

Positronium Annihilation in Molecular Substances

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¹² T. J. Cook and D. H. Levy, to be published.

¹³ T. R. Carver and R. M. Partridge, *Am. J. Phys.* **34**, 339 (1966).

¹⁴ M. C. Pease III, *Methods of Matrix Algebra* (Academic, New York and London, 1965), p. 76.

¹⁵ This is an example of the general theory stating that for any matrix A which can be diagonalized by a transformation T according to the equation $T^{-1}AT = A_D$, any function $f(A)$ is given by $Tf(A_D)T^{-1} = f(A)$ where $(f(A_D))_{aa} = f((A_D)_{aa})$ for all values of a .¹⁶

¹⁶ G. Goertzel and N. Tralli, *Some Mathematical Methods of Physics* (McGraw-Hill, New York, 1960), Chap. 2.

¹⁷ By effective oscillator strength we mean the true oscillator strength multiplied by any instrumental effects such as the use of filters or polarizers. In our experiments the CN red bands have zero effective oscillator strength since the detector includes a uv transmitting-visible absorbing filter.

¹⁸ Because of the pressure drops in the outlet tubulation, the pressure in the cell was always somewhat higher than the pressure at the gauge tube.

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Positronium Annihilation in Molecular Substances

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The behavior of the Ps atom in molecular substances, particularly liquids, is investigated. The pickoff rates of o-Ps in various liquid compounds are found to have a simple empirical relationship to the values of the surface tension of the liquids. The relationship is found to have a theoretical foundation. The Ps atom is highly localized in a cavity created by the balance of various molecular forces inside the liquid. From the above relationship, other simple relationships between the pickoff rates of o-Ps and the various properties of the medium, e.g., polarizability, cohesive energy density, etc., and the temperature or pressure changes can be derived and explained. The diffusion of o-Ps is discussed. A similar approach can also be used for molecular solids.

I. INTRODUCTION

Positron annihilation in various substances has been investigated for many years.¹ Inside substances positrons from a β^+ emitter are expected to lose most of their energies, becoming slow positrons with energies less than several electron volts in times that are small compared to their lifetimes.² During the slowing down process, positrons can capture an electron from the medium substance within a narrow range of kinetic energies (Ore gap or positronium formation gap³) to form the atom (e^+e^-), positronium Ps.⁴

Positrons annihilate with electrons in the medium into gamma quanta. This type of annihilation is commonly called either free or direct annihilation. Laws of conservation require an even number of quanta be emitted for an electron-positron system with total spin of $S=0$ and an odd number (greater than one) of quanta be emitted for an electron-positron system with total spin of $S=1$. As a unit increase in the number of photons emitted means that the cross section for the process is multiplied (decreased) by a factor of the order of the fine structure constant, $\alpha=1/137$, two quanta and three quanta annihilation processes are the most probable ones. If the electrons are treated as free, the ratio of the cross sections for three quanta and two quanta annihilation is $1/372$.⁵ The two quanta emitted will be colinear and the three quanta coplanar in space. The annihilation rate is $\lambda_f = N_e \sigma v = N_e \pi r_0^2 c$, with $r_0 = 2.8 \times 10^{-13}$ cm, c the velocity of light, and N_e the number density of electrons.

There are two ground ($n=1, 1S$) states of positro-

nium due to the total spin of the atom. The state with total spin $S=1$, called orthopositronium (o-Ps), is a triplet and the state with total spin $S=0$, called parapositronium (p-Ps), is a singlet. The statistical weight of the triplet state is three times as large as that of the singlet state. Therefore, in normal cases, there is three times more orthopositronium formed than parapositronium. The mean life (lifetime) of parapositronium in free space is 0.125 nsec and two quanta are emitted during the annihilation. The mean life of orthopositronium in free space is 140 nsec and three quanta are emitted during the annihilation. In a medium the mean life of positronium, particularly orthopositronium, will be modified. The positron in the o-Ps atom has an opportunity to sense the electrons with opposite spin and annihilates in the two quanta mode. The mean life will be reduced. This process takes place in all the substances and is called pickoff.⁶ In a medium with substances possessing unpaired electrons in their atomic or molecular structure o-Ps may change into p-Ps and vice versa. This process is called conversion and has been explained by Ferrell.⁷

