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

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ABSTRACT: We discuss the theoretical basis for relating the mean ortho-positronium (o-Ps) lifetime to free-volume hole sizes using a finite spherical potential well model. The status of the localized o-Ps atom in amorphous polymers is evaluated by calculation of the o-Ps barrier transmission probability. The results indicate that the relative probability for an o-Ps atom to remain in a particular hole during its entire lifetime is on the order of 10^{-2}. We conclude that there is no justification for a one-to-one correlation of o-Ps lifetime components with specific hole sizes.

Background

The positron annihilation lifetime technique provides a unique way of obtaining information about the internal structure of amorphous polymers. In molecular materials, a positron from a radioactive source reaches thermal energy in a very short time (on the order of 1 ps), after which it may diffuse through the material as a free particle or capture an electron to form an atom of positronium. The free-volume model, proposed and developed by Brandt et al.,[1] assumes that positronium is formed only in a free-volume hole which is larger than a certain critical value. Unlike metals, molecular materials always contain a large fraction of imperfect sites, such as impurities, defects, voids, grain boundaries, etc. These sites can serve as free volume for positronium formation.

Positronium (Ps) atoms tend to remain in low electron density areas in macromolecular substances; i.e., they become localized in free-volume holes. Such behavior is described as a self-trapping state of Ps, which is a bound state with an induced local potential.[2,3] Thus the information about free-volume hole size and hole density is carried out of the material through the annihilation γ-rays. Several groups find that connections can be made between o-Ps annihilation data and fractional free-volume values obtained by other experimental techniques.[4] A well-established relation between o-Ps lifetime and free-volume hole size is required to obtain accurate structural information via positron annihilation lifetime analysis.

Several models have been proposed to interpret Ps behavior in molecular liquids.[5] Of these, the "bubble" model[6,7] appears to be most successful. For molecular solids, however, the behavior of Ps remains essentially unsolved. Because of the relatively rigid structure of molecular solids, the Ps atom cannot create additional spaces and the bubble model is no longer valid.

A new challenge to the positron annihilation lifetime method is the potential to obtain information on the distribution of free-volume hole sizes in polymer materials, which could be compared with theoretical predictions, e.g., by molecular dynamics and kinetic theory.[8] Experimentally, a computer code called CONTIN,[9] which uses a numerical Laplace inversion method, can fit the positron annihilation lifetime spectrum to a continuous distribution of intensities as a function of mean lifetime, and experimental measurements of such distributions of mean lifetimes have been reported on several polymers.[10] However, it has been observed that such experimental free-volume hole size distributions do not match those predicted by molecular dynamics and kinetic theory.[10,11]

We have carried out numerical analyses of simulated positron lifetime spectra containing a noise component and a distribution of o-Ps lifetimes. In agreement with the work of Gregory and Zhu,[9] we find that it is difficult to unambiguously resolve discrete lifetime components when two of the lifetimes differ by less than a factor of 2. On the basis of these simulation studies, we are not convinced that the lifetime distributions extracted from CONTIN can accurately reveal the distribution of hole sizes in polymers, unless experimental resolution as well as counting efficiency is greatly improved. Here, however, we consider a more fundamental question, i.e., whether, from quantum mechanical principles, we should expect a hole size distribution to result in a distribution of ortho-positronium lifetimes. Clearly this depends on the degree to which the positronium atoms are localized in free-volume holes. If each ortho-positronium atom remains in a single hole during its entire existence, its lifetime will evidently be correlated to the size of that particular hole. If o-Ps does not remain in a single hole during its lifetime, then one can determine only average hole sizes rather than hole size distributions.

In this work, we first review the theoretical basis for relating the mean o-Ps decay lifetime to the free-volume hole size, and then evaluate the degree to which a Ps atom is located in a free-volume hole, by calculating the one-dimensional transmission probability of quantum barrier tunneling and the three-dimensional escape probability of a Ps atom from a given hole to its neighbors.

