Spin-Orbit Quenching of Positronium during Atomic Collisions

J. Mitroy and S. A. Novikov

Faculty of SITE, Northern Territory University, Darwin NT 0909, Australia

(Received 25 October 2002; published 8 May 2003)

When positrons are injected into a gas, 75% of the positronium (Ps) is likely to be formed as long-lived ortho-Ps. The main decay mechanisms for the ortho-Ps have been assumed to be natural decay of ortho-Ps and pickoff annihilation of the positron during Ps-atom collisions. A third possibility for annihilation is ortho-Ps $\rightarrow$ para-Ps conversion due to the spin-orbit interaction between the atom and colliding Ps. This extra quenching mechanism may explain a number of phenomena observed in the annihilation spectrum of Kr and Xe, including the very small Ps fraction of 3% seen for Xe.

DOI: 10.1103/PhysRevLett.90.183202 PACS numbers: 34.85.+x, 36.10.Dr, 78.70.Bj

When positrons are injected into an atomic or molecular gas, the result is a complex sequence of inelastic, elastic, and annihilating collisions [1,2]. The positrons slow down with inelastic collisions until the energy is sufficiently low that electronic excitations are no longer possible. At this point, further energy loss to thermal energies occurs through excitation of the molecular degrees of freedom (e.g., vibrational or rotational excitations) and momentum transfer through elastic collisions.

Besides the free positrons, another group of positrons is present in the gas. During the collision processes, it is possible for the positron to capture an electron, forming positronium (Ps). Fast moving Ps can typically be expected to ionize, releasing the positron, but as the energy gets lower, it is possible for the Ps atoms to experience inelastic collisions with the gas, and therefore a portion of the positrons are trapped in the form of low energy Ps [1–3]. The Ps formed in the para(singlet)p-Ps state annihilates via the emission of 2γ rays with an annihilation rate of 7.985×10^9 s^{-1}. The ortho(triplet)o-Ps state decays more slowly via the 3γ process with an annihilation rate of 7.04×10^6 s^{-1}. In an atomic gas, the slow moving Ps is thermalized by momentum transfer collisions.

There are three parameters that are used to summarize the annihilation properties of positrons in gases. They are $Z_{\rm eff}$, ${}_1Z_{\rm eff}$, and the Ps fraction F. The parameter $Z_{\rm eff}$ is proportional to the annihilation cross section during a positron-atom collision. The parameter ${}_1Z_{\rm eff}$ describes pickoff annihilation between the positron and atomic electrons during Ps-atom collisions. Finally, the Ps fraction F denotes how many positrons survive the sequence of events to form Ps. The Ps fraction is usually extracted from the long-time tail of the annihilation spectrum.

This Letter shows that the spin-orbit interaction opens another avenue for the quenching of Ps in positron annihilation experiments. During collisions with a heavy atom such as Xe, the spin-orbit interaction between the atom and the electron and positron in the Ps can result in a o-Ps $\rightarrow$ p-Ps reaction. Since p-Ps has a lifetime about 1000 times shorter than o-Ps, this provides an additional mechanism for the quenching of o-Ps. The possibility of o-Ps $\rightarrow$ p-Ps mixing caused by the spin-orbit interaction has also been invoked to explain anomalies in the magnetic field dependence of the positron lifetime spectrum for mylar [4]. The possibility of spin-orbit quenching in Ps-atom (molecule) collisions has been largely ignored since early estimates deemed the effect to be very small [5,6].

The existence of spin-orbit quenching provides an explanation to one of the oldest conundrums in positron annihilation physics, namely, the question: why is the Ps fraction so small for xenon and to a lesser extent krypton [7–9]? An examination of the tail of the annihilation spectrum for Xe reveals that only 3% of the positrons have survived the thermalization process as o-Ps. This result contradicts the predictions of the Ore model [2] which gives reasonable estimates of the Ps fraction for a number of other gases (Table I) with the exception of Kr. This dearth of long-lived o-Ps in Kr and Xe is accompanied by the appearance of annihilation events close to time zero in the spectrum (usually called the fast component). This fast component occurs before the Ps atoms have thermalized and is thought to be responsible for the small Ps fraction of Kr and Xe [8–10].

