge parameter ξ for a given set of approximate eigenstates for the matter. The basic goal is the improvement of the *full* matter-radiation eigenfunction, as opposed to the conventional procedure of optimizing the matter eigenstates alone then using a fixed gauge form, either **E** • **r** or **A** • **p**, for matter-radiation interaction calculations. When the approximate eigenfunctions are chosen so that they *share a common basis with the true eigenfunctions* (Hartree–Fock functions do not qualify), then the exact result seems to lie in the range $0 \leqslant \xi \leqslant 1$. Upper and lower bounds are thereby set. (These last two statements have not been proved rigorously, however.) In simple cases, such as the H_2^+ molecular ion, the optimization procedure can be performed by an extended variational method (Brown and Robinson 1984).

For one-photon absorption in H, the matter eigenfunctions are known exactly and further optimization is not required. However, for two-photon absorptions, the field of the 'first' photon perturbs the electronic states of the atom. A state of the perturbed atom becomes a mixture of the complete set of states of the system, discrete and continuous, requiring infinite sums and integrals to be evaluated. When this set of states is not known, or when it is impractical to carry out the full summation process, gauge optimization can be used to reduce or eliminate the importance of the missing knowledge.

4. Two-photon probabilities

Great care must be exercised when attempting to compute absolute transition probabilities of two-photon absorption or emission, including Raman scattering. An excellent description of this procedure has been set down by Craig and Thirunamachandran (1984). Their results will be adopted here, except that, to deal with intermediate state resonances, damping is included. This formalism has recently been described by Bonin and McIlrath (1984) in their presentation of two-photon, electric-dipole selection rules for atoms.

The starting point is to write down the basic equation for the probability per unit time (*transition rate*) for two-photon absorption from two statistically independent beams for N absorbers,

$$\langle P^{(2)}_{\mathrm{i}\to\mathrm{f}}\rangle(\mathrm{s}^{-1})=\left(\frac{N}{30\hbar^2}\right)\left(\frac{1}{4c\varepsilon_0^2}\right)\bar{\mathscr{I}}_1\bar{I}_2\langle|S_{\mathrm{fi}}|^2\rangle \tag{2}$$

where $\bar{I}_j=\langle n_j\rangle c\hbar\omega_j V^{-1}$ ($\mathrm{J\,m^{-2}\,s^{-1}}$), $\langle n_j\rangle$ being the averaged single mode $(\mathbf{k},\lambda)$ occupation number for wavevector $\mathbf{k}$ and polarization λ in beam j having quantization volume V; $\bar{\mathscr{I}}_j=2\pi\hbar\bar{I}_j\rho(\hbar\omega_j)c^{-1}\approx\bar{I}_j(c\Delta\nu_j)^{-1}$, the radiant energy density of beam j per unit frequency interval ($\mathrm{J\,m^{-3}\,Hz^{-1}}$); $\rho(\hbar\omega_j)$ (J^{-1}) is the density of field states and $\Delta\nu_j$ is the laser linewidth; $\hbar$ is Planck's constant divided by 2π, c is the velocity of light in vacuum, and ε_0 is the permittivity in free space. Multiplying (2) by $(4\pi\varepsilon_0)^2$ transforms the equation to c.g.s. units. Near an intermediate state resonance, dephasing occurs, and the 'sequential' part must be treated as two independent one-photon absorptions.

In (2), the amplitude function,

$$S_{\mathrm{fi}}=\mathrm{e}_j^{(\lambda_2)}(\mathbf{k}_2)\mathrm{e}_k^{(\lambda_1)}(\mathbf{k}_1)\sum_r\left[\frac{\mu_j^{\mathrm{f}r}\mu_k^{r\mathrm{i}}}{E_{r\mathrm{i}}-\hbar\omega_1+i\hbar\gamma_r}+\frac{\mu_k^{\mathrm{f}r}\mu_j^{r\mathrm{i}}}{E_{r\mathrm{i}}-\hbar\omega_2+i\hbar\gamma_r}\right] \tag{3}$$

(where i, f represent initial and final states, respectively, and γ_r is the half-width of an intermediate state r), has been spatially averaged over random dipole orientations, though for spherically symmetric atoms this may be considered merely a formal device; $\langle|S_{\mathrm{fi}}|^2\rangle$ then separates into two distinct tensor contributions, one describing the polarizations (j,k) of the two beams, the other a tensor of the dipole matrix elements μ. The spatial averaging procedure is described in detail in the book by Craig and Thirunamachandran (1984). Their molecular icosahedral symmetry example applies to two-photon transitions in atoms, $|\Delta F|\leqslant 2$, F representing the total angular momentum.