Correlation between o-Ps Lifetime and Free-Volume Hole Size

Experimental correlation of o-Ps lifetime with molecular volume was reported by Eldrup et al.[12] on solid pivalic acid, with pore radius by Nakanishi et al.[13] on zeolites, with total free volume by Kobayashi et al.[14] on both molecular liquids and polymers, and with bubble radius by Ujihira et al.[15] on several organic molecular liquids. The theoretical interpretations of such rela-

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tionships have been based on the bubble model[6,7] and the polaron concept[16] for molecular liquids.

For molecular solids, an analysis adapted from the bubble model of liquids has been proposed. A simple model,[12,17,18] in which o-Ps resides in a spherical potential well of radius R_0 having an infinite potential barrier with an electron layer in the region $R < r < R_0$, gives a connection between o-Ps lifetime τ_3 and free-volume hole size. Using this semiempirical approach, one can determine the absolute size of free-volume holes from the following equation (see ref 18 for details):

$$\tau_3 = \frac{1}{\pi r_0^{2} c \varrho_0}\left[1 - \frac{R}{R_0} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R_0}\right)\right]^{-1} \tag{1}$$

where r_0 is the classical radius of the electron, c is the speed of light, and ϱ_0 is the bulk electron density. Instead of pursuing a calculation of ϱ_0, the o-Ps annihilation rate in the electron cloud was assumed to be 2.0 ns^{-1}, i.e., $\pi r_0^2 c \varrho_0 = 2.0$ (ns^{-1}). With $R_0 = R + \Delta R$, the value of ΔR was determined by fitting eq 1 to experimental τ_3-values and free-volume hole sizes obtained from other methods for molecular solids.

However, there are several problems associated with this model:

(i) To derive eq 1, an infinite spherical potential well was used to calculate the positronium wave function in the free-volume hole. Subsequently, in order to produce a finite overlap between the positronium density and the electron density, an electron shell was placed inside the infinite potential well without considering any perturbation of the positronium wave function.

(ii) As a fitting parameter, the thickness of the electron layer ΔR is numerically comparable to, and indeed could be larger than, the potential well radius and, in principle, can differ from one material to another. The free-volume radius R is allowed to decrease continuously to zero to satisfy the assumption that the annihilation rate of o-Ps in the electron layer is 2 ns^{-1}. No consideration of the conditions for bound states of positronium was given.

(iii) To our knowledge, there are no experimental techniques other than positron annihilation lifetime spectroscopy capable of measuring free-volume hole sizes directly. Therefore, we lack independent data on free-volume hole sizes to determine the fitting parameter ΔR.

Strictly, eq 1 is an empirical expression which applies only to the bubble model for molecular liquids. However, for molecular solids, the bubble model is no longer valid, because of the rigidity of macromolecular chains.

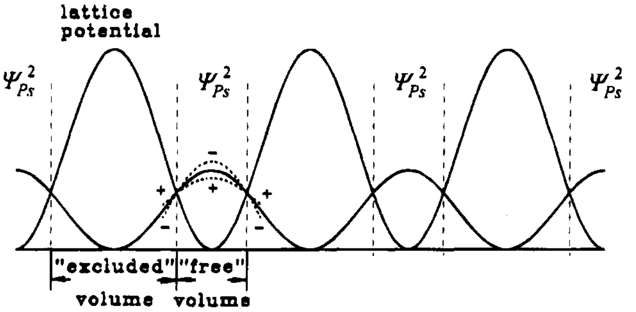

Figure 1. Probability–density distribution of Ps, e$^+$, and e$^-$ in the lattice model.

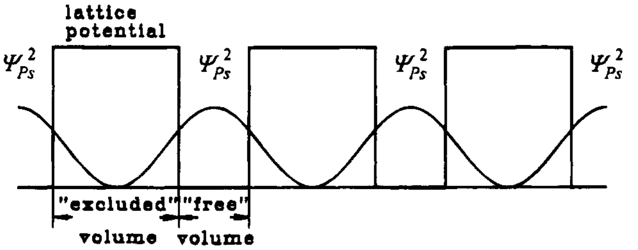

Figure 2. Square well potentials are used to approximate the lattice interaction.