Since positronium is a hydrogenlike atom, naturally it is expected to undergo chemical reactions with the medium molecules just like a hot radical. The monograph by Green and Lee⁸ and the review article by Goldanskii² both describe the field of positron annihilation from a chemical point of view. A systematic introduction to positronium chemistry has been given by Tao and Green.⁹

One of the experimental methods employed in the study of positron annihilation is that of measuring the

annihilation mean life of positrons. In gaseous media, in general, the annihilation lifetime spectra (output data) can be separated into three components. The one with an intermediate mean life is attributed to the free-positron annihilation. The one with the longest mean life, approaching the mean life of o-Ps in free space (140 nsec), is attributed to the annihilation of o-Ps modified by various processes. The shortest lifetime component with a mean life of the order of a few tenths of a nanosecond is attributed to p-Ps annihilation. In condensed molecular substances, in general, two positron lifetime components are observed. The long lifetime component with a mean life of an order of a few nanoseconds is believed to be due to the annihilation of o-Ps principally by the pickoff process. The short lifetime component with a mean life of the order of a few tenths of a nanosecond is attributed to free-positron annihilation and p-Ps annihilation. With the advent of the improved time resolution of the apparatus, this component has been further separated into more than one component.¹⁰

Another experimental method used in the study of positron annihilation is angular correlation of the annihilation radiation. The angular deviation of the two annihilation quanta from 180° is determined. From this one can calculate the momenta or the distribution of the momenta possessed by the annihilating electron-positron pairs. If the positrons are assumed to be thermalized the momenta can be attributed to the electrons. The result will be the momentum distribution of the electrons annihilating with the positrons.

Attempts have been made to understand the pickoff behavior of the positronium in molecular substances. Ferrell¹¹ has made a theoretical study using liquid helium as a simple example. He pointed out that there are two different types of forces acting on the positronium atoms which tend to compensate one another. Besides the attractive van der Waals dispersion force there is the repulsive exchange force. In general, the exchange force works against the pickoff force (attractive van der Waals force) and is probably the dominant reason for the long lifetime in most materials. From the calculations he made, he concluded that if positronium is formed at all in an insulator the atoms in the triplet state will exhibit the long τ_2 lifetime. He also pointed out that a narrow component in the two quanta angular correlation is strong evidence of p-Ps.

Later a theoretical treatment was given by Brandt, Berko, and Walker.¹² They used an ultrasimplified theory in which the wavefunction of the positron in the field of the electron to which it is bound is replaced by the wavefunction of the positronium atom, then the Ps wavefunction is calculated for different lattice structures in the Wigner-Seitz approximation. This theory has had some limited success.^{10,12} Since "free volume" (as defined in their theory¹²) is used as one of the parameters in their calculation, this theory is in general called the "Free-Volume" theory.

A similar approach has also been used by Tabata¹³ and Ogata and Tao.¹⁴ In their approach the center of the unit cell is the center of the Ps atom instead of the center of the molecule of the surrounding substance as used by Brandt *et al.*¹² The results obtained using either approach are the same for a one dimensional lattice but are different for a two or three dimensional lattice. Recently, a Russian group¹⁵ has also tried to use a simple square well, called a "bubble," to study the pickoff rate and the width of the narrow component of the angular correlation.

A different approach, an empirical one, has been tried by many workers. Story¹⁶ suggested a correlation between the lifetimes of o-Ps in a number of plastic materials with their dielectric constants. Khan¹⁷ suggested a correlation between the lifetime of o-Ps in a number of polymers with their molecular cohesive energy density. The most successful attempt was made by Gray, Cook, and Sturm.¹⁸ They found that the quenching cross sections of the o-Ps in the *n*-alkanes correlate directly with the electron polarizability of the molecule. Measurements of other classes of organic liquids have shown a similar relationship. Their success was largely due to their great effort in experimental measurements. They carefully measured the mean lives of the long component (o-Ps) for positron annihilation in 193 pure organic liquids. However, no theoretical explanation was given by them.