5. Application to positronium

Following Quattropani and Bassani (1983), a constant $e^2a_0'^2\mathscr{R}'^{-1}$ is factored out of S_{fi} to make it dimensionless. The new amplitudes S^0_{fi} are then identical for Ps and H (Bassani *et al.* 1977). The primes here denote the Ps Bohr radius $(2a_0)$ and the Ps Rydberg energy $(\frac{1}{2}\mathscr{R})$, respectively, while e is the electronic charge. For $S_{\mathrm{g}}-S_{\mathrm{g}}$ two-photon transitions in atoms, zz-ploarization can be assumed without losing generality, in which case spatial averaging contributes an additional factor of $\frac{10}{3}$ (i.e. $\frac{1}{9}$ for the overall average) to (2). Since linewidth contributions from 3γ annihilation are negligible, natural radiative widths, half those for H (Bethe and Salpeter 1957), are used in (3).

Gauge optimization for Ps, as for H, requires the addition of a sum-completing term to S_{fi}. This term takes the form of an average energy contribution (Robinson 1982), but, unlike conventional approximations of this kind, gauge invariance is preserved through a special sum rule (Dirac 1947). Discrete intermediate states up to and including $n_{\max}=4$ are employed, and as in H (Robinson 1982) the average energy value for $n_{\max}=4$ is taken to be $+0{\cdot}174\mathscr{R}'$ for $1^3\mathrm{S}_1$–$2^3\mathrm{S}_1$ and $+0{\cdot}083\mathscr{R}'$ for $1^3\mathrm{S}_1$–$3^3\mathrm{S}_1$.

Results are presented in the table and figures 1–3. An interesting feature in the $1^3\mathrm{S}_1$–$3^3\mathrm{S}_1$ transition (figure 1) is a *destructive interference profile* (DIP) (Robinson and Auerbach 1981) just below the 2P resonance region caused by nearly complete cancellation of the sum over states. Without the linewidth term, cancellation would have been complete. This type of feature, *on the long wavelength side* of the lowest

Calculated two-photon amplitudes and probabilities.†

	1^3S_1–2^3S_1		1^3S_1–3^3S_1	
ν_1 (Hz)	Re S^0_{if}	$\mathscr{F}\lvert S^0_{\mathrm{if}}\rvert^2$	Re S^0_{if}	$\mathscr{F}\lvert S^0_{\mathrm{if}}\rvert^2$
6·168 (14)‡	−2·357 (1)	1·370 (−5)	−6·495 (0)	1·041 (−6)
6·468	−2·364	1·379	−6·465	1·031
6·768	−2·386	1·405	−6·442	1·024
7·068	−2·424	1·450	−6·428	1·019
7·311 §	−2·467	1·501	−6·425	1·018
7·668	−2·552	1·606	−6·432	1·021
7·968	−2·646	1·727	−6·450	1·026
8·268	−2·766	1·887	−6·476	1·035
8·568	−2·915	2·096	−6·508	1·045
8·868	−3·101	2·373	−6·540	1·055
9·168	−3·334	2·743	−6·565	1·063
9·468	−3·629	3·248	−6·569	1·065
9·768	−4·006	3·958	−6·530	1·052
1·007 (15)	−4·497	4·990	−6·409	1·013
1·037	−5·158	6·562	−6·137	9·291 (−7)
1·067	−6·078	9·114	−5·584	7·692
1·097	−7·432	1·363 (−4)	−4·485	4·963
1·127 ¶	−9·590	2·269	−2·240	1·238
1·157	−1·350 (2)	4·498	+2·774	1·899
1·187	−2·257	1·257 (−3)	+1·656 (1)	6·761 (−6)
1·217	−6·450	1·026 (−2)	+8·893	1·951 (−4)

† The imaginary parts of S^0_{if} are negligible throughout this frequency range. Numbers in parentheses refer to powers of 10 by which the data point and subsequent entries are to be multiplied. Absorption probabilities are proportional to $\mathscr{F}\lvert S^0_{\mathrm{if}}\rvert^2$.

‡ 1^3S_1–2^3S_1 half-resonance frequency.

§ 1^3S_1–3^3S_1 half-resonance frequency.

¶ 1^3S_1–3^3S_1 DIP frequency = 1·144 × 10^6 GHz.