Both Kr and Xe are heavy atoms and their spectra are influenced by relativistic effects. The spin-orbit interaction between the target atom and the e^- and e^+ comprising the Ps atom are stronger for Kr and Xe than for Ne and Ar. Therefore, it is possible that spin-orbit quenching could be significant for Xe but of only minor importance for Ne. However, this explanation is viable only if the

TABLE I. The upper and lower estimates of the Ps fraction as given by the Ore model. Also tabulated are the experimental $\langle {}_1Z_{\rm eff}\rangle$ at thermal energies. All data are taken from Ref. [2].

System	Ps fraction Ore model	Ps fraction Expt.	$\langle {}_1Z_{\rm eff}\rangle$ Expt.
He	0.14–0.28	0.23	0.125 ± 0.002
Ne	0.09–0.32	0.26	0.235 ± 0.008
Ar	0.17–0.43	0.33	0.314 ± 0.003
Kr	0.20–0.49	0.11	0.478 ± 0.003
Xe	0.26–0.56	0.03	1.26 ± 0.01

spin-orbit quenching rate has the correct energy dependence. While the fast components in the annihilation spectrum can be attributed to spin-orbit quenching, the existence of a slow decay of Ps in the tail of the annihilation spectrum requires this reaction to be suppressed at thermal energies. It will be shown that the o-Ps $\rightarrow$ p-Ps reaction does not occur for s-wave scattering and should have a very small cross section close to threshold.

The spin-orbit operator to a first approximation is

$$V_{\rm so} = \alpha^2 \frac{1}{r_0}\frac{dV_0}{dr_0}\mathbf{l}_0 \cdot \mathbf{s}_0 + \alpha^2 \frac{1}{r_1}\frac{dV_1}{dr_1}\mathbf{l}_1 \cdot \mathbf{s}_1, \qquad (1)$$

where 0 (1) refers to the positron (electron) coordinate and $V_{0(1)}$ is the effective potential acting on the positron (electron).

The wave function for the Ps scattering state with spin S can be written in the partial-wave form as

$$\Psi(S, M_S, \mathbf{k}) = \sum_{LM_L} i^L \phi(\rho) Y_{00}(\hat{\boldsymbol{\rho}}) \Phi_L(k, R) Y_{LM_L}(\hat{\mathbf{R}}) \times Y^*_{LM_L}(\hat{\mathbf{k}}) \chi(S, M_S), \qquad (2)$$

where $\chi(S, M_S)$ is the electron-positron spin function, $\mathbf{R}$ is the Ps center-of-mass coordinate, L is the angular momentum of the center of mass, and $\boldsymbol{\rho}$ describes the internal motion of the Ps. The spin-orbit conserves the total angular momentum $J(= L + S)$ and parity $\Pi = (-1)^L$ quantum numbers of the partial-wave components of the wave function $|\Psi(S, M_S, \mathbf{k})\rangle$ during the collision.

Simple arguments can be used to determine the conditions under which the ${}^S\text{Ps} \leftrightarrow {}^{S'}\text{Ps}$ transitions are possible for the different (L, L') partial waves. Let $T^{S'S}_{L'L}$ symbolically represent the T-matrix element for this transition. First of all, consider the p-Ps $\leftrightarrow$ p-Ps transition. The only transitions that are possible are those of the type T^{00}_{LL} since $J = J' = L$ must be conserved.

Things are different for the o-Ps $\leftrightarrow$ p-Ps transition. The T^{10}_{LL} matrix element is zero when $L = 0$ since the initial state has $J = 1$ while the final state has $J = 0$. When $L \geq 1$, this T-matrix element can be finite since the initial state with $(S, L) = (0, L)$ and final state with $(S', L') = (1, L)$ can be coupled together to get $J = J' = L$. Despite the possibility of $S' = S \pm 1$, the $L' = L \pm 1$ case is forbidden since this would change parity. Therefore, the o-Ps $\leftrightarrow$ p-Ps transition is possible for all partial waves except for $L = 0$ where it is suppressed.

