Comments on the Paper "Can Positron Annihilation Lifetime Spectroscopy Measure the Free-Volume Hole Size Distribution in Amorphous Polymers?"

Y. C. Jean

Department of Chemistry, University of Missouri—Kansas City, Kansas City, Missouri 64110

Received January 22, 1996
Revised Manuscript Received June 4, 1996

Yu *et al.* recently published an article[1] entitled "Can Positron Annihilation Lifetime Spectroscopy Measure the Free-Volume Hole Size Distribution in Amorphous Polymers?" and drew a negative conclusion. Their conclusion was based on a theoretical model using a finite spherical potential well and assuming the positronium atom, Ps (an atom which consists of a positron and an electron), is an inert particle. The key factor leading to these authors' negative conclusion that "there is no justification for one-to-one correlation of o-Ps [ortho-Ps, the triplet state] lifetime components with specific hole sizes" is an estimate of the relative probability for an o-Ps atom to remain in a particular hole during its entire lifetime (on the order of 10^{-2}). This conclusion indicates that their theoretical model is inconsistent with recent experimental Ps diffusion coefficients in amorphous polymers on the order of 10^{-6} cm^2 s^{-1}.[2]

Since the original Ps−free volume theory by Brandt *et al.* more than three decades ago,[3] at least three different theoretical models have been developed to correlate experimentally observed o-Ps lifetimes and free-volume hole dimensions in molecular substrates: (1) an infinite spherical potential with a uniform electron layer;[4−6] (2) a finite one-dimensional square-well potential model;[7] and recently (3) a finite spherical potential well model.[1] Each model leads to a correlation between the o-Ps lifetime and the hole dimension by incorporating additional empirical parameters. For example, for the infinite spherical potential model, the o-Ps lifetime (τ) and the hole radius (R) have the relationship

$$\tau = 0.5\left[1 - \frac{R}{R_0} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R_0}\right)\right]^{-1} \tag{1}$$

where τ and R are expressed in ns (10^{-9} s) and Å (10^{-10} m), respectively, and R_0 is an empirical parameter ($R_0 = R + \Delta R$). The estimated value of ΔR for substrates which contain simple covalent bonds and no strong Ps-quenching functional groups is found to be 1.656 Å.[6] Equation 1 has frequently been used in the scientific community, including by Yu *et al.* themselves,[8] because of its conceptual and mathematical simplicity. The good agreement obtained by applying eq 1 to systems having static holes and pores has recently been extended with experiments using both PAL and other techniques in silica and alumina.[9]

Since eq 1 suggests that the o-Ps lifetime and the hole radius have a one-to-one relationship, Jean *et al.* developed a method of directly measuring the free-volume hole distribution in polymers using the PAL technique.[10,11] In amorphous polystyrene,[12] they obtain excellent agreement between the experimental free-volume distribution and the free volume computed according to the Simha−Somcynsky theory[13] and fairly good agreement with the cumulative free-volume distribution predicted by the Turnbull−Cohen theory.[14]

In Yu *et al.*'s paper,[1] a calculation of the tunneling probability for an inert particle passing through a finite spherical potential well with radius R, barrier height V_0, and barrier thickness a was carried out. The transmission probability T of the particle was found to be[1]

$$T = \left[1 + \frac{V_0^{\,2}\sinh^2(\beta a)}{4E(V_0 - E)}\right]^{-1} \tag{2}$$

where $\beta = [2m(V_0 - E)/\hbar^2]^{1/2}$, m is the o-Ps mass (2 × electron mass), and E is the zero-point kinetic energy of Ps. These authors assumed $V_0 = 1.1$ eV, $E = 0.6$ eV, and $a = 10$ Å and obtained a value of $T = 1.2 \times 10^{-4}$ for a typical (5% or more) hole fraction and a hole of radius = 4 Å.

Yu *et al.* then expressed the probability of Ps escape from a hole (p) as the product of T and the number (n) of times a Ps strikes the barrier during its lifetime of about 1 ns. By considering Ps a classical particle[15] with kinetic energy = 0.6 eV and therefore velocity $\simeq 3 \times 10^{15}$ Å/s, the time to make a round trip across the hole was estimated as 10^{-15} s. Thus, during its lifetime of 1 ns, the number n of times a Ps strikes the barrier was estimated to be 10^6. Yu *et al.* finally derived a value of the probability of Ps escape $p = 10^2$, or a mean time for Ps escaping the hole on the order of 10^{-2} ns. From this series of estimates and assumptions, the authors concluded that there is no justification for a one-to-one correlation of o-Ps lifetime components with specific hole sizes. The argument is thus based on a single theoretical result: that the probability that an o-Ps atom will remain in a particular hole during its entire lifetime is estimated to be on the order of 10^{-2}. The central point of our counterargument is that the 10^{-2} value is (far) too small for amorphous polymers, when one considers the recent experimental estimates of Ps diffusion coefficients in polymers.[2]