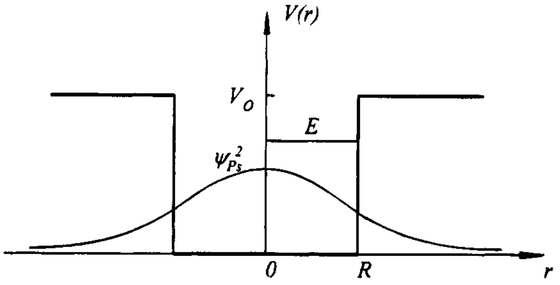

Figure 3. Finite spherical potential well with radius R and height V_0. Also plotted is the schematic probability density of Ps.

Since the de Broglie wavelength of thermalized positronium is much larger than the mean interatomic distance in most molecular solids, a Ps atom interacts simultaneously with many atoms, and we expect that such interactions can be related to the lattice potentials as shown schematically in Figure 1. To simplify our efforts to derive a quantitative relation between o-Ps lifetime and free-volume hole sizes in molecular solids, we represent the lattice potentials as square well potentials in Figure 2. We consider a finite spherical potential well, illustrated in Figure 3, with potential barrier V_0 and well radius R, which is defined as the free-volume hole radius. Neglecting the internal structure of positronium, i.e., treating positronium as a single particle, and approximating the electron density as a constant ϱ_0 outside of the potential well, we can express the pick-off annihilation rate of the o-Ps as:

$$\lambda = \pi r_0^{2} c \varrho_0 \int_{v_0} \psi_{\rm Ps}^{*} \psi_{\rm Ps} \, d\vec{r} \tag{2}$$

where v_0 is the volume outside of the wells, and ψ_{Ps} is the wave function for the center-of-mass motion of Ps atom in the well.

The ground-state wave function in spherical polar coordinates for the Ps atom can be written as:[19]

$$\psi_{\rm Ps} = \frac{B \sin(kr)}{r}, \quad 0 < r < R \tag{3}$$

$$\psi_{\rm Ps} = \frac{C e^{-\alpha r}}{r}, \quad r > R$$

with

$$k \equiv (2mE/\hbar^2)^{1/2}$$

$$\alpha \equiv (2m(V_0 - E)/\hbar^2)^{1/2}$$

$$\beta \equiv (2mV_0/\hbar^2)^{1/2}$$

where constants B and C are determined by the boundary conditions (which require both the wave function and its first derivative to be continuous at $r = R$) and the normalization of the wave function, and m is the mass of the positronium.

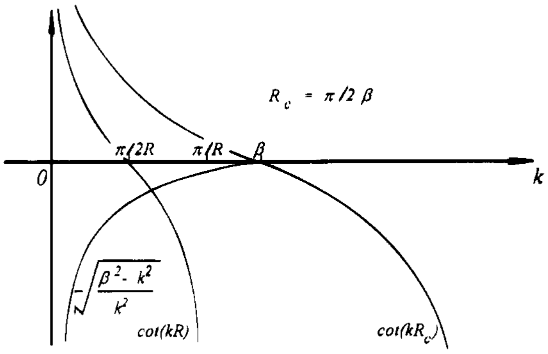

Figure 4. Graphs of cot(kR) with different R values and $[(\beta^2 - k^2)/k^2]^{1/2}$.