The small energy difference of 0.84 meV between the p-Ps and o-Ps states means the reaction can be treated as elastic scattering. The cross section near threshold is proportional to E^2 since the lowest order contribution goes by p-wave scattering [11]. Two step processes involving virtual excitations can contribute to the spin-conversion cross section, but these also lead to a cross section that increases at least as fast as E^2 close to threshold. The spin-conversion cross section $\sigma_{\rm so}(k)$ for the o-Ps $\rightarrow$ p-Ps reaction is parametrized as $\sigma_{\rm so}(k) = F_{\rm so}\sigma_p(k)$, where $F_{\rm so}$ is the conversion probability per elastic p-wave collision. The functional form for the p-wave elastic cross section $\sigma_p(k)$ is calculated from the effective range expression for the p-wave phase shift δ_1 for Ps-H scattering in the electron spin triplet state [12], i.e.,

$$k^3 \cot(\delta_1) = -1/6.8 - \tfrac{1}{2}4.0k^2. \qquad (3)$$

The model of Sauders [13] is used to estimate the survival probability of Ps when thermalizing in a gas. It is assumed that monoenergetic Ps is initially produced in its singlet-triplet forms according to the 1:3 statistical ratio at an energy E_0, where E_0 is the energy at which Ps forms below the Ps-formation threshold. During collisions the Ps will experience a fractional energy loss given by $\delta E/E = m_{\rm Ps}/M$, where M is the atomic mass. Assuming the gas molecules are at a temperature of T, the Sauders model predicts the time dependent energy during thermalization to be

$$E = E_{\rm th}\coth^2[\beta + Gnt], \qquad (4)$$

where $E_{\rm th}$ is the average thermal energy $\frac{3}{2}kT$, n is the gas density, and β is defined by $E_0 = E_{\rm th}\coth^2[\beta]$. The factor G is

$$G = p_{\rm th}\sigma M/(m_{\rm Ps} + M)^2, \qquad (5)$$

where $p_{\rm th}$ is the Ps momentum at thermal energies and σ is the momentum transfer cross section.

The rate at which o-Ps disappears is given by

$$\frac{dn_T}{dt} = -n_T\Gamma_T - 4\pi r_0^2 c n_T n_1 Z_{\rm eff} - n_T\sigma_{\rm so}\upsilon_{\rm Ps}n + 3n_S\sigma_{\rm so}\upsilon_{\rm Ps}n. \qquad (6)$$

The first term is the rate for 3γ decay of o-Ps while the second term is due to pickoff annihilation. The third term describes the conversion of o-Ps into p-Ps during the collision. The fourth term accounts for the p-Ps $\rightarrow$ o-Ps reaction with the factor of 3 coming from the principle of detailed balance.

The rate at which p-Ps disappears is

$$\frac{dn_S}{dt} = -n_S\Gamma_S - 4\pi r_0^2 c n_S n_1 Z_{\rm eff} - 3n_S\sigma_{\rm so}\upsilon_{\rm Ps}n + n_T\sigma_{\rm so}\upsilon_{\rm Ps}n, \qquad (7)$$

where Γ_S is the decay rate for p-Ps. Most of the terms in this equation are analogous to those in Eq. (7). This pair of coupled differential equations was integrated numerically. Once the time dependent density of Ps is known, the rate at which γ quanta are emitted is

$$\lambda = 3n_T\Gamma_T + 2n_S\Gamma_S + 8\pi r_0^2 c(n_T + n_S)n_1 Z_{\rm eff}. \qquad (8)$$

Figure 1 shows a simulated decay spectrum for Ps in Xe. The parameters used in the simulation were initially estimated using criteria that were deemed to be physically sensible. However, some of the parameters