The diffusion coefficient of a particle is one of its most important properties. For a particle undergoing three-dimensional Brownian motion, the mean diffusion length, l_{Ps}, is estimated from the following equation:[16]

$$l_{\mathrm{Ps}} = (6D_{\mathrm{Ps}}\tau_{\mathrm{Ps}})^{1/2} \tag{3}$$

where D_{Ps} and τ_{Ps} are the diffusion coefficient and the hopping time of the Ps. While positron diffusion coefficients have often been measured and documented,[17] D_{Ps} data have been reported for only a few molecular systems. This is partly due to the difficulty of selecting molecular systems with well-defined void properties. The existing D_{Ps} data for systems such as oxide powders,[18] porous organic resins,[19] and polymers[2] have been estimated by measuring o-Ps lifetimes in samples with varying surface areas (voids) or by measuring o-Ps quenching rates with chemical quenchers dissolved in the matrix. It is known that D_{Ps} is relatively small in substrates which contain defects. In oxides and organic resins, D_{Ps}'s have been reported to be on the order of 10^{-5}−10^{-6} cm^2 s^{-1}.[18,19] Recently, Hirata *et al.*[2] estimated D_{Ps} in a variety of amorphous polymers at room temperature, such as polycarbonate, polystyrene, and polysulfone, and found $D_{\mathrm{Ps}} = (2.6−3.2) \times 10^{-6}$ cm^2 s^{-1}. In these experiments, D_{Ps} was calculated from the variation of o-Ps lifetimes due to a chemical reaction

S0024-9297(96)00085-X CCC: $12.00

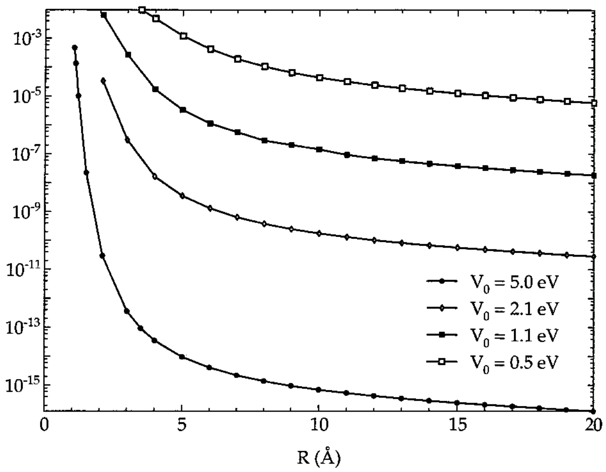

Figure 1. Tunneling probability (*T*) vs hole radius in 3D framework. The plot follows eq 4 according to ref 1, with some corrections (see note 20).

between the Ps and a quencher (2,2′-dinitrophenyl) added to the polymer matrix. The calculated D_{Ps}'s are consistent with D_{Ps}'s reported in molecular substrates which contain defects, such as oxide powders and porous organic resins.[18,19]

Taking $D_{Ps} = 3 \times 10^{-6}$ cm^2 s^{-1} and $\tau_{Ps} = (2-3) \times 10^{-9}$ s, eq 3 gives a diffusion length for Ps in an amorphous polymer of about 20 Å (2 nm). This diffusion length, 20 Å, is only twice the barrier width (10 Å) and about the same distance as the center of one hole is from the center of the nearest-neighbor hole (17.5 Å), according to Yu *et al.*[1] This experimental result suggests that Ps is trapped in or near a single free-volume hole in an amorphous polymer during its entire lifetime. It also suggests that the quantum tunneling model used by Yu *et al.* is not appropriate for Ps diffusion in amorphous polymers.

Let us consider why Yu *et al.*'s model result and the experimental D_{Ps} data may be inconsistent. The value of 10^{-2} ns for Ps remaining in a hole could easily be wrong by several orders of magnitude, since the transmission probability *T* depends strongly on three unknown quantities: the barrier height V_0, the barrier width *a*, and the zero-point kinetic energy *E*. Since *E* (0.6 eV) was estimated from the bubble model of liquids, it may vary much as *a* and V_0 vary in polymers. In Figure 1, we show the sensitivity of *T* to the value of V_0 as a function of *R*. A small error in estimating either *a* or V_0 can easily lead to a completely misleading conclusion. This is possibly what has occurred in the calculations of Yu *et al.* In order to fit the Ps diffusion data in amorphous polymers using Yu *et al.*'s model, V_0 must be on the order of several eV.[20]

As shown in Figure 1, according to Yu *et al.*'s model, the value of $T \simeq 10^{-4}$ (*i.e.*, 10^{-2} of Ps entire lifetime in a hole) was derived from $V_0 = 1.1$ eV, $a = 10$ Å, and $f_v = 5\%$. The high sensitivity of *T* with respect to V_0 is easily seen in Figure 1. For example, at $R = 4$ Å, when $V_0 = 2.1$ and 5.0 eV, *T* dramatically decreases to 10^{-8} and 10^{-14}, respectively. It is also seen that for any $V_0 \geq 3$ eV, Ps will spend its entire lifetime in any hole with $R > 1.5$ Å, according to their model (*i.e.*, the region of $T < 10^{-6}$ in Figure 1). A large value of V_0 for Ps in amorphous polymers can be understood as being due to the repulsive force between the ion cores and the positron of Ps, when the positron penetrates the valence shells of polymer molecules. This is also consistent with the fact that Ps is thermodynamically more stable in vacuum than in the bulk of solids.[21] The large polarizability (8 times that of H) of Ps can also further contribute to a large potential barrier for Ps in a polymer matrix. This effect is seen in the Ps bubble formation of liquids.[22] The existing Ps diffusion data imply that Ps is deeply localized in most free-volume holes and spends most of its entire lifetime in the vicinity of significant holes in amorphous polymers. This is perhaps also the main reason that the infinite potential model works so well for Ps in amorphous polymers.[4-6]