The kinetic energy of the positronium, E, is then determined by:

$$\cot(kR) = -\frac{\alpha}{k} = -\left(\frac{\beta^2 - k^2}{k^2}\right)^{1/2} \tag{4}$$

Figure 4 shows the graphical solution of the above equation. To have a bound state solution for positronium, we must have

$$R > R_c \equiv \frac{\pi}{2\beta} = \frac{\pi}{2}\left(\frac{\hbar^2}{2mV_0}\right)^{1/2} \tag{5}$$

The positronium binding energy ($V_0 - E$) in free-volume holes is unknown for molecular solids but should be on the same order as for molecular liquids,[15] where it is about 1 eV. Equation 5 sets a threshold, R_c, in the free-volume hole size for localization of positronium; i.e., the positronium can be localized only in free-volume holes with radii bigger than R_c. Evidence for this threshold is seen in the temperature dependence of the o-Ps intensities. As the temperature is reduced and hole sizes become smaller, fewer holes are large enough to trap Ps, and the Ps intensity is reduced. This result is consistent with experimental o-Ps annihilation data on glassy polystyrene, as discussed elsewhere.[4]

The relation between o-Ps pick-off annihilation mean lifetime and free-volume hole sizes can be worked out[20] from eqs 2–4 as:

$$\tau = \tau^*(1 - \Omega \cot \Omega + \cot^2 \Omega - \Omega \cot^3 \Omega) \tag{6}$$

$$R = R^* \frac{\Omega}{\sin \Omega} \tag{7}$$

with the condition (see eq 4 and Figure 4):

$$\pi/2 < \Omega < \pi \tag{8}$$

where

$$\Omega \equiv kR$$

$$\tau^* = \frac{1}{\pi r_0^2 c \varrho_0}$$

$$R^* = \left(\frac{\hbar^2}{2mV_0}\right)^{1/2}$$

The scaled o-Ps lifetime, τ/τ^*, is plotted vs the scaled free-volume hole size, $V/V^* = (4\pi R^3/3)/(4\pi R^{*3}/3)$, in Figure 5. The precise values of the bulk electron density and the positronium binding energy are selected by fitting these equations to known experimental results. Subsequently, eqs 6 and 7 can serve as working equations to correlate o-Ps annihilation lifetime to free-volume hole size for molecular solids and for molecular liquids as well.

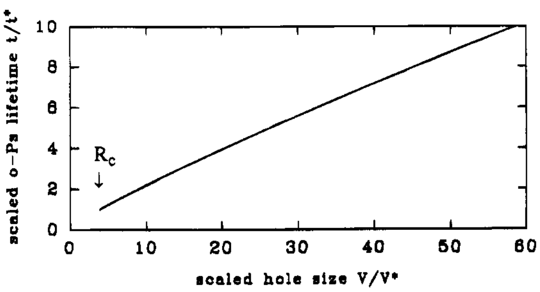

Figure 5. Scaled o-Ps lifetime, τ/τ^*, vs the scaled free-volume hole size, V/V^*.

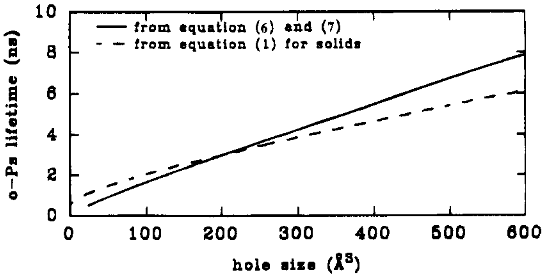

Figure 6. Comparison of eq 1 with eqs 6 and 7. We set the scaling parameter τ^* to 0.5 ns and the potential barrier V_0 to 1.4 eV.

Unfortunately, as noted above, there are no independent experimental data on free-volume hole sizes available, except those calculated from the bubble model for molecular liquids.[15] A qualitative comparison of eq 1 with eq 6 and 7 is made in Figure 6, where we set the scaling parameter τ^* to 0.5 ns, which is the mean lifetime of free positrons, and the potential barrier V_0 to 1.4 eV, so that each set of equations agrees in the region of interest (hole sizes around 200 Å^3).