We attempt to make a systematic analysis of the behavior of Ps, particularly the pickoff process in molecular liquids. We hope we can obtain some insight which will shed some new light on this problem by using this approach. Although it is still a simplified theory, it enables us to explain the various theories and relationships in a more unified way. This approach can also be applied to molecular solids and polymers with slight modification.

II. THEORETICAL CONSIDERATIONS

A. Molecular Forces

We shall treat the positronium atom as an entity and neglect the interaction between the medium and the positronium electron and the one between the medium and the positronium positron. The attractive van der Waals force between the medium molecules and the positronium atom is separated into two parts, the attractive force between the medium molecules and the attractive force between Ps and the surrounding medium molecules. The attractive force of the medium molecules surrounding the Ps atom exerts a pressure on the Ps atom. This type of force is indicated macroscopically by the surface tension of the medium liquid. The existence of an attractive force between Ps and the surrounding medium molecules has been further supported by the experimental evidence in the adsorption of o-Ps on the surface of silica gels.¹⁹ Under an equilib-

rium condition, neglecting other interactions, we have

(exchange force between Ps and medium molecules)

$$= (\text{attractive force between Ps and medium molecules}) \\ + (\text{attractive force between medium molecules exerted on the Ps atom}).$$

The magnitude of the exchange energy has been estimated by Ferrell¹¹ for liquid helium. He has also pointed out that the exchange energy is negligible for separations greater than 3 Å. It increases rapidly with less separation and tends to prevent separations of less than 1 Å. The value of the exchange energy can also be estimated by another method. If the o-Ps atom is considered to be confined inside a rigid sphere, the change of the energy of the electron-positron pair and the pressure of the pair exerted onto the wall can be calculated.^{20,12} The results are shown in Fig. 1 where for the sake of convenience the energy scale is set such that the ground level of Ps atom in free space is zero. The energy of the Ps atom becomes zero when the radius of the sphere is 1.835 a_0 (about 0.97 Å).¹⁵ When the radius of the sphere is less than 0.97 Å the electron-positron pair is no longer bound to each other. The pressure of the positronium wave applied to the wall rises approximately exponentially with decreasing radius. Or we can write

$$P \simeq P_0 \exp(-r/R_p),$$

with $R_p = 0.56a_0$. The pressure is 1.1×10^4 atm at $r = 3a_0$ and 7×10^4 atm at $r = 2a_0$. Incidentally, if a pressure of 9×10^4 atm or higher is applied to an electron-positron pair it will become a plasma instead of a bound Ps atom.

The intermolecular force of the medium molecules is more conveniently represented by the macroscopic property of the liquid, surface tension γ . The surface tension values for many liquids have been precisely measured. The relationship between surface tension and other properties of the liquids have been well investigated and documented.²¹ A discussion of surface tension and intermolecular forces is beyond the scope of this paper. Since our discussion will be centered on surface tension we shall discuss it briefly.

Hildebrand and Scott²² have developed some simple relationships between surface tension and latent heat of vaporization, and latent heat of vaporization and the parameter a in the van der Waals equation. If the radial distribution function does not vary with temperature, the energy of the liquid can be calculated to be

$$E = -a'/V_m,$$

where V_m is the molar volume and a' is the constant of the van der Waals equation or something very similar. The internal pressure can be expressed as