In conclusion, the recent diffusion data for Ps in amorphous polymers are incompatible with the conclusions of Yu *et al.*[1] We conclude that the PAL method is a promising approach to measuring free-volume hole size distribution in amorphous polymers.

Acknowledgment. I wish to thank Dr. Y. Kobayashi *et al.* for supplying their experimental D_{Ps} data prior to publication. I would like to acknowledge the assistance of G. H. Dai and J. Liu in preparing the manuscript. This research is supported by NSF (Grant DMR-9402655) and Eastman Chemical Co.

References and Notes

(1) Yu, Z.; McGervey, J. D.; Jamieson, A. M.; Simha, R. *Macromolecules* **1995**, *28*, 6268.
(2) Hirata, K.; Kobayashi, Y.; Ujihira, Y. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 985.
(3) Brandt, W.; Berko, S.; Walker, W. W. *Phys. Rev.* **1960**, *120*, 1289.
(4) Tao, S. J. *J. Chem. Phys.* **1972**, *56*, 5499.
(5) Eldrup, M.; Lightbody, D.; Sherwood, J. N. *Chem. Phys.* **1981**, *63*, 51.
(6) Nakanishi, H.; Wang, S. J.; Jean, Y. C. In *Positron Annihilation Studies of Fluids*; Sharma, S. C., Ed.; World Science Pub.: Singapore, 1988; p 292.
(7) Zerda, T. W.; Hoang, G.; Miller, B.; Quarles, C. A.; Orcel, G. *Mater. Res. Soc. Symp. Proc.* **1988**, *121*, 65.
(8) For example, see: McCullagh, C. M.; Yu, Z.; Jamieson, A. M.; Blackwell, J.; McGervey, J. D. *Macromolecules* **1995**, *28*, 6100.
(9) Hasagawa, Y.; Tabata, M.; Miyamoto, T.; Nagashima, Y.; Hyodo, T.; Fujinami, M.; Yamaguchi, S. *Mat. Sci. Forum* **1995**, *175–178*, 269.
(10) Jean, Y. C.; Deng, Q. *J. Polym. Sci., B: Polym. Phys.* **1992**, *30*, 1359.
(11) Deng, Q.; Zandiehnadem, F.; Jean, Y. C. *Macromolecules* **1992**, *25*, 1090.
(12) Liu, J.; Deng, Q.; Jean, Y. C. *Macromolecules* **1993**, *26*, 7149.
(13) Simha, R.; Somcynsky, T. *Macromolecules* **1969**, *2*, 342.
(14) Cohen, M. H.; Turnbull, D. *J. Chem. Phys.* **1959**, *31*, 1164.
(15) For Ps with a kinetic energy $E = 0.6$ eV, velocity $v = (E/2m)^{1/2} = 3.2 \times 10^5$ m s^{-1}, and the time of traveling a distance of $2R$ (8 Å) $= 2 \times 10^{-15}$ s. Then the number of Ps striking a well in 10^{-9} s $= 5 \times 10^5$. Therefore the estimated probability of escape (p) = 50 for 4 Å radius and 5% of free-volume holes, according to ref 1.
(16) For example, see: Wang, S. J.; Jean, Y. C. In *Positron and Positronium Chemistry*; Schrader, D. M., Jean, Y. C., Eds.; Elsevier Science Publ.: Amsterdam, 1988; p 259.
(17) Brandt, W. *Appl. Phys.* **1974**, *5*, 1.
(18) Brandt, W.; Paulin, R. *Phys. Rev. Lett.* **1968**, *21*, 193.
(19) Venkateswaran, K.; Cheng, K. L.; Jean Y. C. *J. Phys. Chem.* **1984**, *88*, 2465.
(20) In Figure 1, we plot the transmission probability (*T*) according to eq 4 as presented in Yu *et al.*'s paper (ref 1). Here we adopt their assumptions (barrier width $a = 10$ Å and fraction of holes = 5%), and we also have corrected *T* values from a one-dimensional to a three-dimensional framework by recalculating the solid angles and distances according to their cubic lattice model.
(21) For example, see: Dale, J. M.; Hulett, L. D., Jr.; Pendyala, S. *Appl. Spectrosc. Rev.* **1983**, *19*, 105.
(22) For example, see: Nakanishi, H.; Jean, Y. C. In *Positron and Positronium Chemistry*; Schrader, D. M., Jean, Y. C., Eds.; Elsevier Science Publ.: Amsterdam, 1988, p. 164.

MA960085H