Localization of o-Ps and Distribution of Its Mean Lifetimes

Clearly we can use the mean value of the o-Ps lifetime, τ_3, to determine an average hole size and can apply such measurements to observe how that average size changes with changes in pressure,[21] temperature,[4] or tensile stress.[22] However, if we analyze the o-Ps component to obtain a distribution of o-Ps lifetime components, either discrete as in POSITRONFIT[23] or continuous as in CONTIN, it remains unclear whether we can determine from this the true distribution of hole sizes. The connection between the distribution of free-volume hole sizes and the distribution of o-Ps pick-off annihilation lifetimes depends on the degree to which positronium is localized in free-volume holes.

We consider two extreme situations. First, Ps is assumed to preferentially reside in areas of lower electron density, i.e., in free-volume holes, but does not remain in a particular hole. This means that o-Ps samples a number of holes with different sizes. We assign P_i as the probability and λ_i as the pick-off annihilation rate of an o-Ps atom which is located in a hole with size V_i. The decay of the o-Ps can be represented as:[20]

$$N = N_0 e^{-\Sigma_i P_i \lambda_i t} = N_0 e^{-\lambda t} \tag{9}$$

where N_0 is the total number of o-Ps, and $\lambda = \Sigma_i P_i \lambda_i$. The decay can be presented as a single exponential function with mean lifetime $\tau = 1/\lambda$.

The second situation is that a positronium atom stays in a particular hole for its entire lifetime after being thermalized. The decay function of o-Ps can then be represented as:[20]

$$N = N_0 \sum_i P_i e^{-\lambda_i t} \tag{10}$$

In this case, each hole with a specified size gives an annihilation rate λ_i, and the decay function contains a distribution of o-Ps pick-off annihilation lifetimes. If the o-Ps atom remains in a single hole after it is trapped, we can, of course, determine the hole size distribution from the lifetime distribution, knowing the relation between o-Ps lifetime and free-volume hole size. However, as we show below, it is highly unlikely that an o-Ps atom will stay in a single hole.

In previous discussions[10] of free-volume hole size distributions measured by the positron annihilation lifetime method, it is assumed that, because of "the large Ps-binding energies with holes (in the order of 0.5 eV)...the chance of the Ps escaping from a hole or diffusing to another before it annihilates is almost zero."[24] However, the escape probability and the diffusion rate cannot be analyzed without taking account of quantum mechanical barrier penetration. This cannot be negligible for o-Ps in polymers with a typical free-volume distribution. We now examine this process. Consider a hole of radius 4 Å, and let its surface be 10 Å from the surface of another hole of any size. (This is typical when the free-volume fraction is 5% or more.) Although this is not a one-dimensional problem, we can estimate the transmission probability, T, of barrier penetration to the second hole using the equation:[25]

$$T = \left[1 + \frac{V_0^2 \sinh^2(\alpha a)}{4E(V_0 - E)}\right]^{-1} \tag{11}$$

where $\alpha = [2m(V_0 - E)/\hbar^2]^{1/2}$. Here, a is the barrier width of 10 Å, m is the o-Ps mass, V_0 is the barrier height (1.1 eV) (the basis for using this value will be given later), E is the zero-point kinetic energy of the o-Ps atom (0.6 eV in a hole of size 4 Å), and $V_0 - E$ is therefore the binding energy of 0.5 eV as quoted above. The resulting value of T is about 1.2×10^{-4}.

To determine the probability of escape, we must now estimate the number of times that an o-Ps atom will strike this barrier during its lifetime of about 1 ns, considering its kinetic energy of 0.6 eV. Setting $mv^2/2 = 0.6$ eV, with $mc^2 = 1$ MeV, we find that $v \cong 3 \times 10^{15}$ Å/s. Thus, by this semiclassical computation,[26] o-Ps will take about 10^{-15} s to make a round trip across the hole and back and hence will strike the barrier 10^6 times during its lifetime of 1 ns. This results in a mean time for escaping the hole of order 10^{-2} ns, and hence the chance of o-Ps remaining in the hole is virtually zero. Obviously, this one-dimensional calculation cannot be viewed as precise, but it does suggest that tunneling of o-Ps from one hole to another can happen and cannot be overlooked.