$$P_i = (\partial E / \partial V)_T + T(\partial P / \partial T)_V - P.$$

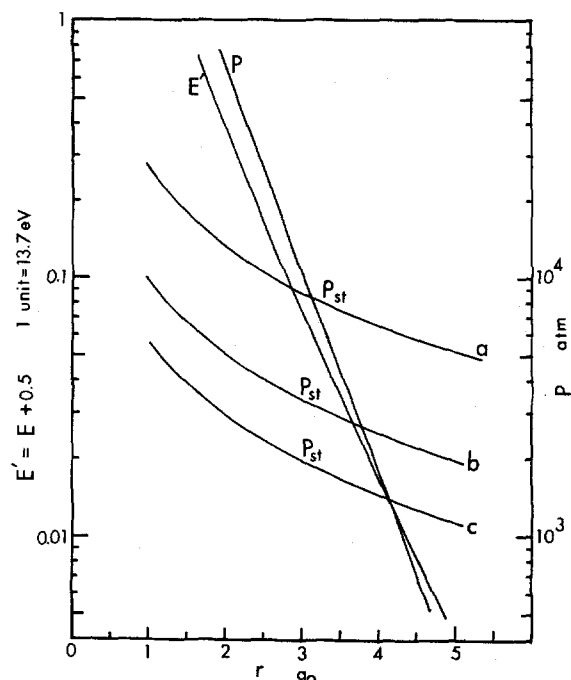


FIG. 1. Binding energy and the pressure of Ps atom inside a rigid sphere and the pressure applied to a sphere by surface tension. ($E' = 0.5 + E$, E = binding energy; P , pressure of Ps; P_{st} , pressure of surface tension; a , $\gamma = 72$ dyn cm^{-1} , water; b , $\gamma = 28.3$ dyn cm^{-1} , benzene; c , $\gamma = 15.5$ dyn cm^{-1} , n -pentane.)

Actually, it is more general to write

$$E = -a/V_m^n,$$

where a is the constant of the van der Waals equation. Then we have

$$P_i = -n(a/V_m^{n+1}) = -n(E/V_m) = n[(\Delta H_v - RT)/V_m].$$

From the ratio of $(\partial E / \partial V_m)_T$ and $(\Delta H_v - RT)/V_m$ the value of n can be measured. For an ideal van der Waals liquid n equals 1. For most of the nonpolar liquids the value n is very close to 1 and the value of the internal pressure is very close to $(\Delta H_v - RT)/V_m$, the cohesive energy density (CED).

There is also a simple relation between the free energy of surface formation per mole and the latent heat of vaporization. Hildebrand and Scott²² have pointed out a direct proportional relationship between $\gamma/V_m^{1/3}$ and $\Delta H_v/V_m$ would be satisfactory for many liquids. However, a better agreement can be shown by the following empirical formula:

$$\delta = 4.1(\gamma/V_m^{1/3})^{0.43},$$

and

$$\delta^2 = \text{CED} = (\Delta H_v - RT)/V_m,$$

where δ is the solubility parameter. Such a relationship has been further investigated by Lee.²³

If we want to calculate the exact energy required for creating a void cavity with the dimension of inter-

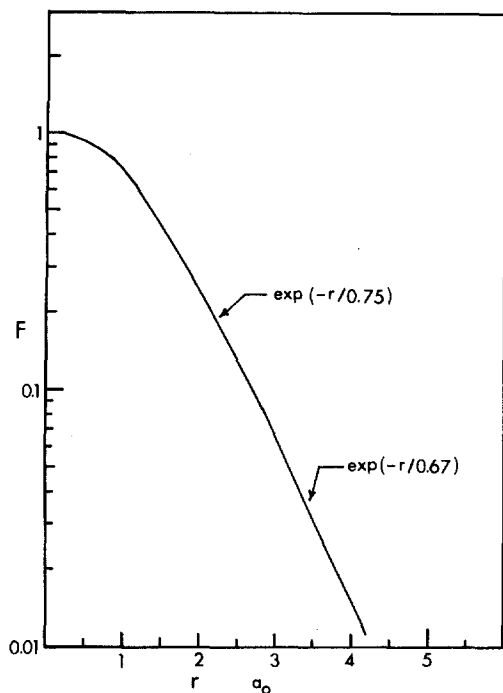


FIG. 2. The fraction F of the total amplitude of Ps wave outside a radius r .

molecular distances in liquids, it will not be a simple task because the knowledge of the exact shape of the potentials is not known. One of the simplest ways is to estimate the energy from surface tension classically. The energy required to create a spherical cavity with radius r is

$$E = 4\pi r^2 \gamma,$$

and the pressure applied on the cavity is

$$P = 2\gamma/r.$$

This type of pressure variation is shown in Fig. 1 using water ($\gamma = 72 \text{ dyn cm}^{-1}$ at 25°C), benzene ($\gamma = 28.3 \text{ dyn cm}^{-1}$), and *n*-pentane ($\gamma = 15.5 \text{ dyn cm}^{-1}$ at 25°C) as examples. If the intermolecular attractive forces between Ps and the surrounding liquid molecules are neglected, the range of the equilibrium cavity radii will be about $3.5a_0$ to $4.5a_0$. The change to the Ps wavefunction will be quite small since the energy change in the binding energy of Ps is only 0.24 eV in water.