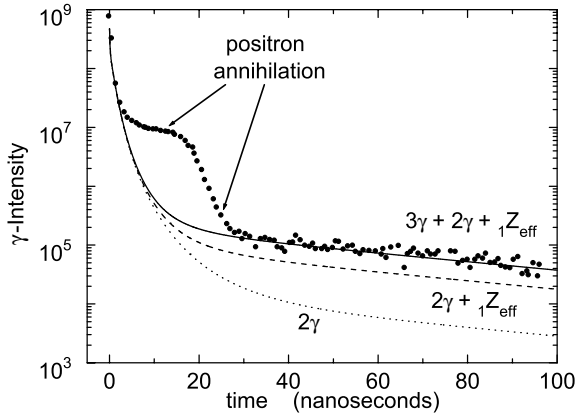

FIG. 1. The intensity of the emitted γ spectrum versus time for Ps thermalizing in Xe. The incremental contributions to the spectrum from (a) the 2γ decay of p-Ps, (b) pickoff annihilation of both p-Ps and o-Ps, and (c) the 3γ decay of o-Ps. The experimental data of Heyland *et al.* [7] were digitized and plotted on the same scale as the present simulation. Those parts of the spectrum traditionally ascribed to free positron annihilation are identified.

(e.g., F_{so}, σ, ${}_1Z_{\text{eff}}$, E_0) were then fixed by manual adjustment to give a reasonable fit to the spectrum for pure Xe [7] while ensuring that the parameters did not become unphysical. The density of the gas was chosen as 9.64 amagats (1 amagat $= 2.69 \times 10^{25}$ atoms/m^{-3}) as this is the same density as Fig. 3 in Ref. [7]. A scattering length of $2.5a_0$ (recent calculations and analysis of experimental data suggest a value between 1.5 and $3.2a_0$ [9,14]) results in a momentum transfer cross section of $25\pi a_0^2$. The gas temperature was taken as 297 K. The initial Ps fraction was taken as 0.52 with the singlet:triplet ratio 0.13:0.39. This fraction was based on a Ps fraction of 0.51 for Xe:He mixtures with 90% of the mixture comprised of He [10]. The initial Ps energy E_0 was taken as 2.5 eV. Finally, the conversion factor F_{so} was set to 0.000 53 by requiring it to reproduce the experimental Ps fraction. This value is reasonable given that the $6s6p\,{}^3P^0 \rightarrow 6s^2\,{}^1S^e$ oscillator strength for Ba of $\sim$0.0083 [15] suggests that the spin-orbit interaction leads to an 0.0005 admixture of the $6s6p\,{}^1P^0$ state into the ${}^3P^0$ state. The pickoff parameter ${}_1Z_{\text{eff}}$ was chosen as 1.03 and was independent of energy (the reason this value is smaller than the measured $\langle {}_1Z_{\text{eff}} \rangle$ for Xe will be apparent later).

The simulated spectrum of Fig. 1 exhibits a very rapid initial decrease, which becomes much slower as the Ps projectile thermalizes. During the rapid decrease some 95% of the Ps is annihilated before 5.0 ns have elapsed. Once the Ps has thermalized, the decay approaches a constant. In a typical experimental situation, the part of the curve for $t > 30$ ns would be extrapolated backwards to zero and then integrated and multiplied by 4/3 to get the total Ps fraction. The Ps fraction of the simulation that would be deduced from an experimental analysis is determined by fitting the decay to an exponential at $t =$ 70 ns and extrapolating back to $t = 0$. Doing this for the curve shown in Fig. 1 gives an estimated Ps fraction of 0.029. There was one feature of the simulation that caused concern: the Ps atoms were not completely thermalized at $t = 70$ ns and had an average energy 1% larger than the thermal energy.

It is apparent from Fig. 1 that the long-time annihilation spectrum might not give a pure estimate of ${}_1Z_{\text{eff}}$. According to Eq. (8), the long-time spectrum also has a contribution from the p-Ps created from the spin-conversion reaction. The value of ${}_1Z_{\text{eff}}$ obtained from the long-time part of the simulated spectrum was 1.26; therefore, 20% of the apparent ${}_1Z_{\text{eff}}$ comes from spin-orbit quenching. The contribution from spin-orbit quenching may make it necessary to revise current interpretations of the slow annihilation component.

The short-time part of Fig. 1 is consistent with experiment. As the Ps atoms slow down, $\sigma_{\text{so}}(k)$ decreases and the slope of the curve decreases. The fast component in the experimental Xe spectrum also shows this feature and is fitted to two exponentials [7].