The above result encourages us to make a further investigation, within a three-dimensional framework, of the escaping probability of the Ps atom from one hole to another. We use the same free-volume model used in the last section, based on a finite spherical potential well, illustrated in Figures 2 and 3, with potential barrier V_0 and well radius R. The positronium wave function was given in eq 3. Consider a cubic lattice, shown in Figure 7, consisting of free-volume holes, each with the same radius $R = 4$ Å, and a free volume fraction of 5%. Then the distance from the center of one hole to the center of a nearest-neighbor hole (referred to as d in the figure) is 17.5 Å. The probability of escape can be represented as:

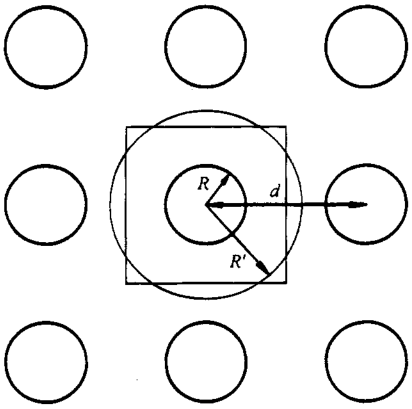

Figure 7. Cubic lattice with holes on the lattice sites. d is the distance between the center of one hole to the center of the nearest hole. R' satisfies $4\pi R'^3/3 = d^3$.

$$P = \int_v |\psi_{Ps}|^2 \, d\vec{r} \tag{12}$$

where v is the volume excluding the cube of edge d shown in Figure 7. Since the wave function is spherically symmetric, an integral with a spherical boundary is much easier to evaluate than one with a cubic boundary. We define R' in the following equation:

$$\frac{4}{3}\pi R'^3 = d^3 \tag{13}$$

and

$$P' = \int_{R'}^{\infty} |\psi_{Ps}|^2 \, d\vec{r} = 4\pi C^2 \int_{R'}^{\infty} e^{-2\alpha r} \, dr = \frac{2\pi C^2}{\alpha} e^{-2\alpha R'} \tag{14}$$

Therefore, we have

$$P > P' \tag{15}$$

We set the free-volume hole radius to a typical number, $R' \approx 4$ Å, and the binding energy of a Ps atom in the hole ($V_0 - E$) to 0.5 eV. From eq 4, we obtain $E = 0.63$ eV and then $V_0 = 1.13$ eV. Combining eq 14 with the boundary condition and the normalization of the wave function, noted earlier, we have $P' = 1.6 \times 10^{-4}$. Therefore, the probability of escape is greater than 1.6×10^{-4} which is even larger than the transmission probability ($T = 1.2 \times 10^{-4}$) obtained from one-dimensional barrier tunneling of Ps atoms.

With the same method used before, we obtain a mean time for escaping the hole of order 10^{-2} ns, which suggests that it is almost impossible for a Ps atom to remain in a specific hole during its entire lifetime. Note that this result does not necessarily imply that each o-Ps atom samples holes of all possible sizes; a distribution of mean lifetime in the o-Ps component may still occur due to variation in the Ps trapping probability as a function of hole size and some other factors. However, there seems to be little justification for a one-to-one correlation of lifetime components with specific hole sizes.

Conclusions

Following the free-volume concept, we have used a finite spherical potential well to elucidate a relationship between mean o-Ps annihilation lifetime and free-volume hole size. We conclude that positronium has a threshold for detecting free-volume holes; i.e., it can probe only holes larger than a size corresponding to the minimum for o-Ps localization. Calculations of the one-dimensional transmission probability and the three-dimensional escape probability indicate that the chance for a Ps atom to remain in one particular hole for its entire lifetime is on the order of 1%; i.e., it appears that each positronium will sample a number of holes of different sizes before annihilating with an electron. The lifetime of o-Ps therefore reflects an average over the distribution of free-volume hole sizes in polymer materials. Even if a reliable measurement of the o-Ps lifetime distribution has been obtained, we conclude that there is no reason to believe that this lifetime distribution is a direct measure of the hole size distribution.

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