If the Ps wavefunction is not distorted inside such a cavity, the part of either the e^+ wave or the e^- wave stretching outside the cavity ($r > 3.5a_0$) is less than 0.4% as shown in Fig. 2. The high pickoff quenching rates of 0.25–0.5 nsec^{-1} are unlikely to all be attributed to this effect. This naturally indicates that the attractive forces between the Ps atom and the surrounding molecules must play a role here. This is just what has been pointed out by Ferrell.¹¹ At present, we do not know exactly the size of this potential for various

substances. The only substances for which we have a fair idea are silica gels. It has been found that o-Ps atoms are adsorbed on the surface of the silica gels, and the potential of this attractive force has been estimated to be about 0.2 eV deep and 7 \AA wide.¹⁹ A force of this magnitude certainly must be taken into consideration in the investigation of the behavior of Ps atoms in various substances. This attractive force will reduce the equilibrium cavity radius for Ps atoms to, say, $2.5a_0$ to $3.5a_0$. The interaction between the e^+ in the Ps atom and e^- in the medium substance will be increased greatly, too.

B. Pickoff Rate

The pickoff rate of o-Ps in condensed molecular substances can be estimated theoretically using certain assumptions. Excluding other complications, such as conversion quenching, one has the pickoff rate λ_p , of o-Ps in a substance¹²:

$$\lambda_p = \pi r_0 c \int_L \psi_L^*(r) \psi_{+b}^*(r) \psi_{+b}(r) \psi_L(r) d\tau^3, \quad (1)$$

where ψ_{+b} is the wavefunction of the positron in the field of the electron to which it is bound as o-Ps as well as in the field of the surrounding medium molecules, ψ_L is the wavefunction of the electrons in the surrounding medium molecules under the same condition, and L is the volume element. Using a zero-velocity approximation one can set¹²

$$\psi_{+b}(r_+) = \alpha(r_+) \psi_{Ps}(r_0), \quad (2)$$

where α is a polarization function, and $\psi_{Ps}(r_0)$ is the wavefunction of the Ps atom at its center of mass. If α is assumed to be 1, one has

$$\lambda_p = \pi r_0 c \int_L \psi_L^*(r) \psi_{Ps}^*(r) \psi_{Ps}(r) \psi_L(r) d\tau^3. \quad (3)$$

If the part contributed by ψ_L is approximated to have an average electron density of ρ_0 , one can further simplify the formula to

$$\lambda_p = \pi r_0 c \rho_0 \int_L \psi_{Ps}^* \psi_{Ps} d\tau^3. \quad (4)$$

The advantage of using Formula (4) as a starting point in calculation is that the wavefunction ψ_{Ps} can be easily solved if the potential is known. Therefore, one has only to select a suitable potential well to represent the molecular forces involved.

C. Potential Wells

Square well type potentials are generally used as a further simplification. The Schrödinger equations for various regions expressed in terms of an appropriate geometry are

$$\begin{aligned} [\nabla^2 - (4m/\hbar^2)(U_\mu - E)]\phi_\mu &= 0, \\ \mu &= 0, 1, 2, \text{ etc.}, \\ \phi &= \psi_{Ps} \end{aligned} \quad (5)$$

subject to a suitable potential U_μ at various regions denoted by $\mu=0, 1, 2$, etc., and the corresponding boundary conditions.