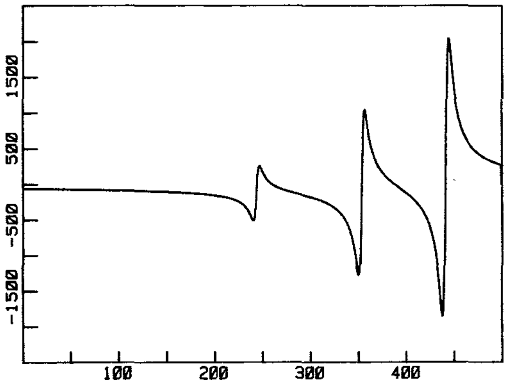

Figure 2. Real part of amplitude function S^0_{if} for 1^3S_1–2^3S_1 in the 2^3P resonance region. The frequency range is 1 233 576·5 to 1 233 601·5 GHz, in units of 0·05 GHz. The ordinate scale has been reduced by a factor of 1 × 10^4. The resonances from left to right correspond to $^3P_0$, $^3P_1$ and $^3P_2$. The amplitude function for 1^3S_1–3^3S_1 in this same region is similar except (1) the sign is reversed, and (2) the absolute magnitudes are about 5·54 × smaller throughout. The 3^3P resonance of this latter transition has the same sign as the 2^3P resonance of 1^3S_1–2^3S_1, but is larger by a factor of about 3·0 to 3·5; and, of course, the energy splittings correspond to the 3^3P fine structure.

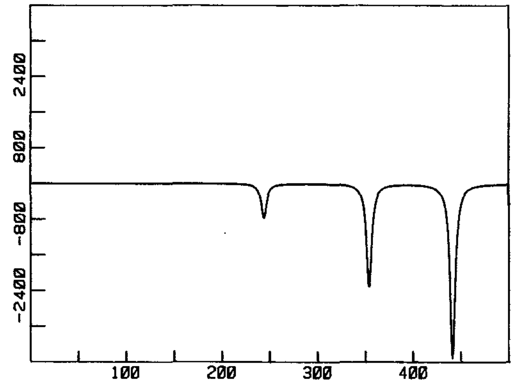

Figure 3. $-\mathrm{Im}\, S^0_{\mathrm{if}}$ for the 1^3S_1–2^3S_1 transition in the 2^3P resonance region. All else is the same as in figure 2. The widths and heights of the resonance peaks of course depend upon experimental linewidths, which may be broader than the natural linewidths used in the figures.

resonance, has been discussed in relation to molecular Raman intensities (Berg and Robinson 1977, Robinson and Auerbach 1981, Robinson and Brown 1983). It should be a common feature in tuned 2C2P absorption, usually as the first intermediate state resonance is approached. This zero was previously reported both by Quattropani and Bassani (1983) and by Tung *et al.* (1984), the latter for two-photon emission decays in hydrogenic atoms. Because of competition with allowed radiative channels, however, it might be difficult to detect DIP spectra except in absorption.

Connection with the experiments of Chu *et al.* (1984) is made by considering the 1^3S_1–2^3S_1 transition for equal laser frequencies ($0{\cdot}6168 \times 10^6$ GHz), where $S^0_{\mathrm{if}}(\nu_1 = \nu_2) = -23{\cdot}569$. The constant factor, $\mathscr{F} = (a_0'^4 e^4)(36\hbar^2 c^2 \varepsilon_0^2 \mathscr{R}'^2)^{-1}$, to be applied to $|S^0_{\mathrm{if}}|^2$ for *zz*-polarization, has a value of $2{\cdot}4669 \times 10^{-8}\,\mathrm{m}^4\,\mathrm{J}^{-2}$. The width Δt of the 'stretched', nearly transform-limited, laser pulse used in the experiments was ~ 40 ns. In addition, the number of absorptions *per pulse*, $\mathscr{N}$, is proportional to the length τ of the Ps-atom burst, ~ 10 ns. Multiplying all the various factors together, $\mathscr{N}(\mathrm{theor}) \approx N\mathscr{F}|S^0_{\mathrm{if}}|^2(\Delta\nu_1)^{-1}\bar{I}_1\bar{I}_2\tau = 32$. Here $N \approx 75$ Ps-atoms per burst; and assuming equal intensity of the pulses, $\bar{I}_1 = \bar{I}_2 \approx \frac{1}{2}P(\Delta t)^{-1}$, where P ($\mathrm{J\,m^{-2}}$ per pulse) corresponds to 20–25 mJ per pulse in a $\sim$6-mm-diameter beam. We have also used the fact that $\Delta\nu\Delta t \approx 4/\pi$ for the Fourier transform limited pulse, assumed of gaussian shape (Levenson 1982). Agreement with experiment (Chu *et al.* 1983), $\mathscr{N}(\mathrm{expt}) \approx 0{\cdot}2$, is satisfactory considering the probable reduced efficiency ($\lesssim 1\%$) of Ps production and detection caused by non-optimum spatial overlap of the Ps-atom bursts and the laser pulses, the lower than unit efficiency of the detection train, and other losses.

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