The possibility of spin-orbit quenching impacting the annihilation spectrum of Kr and Ar has also been studied. The functional form of $\sigma_p(k)$ was not changed. The factor F_{so} is proportional to the square of the spin-orbit matrix element. The manner in which this matrix element scales can be deduced from spin-orbit splitting of the valence np^{-1} level for Ar, Kr, and Xe. Using the orbital energies from a relativistic Hartree-Fock calculation as a guide, one determines the Xe, Kr, and Ar F_{so} to scale as 1:0.265:0.0205. These factors roughly scale as Z^4 which is expected from theoretical considerations [16]. Running the model using the Kr mass, an initial Ps fraction of 0.44, the ${}_1Z_{\text{eff}}$ parameter set to 0.42, and F_{so} set to 1.40×10^{-4} resulted in a Ps fraction of 0.25, about 60% the size of the expected value of 0.44. The contribution of spin-orbit quenching to the apparent ${}_1Z_{\text{eff}}$ of 0.472 at thermal energies was 0.052. The simulation of argon put the initial Ps fraction to 0.32, set the ${}_1Z_{\text{eff}}$ parameter to 0.30, and F_{so} was fixed at 1.09×10^{-5}. The Ps fraction derived from the simulation was 0.314. At thermal energies, 0.004 of the simulation derived ${}_1Z_{\text{eff}}$ of 0.304 was due to spin-orbit quenching. The simulations predict that spin-orbit quenching has a negligible effect upon the Ar Ps fraction and does influence but underestimates the reduction of the Ps fraction for Kr.

These ideas are compatible with a number of variations upon the classic positron annihilation experiment in the rare gas. It is known that the Ps fraction in Kr or Xe increases when it is admixed with H_2 and He. For example, the Ps fraction for a He:Kr gas mixture with 50% Kr is 0.30 [10]. The small admixture of much lighter He leads to much quicker thermalization and will inevitably result in a smaller percentage of the gas undergoing spin-conversion reactions. Experiments using H_2:Xe mixtures have also resulted in a larger Ps fraction [10].

Experiments in a H_2:Xe mixture with Xe at 3.7 amagats and the addition of 10.7% H_2 can also be interpreted as giving further support to the existence of spin-orbit quenching. The thermally averaged ${}_1Z_{\rm eff}$ is known to increase from 1.25 to 1.8 when the temperature increases from 290 to 373 K. This relatively large increase could be an indication that part of the observed $\langle {}_1Z_{\rm eff}\rangle$ is due to spin-orbit quenching since the spin-conversion cross section increases as E^2. When the conditions of the simulation shown in Fig. 1 are changed so that the temperature is 373 K, the decay rate in the long-time part of the spectrum would imply a $\langle {}_1Z_{\rm eff}\rangle$ of 1.39, 0.13 larger than the simulation at $T = 297$ K. This suggests that our model underestimates the size of spin-orbit quenching at thermal energies by a factor of 4. The ability of the simulation to reproduce the positronium fraction is largely determined by the size of $\sigma_{\rm so}$ near E_0. A factor of 4 discrepancy is not excessive, given that $\sigma_{\rm so}$ varies by 2 orders of magnitude from E_0 to $E_{\rm th}$.

In the silica aerogel experiments of Kakimoto and Hyodo [17] upon Kr and Xe, a narrow peak in the angular correlation spectrum was identified and attributed to p-Ps formed from e^+-Kr and e^+-Xe collisions. However, because of the low energies of the positrons at this part of the spectrum it is more likely that they are observing the decay of p-Ps formed by the o-Ps $\rightarrow$ p-Ps reaction.