The Wigner-Seitz approximation has been used by Brandt, Berko, and Walker.¹² The schematic of the potential well is shown in Fig. 3(a). The potentials are

$$U_0 = U_0, \quad r < r_0,$$

$$U_0 = 0, \quad r_0 < r < r_1,$$

and the boundary conditions are

$$\phi_0(r_0) = \phi_1(r_0),$$

$$\phi_0'(r_0) = \phi_1'(r_0),$$

$$\phi_1'(r_1) = 0.$$

The unit cell is centered at one of the medium molecules. They¹² also used the scattering parameter $(4m/\hbar^2)U_0r_0^2$ as a variable. In this approximation the Ps wave is surrounding the medium molecules. It should be a good approximation for cases where the o-Ps wave is highly delocalized.

Another approximation, similar to the above one, was mentioned before. The difference is that the unit cell is centered at the o-Ps atom instead of at one of the medium molecules. It seems this approximation is more suitable for cases where the o-Ps wave is more localized in the cavity occupied by itself. If the potential barrier is high, this approximation is reduced to a simple square well problem with a barrier height extended to a distance of infinity. It is very interesting to point out that in this simplest model there is a minimum value of the scattering parameter for the existence of a bound solution of ϕ . For spherical geometry the condition for the existence of a bound solution is

$$(4m/\hbar^2)U_0r_0^2 > (\pi/2)^2.$$

If the value of the scattering parameter is smaller than $(\pi/2)^2$, the Ps wave will penetrate freely into the barrier.

For o-Ps atoms in the pores (cavities) of silica gels because of the large pore sizes, a potential well of the shape shown in Fig. 3(b) has been used by us.¹⁹ The potential barrier at a distance inside the wall of the pores is assumed to be impenetrable. A layer of electron cloud with an average density of ρ_0 at the surface of this barrier with the thickness of r_2 is assumed to be interacting with the e^+ in the o-Ps atom. There is a shallow square well with depth of U_0 and width of $(r_1 - r_0)$, which represents the attractive force between the o-Ps atom and the surface molecules situated adjacent to the barrier. This type of potential well has been found suitable for explaining the adsorption of o-Ps atoms on the surface of the silica gels. The adsorption of the o-Ps atom on the surface of the silica gels is not very strong.¹⁹ This is due to the fact that the o-Ps atom has a small mass and is very mobile. If the surface is not partially closed such as in the pores inside the

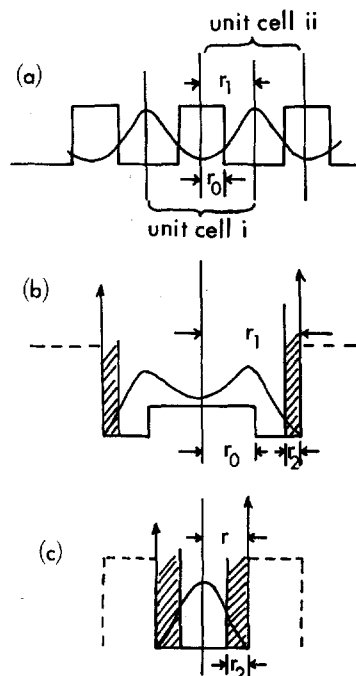


FIG. 3. Schematics of some square well potentials (a, periodic barrier; b, large rigid pore; c, small rigid pore).

solid skeleton of silica gels but instead it is an open surface, there is a great chance that the o-Ps atom may escape the surface and wander into the space before its annihilation.

Now if the size of the pore as shown in Fig. 3(b) is reduced, the radius r_0 of the center region will be reduced. When the pore size is sufficiently small, as in the case of o-Ps atoms in molecular liquids, the potential well of the type shown in Fig. 3(c) will be obtained. Here, we only have one region because there is no center region. If the o-Ps atom is highly localized, this is a suitable model. If the o-Ps atom is not so highly localized, a potential well similar to the one shown in Figure 3(a)(ii) is likely to be a more suitable model.

III. PICKOFF RATE

A. Surface Tension

In the last section we had the force equilibrium condition. The exchange force can be approximated by using the pressure of the wave of the Ps atom applied to the surrounding medium molecules. The attractive force between the medium molecules can be approximated by using the surface tension of the liquid medium. The force about which we know very little is the attractive force between Ps and the medium molecules. However, for a group of compounds with similar structure and properties, such as the homologue of n -alkanes, this force is expected to have a systematic relationship with the surface tension of the medium. Therefore, we should

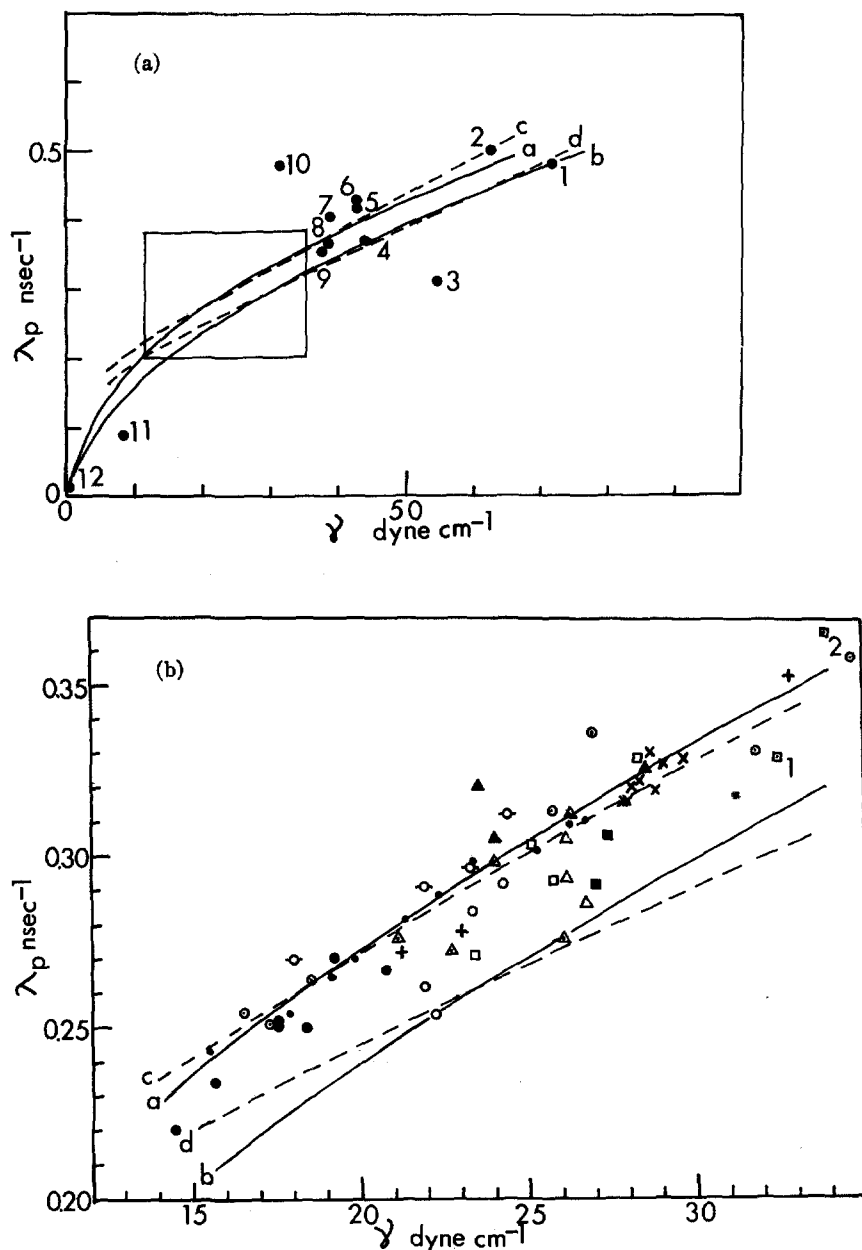


FIG. 4. (a) The relationship between Ps pickoff rate λ_p and surface tension γ {1 water, 2 glycerine,²⁶ 3 H_2SO_4 [S. J. Tao and J. H. Green, *J. Phys. Chem.* **73**, 882 (1969)], 4 ethylene glycol, 5 aniline, 6 dimethylsulphoxide, 7 acetophenone, 8 benzoyl alcohol, 9 pyridine, 10 CS_2 , 11 $\text{N}_2(1)$ ²⁶, 12 $\text{He}(1)$ ²⁶; curve a, $\gamma_p = 0.061 \gamma^{0.50}$; curve b, $\gamma_p = 0.046 \gamma^{0.55}$; curves c and d, results from a simple square well model; other referred to Fig. 4(b)}. (b) The relationship between Ps pickoff rate λ_p and surface tension γ [small dot, *n*-alkanes; large dot, branched alkanes; open circle, alcohols; cross, chloroalkanes; open square, bromoalkanes; closed square, fluoroalkanes; barred circle, other hydrocarbons; open triangle, acids; closed triangle, nitrogen compounds; dotted circle, ethers; dotted triangle, ketones and aldehydes; inclined cross, benzenes and alkylbenzenes; 1, propylene glycol; 2, cyclohexanol; others referred to in Fig. 4(a)].

expect a simple empirical relationship between the pick-off rate of o-Ps in a liquid and the surface tension of the liquid. Indeed, there is a simple relationship between them. The pickoff rates of o-Ps (the inverse of the mean life of the long lifetime component) of various liquids are plotted against the values of the surface tension of the liquids at 25°C²⁴ in Figs. 4(a) and 4(b). Figure 4(b) is an enlarged portion of Fig. 4(a) for most of the organic compounds. The pickoff rate of o-Ps for all the compounds except a few are taken from the work by Gray, Cook, and Sturm measured at 26.5°C.¹⁸ This ensures that the systematic errors in the measurements of the mean lives of positron annihilation in various