The present explanation for the origin of the fast components in the lifetime spectrum to a certain extent complement rather than supplant earlier ideas [7–9]. It has been suggested that a strongly energy dependent mechanism for the quenching of o-Ps must exist. At 2 eV, Heyland *et al.* suggested an o-Ps quenching cross section of $7 \times 10^{-4}\ \pi a_0^2$. This is comparable to the present $\sigma_{\rm so}$, which is about $10 \times 10^{-4}\ \pi a_0^2$ at 2 eV. However, the earlier suggestions about the dynamical mechanism responsible for the quenching are not plausible and none of them has gained widespread acceptance. For example, Heyland *et al.* [7,8] speculated that the existence of some low lying PsXe resonant states could greatly enhance ${}_1Z_{\rm eff}$ as the Ps atoms thermalized through the resonance energy. Although this idea was advanced about 20 years ago, it is based on a number of assumptions that remain to be substantiated. No information about the likely structure of these resonances has been given and the question of why such resonances are not present in the Ps-Ar system warrants some explanation. Furthermore, their model relies upon ${}_1Z_{\rm eff}$ of about 1000 while in the resonant state, and such a large value seems unlikely given that the pickoff contribution to the total annihilation rate in complexes consisting of Ps bound to an alkali atom is quite small [18]. An alternate hypothesis by Tuomisaari *et al.* [9] suggested that a pickoff annihilation parameter ${}_1Z_{\rm eff}(k)$ that increased rapidly with energy could explain the results. However, the authors of Ref. [17] have commented that a ${}_1Z_{\rm eff}$ of about 100 would be needed at a few electron volts incident energy. Such a value is 2 orders of magnitude larger than any existing value [2] and would seem to invalidate this idea. The only calculations of ${}_1Z_{\rm eff}$ for Xe [14] gave ${}_1Z_{\rm eff} \approx 0.1$ for s-wave scattering in the energy range up to 1 eV.

To summarize, a model of Ps thermalization and annihilation involving the conversion o-Ps into p-Ps by the spin-orbit interaction has been advanced that explains the small Ps fraction observed for Xe. A spin-conversion probability of about 10^{-4} per elastic collision at 2 eV incident energy seems quite feasible. A formal validation of the existence of spin-orbit quenching will require an explicit calculation of Ps-Xe scattering. However, the difficulties associated with Ps-atom scattering calculations are severe [12,14] and it could be some time before a calculation of the o-Ps $\rightarrow$ p-Ps cross section is done. Another possibility would be an angular correlation measurement on the long-time component for Xe. The existence of a narrow component in the spectrum that increased in intensity with increasing temperature would be consistent with the existence of the spin-orbit quenching.

[1] T. C. Griffith and G. R. Heyland, Phys. Rep. **39**, 169 (1978).
[2] M. Charlton, Rep. Prog. Phys. **48**, 737 (1985).
[3] P. G. Coleman, T. C. Griffith, G. R. Heyland, and T. L. Killeen, J. Phys. B **8**, L185 (1975).
[4] R. S. Brusa, S. Oss, and A. Dupasquier, Lett. Nuovo Cimento Soc. Ital. Fis. **42**, 45 (1985).
[5] M. Deutsch, Phys. Rev. **82**, 455 (1951).
[6] H. S. W. Massey and C. B. O. Mohr, Proc. Phys. Soc., London, Sect. A **67**, 695 (1954).
[7] G. R. Heyland, M. Charlton, T. C. Griffith, and G. L. Wright, Can. J. Phys. **60**, 503 (1982).
[8] G. L. Wright, M. Charlton, T. C. Griffith, and G. R. Heyland, J. Phys. B **18**, 4327 (1985).
[9] M. Tuomisaari, K. Rystola, and P. Hautojarvi, J. Phys. B **21**, 3917 (1988).
[10] G. R. Heyland, in *Positron Scattering in Gases*, edited by M. R. C. McDowell and J. W. H. Humberston (Plenum Press, New York, 1984), Vol. 18, p. 99.
[11] N. F. Mott and H. S. W. Massey, *Theory of Atomic Collisions* (Clarendon Press, Oxford, 1965).
[12] I. A. Ivanov, J. Mitroy, and K. Varga, Phys. Rev. A **65**, 032703 (2002).
[13] W. C. Sauders, J. Res. Natl. Bur. Stand., Sect. A **72**, 91 (1968).
[14] J. Mitroy and M. W. J. Bromley, Phys. Rev. A **67**, 034502 (2003).
[15] J. Migdalek and W. E. Baylis, J. Phys. B **19**, 1 (1986).
[16] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics (Non-Relativistic Theory)* (Pergamon, Oxford, 1977), Vol. 3.
[17] M. Kakimoto and T. Hyodo, J. Phys. B **21**, 2977 (1988).
[18] J. Mitroy and G. G. Ryzhikh, J. Phys. B **32**, 3839 (1999).