compounds made by various groups of research workers is reduced to a minimum. In order to make the values of the pickoff rate more reliable, the pickoff rates for compounds in which the intensity of this long lifetime component is lower than 10% are not used. The values of the surface tension of the liquids are the values at 25°C. All together there are 72 compounds including the *n*-alkanes, *n*-alkanols, acids, aldehydes, ketones, ethers, benzene and alkyl-benzenes, branched-alkanes, halogenated alkanes, and others. Obviously, except for H_2SO_4 , CS_2 , and perhaps liquid N_2 , all of them lie close to a smooth curve.

The simplest empirical formula which fits the data

representing *n*-alkanes best has been found to be

$$\lambda_p = 0.061\gamma^{0.50}, \quad (6)$$

where γ is the surface tension of the liquid in units of dyne per centimeter, and λ_p is the pickoff rate in units of nanoseconds⁻¹. Using this formula to calculate the value of the pickoff rate from the value of the surface tension for various organic compounds excluding the derivatives of the short chain hydrocarbons, the error is found to be less than $\pm 5\%$. For many hydrocarbons and derivatives of long chain hydrocarbons, the error is found to be less than $\pm 2\%$.

The above formula is not very good for oxygenated short chain hydrocarbons, such as methanol, acetic acid, and acetaldehyde. All of these compounds are polar compounds with hydrogen bonds playing a major role in their properties. It is also possible to find a similar empirical relationship as in Formula (6) for these oxygenated short chain hydrocarbons. The best fit is found to be

$$\lambda = 0.046\gamma^{0.55}. \quad (7)$$

It is also interesting to note that this formula fits the data for ethylene glycol and water. The value for glycerine does not fit this formula as well. However, the value of λ_p for glycerine is obtained from another source.²⁵ Some systematic discrepancy is expected. Both formulas are shown as the solid curves in Figs. 4(a) and 4(b).

Here, we shall show that the Formulas (6) and (7) are not entirely without theoretical foundation. As it has been mentioned before the repulsive pressure of the Ps atom is approximately

$$P = P_0 \exp(-r/R_p) \quad (8)$$

with $R_p = 0.56a_0$. The fraction of the undistorted wavefunction of the Ps atom outside the radius r can be approximated as

$$G = G_0 \exp(-r/R_c) \quad (9)$$

with R_c and G_0 constants, provided the range of r considered is small. Combining Eqs. (8) and (9) we have

$$G = G_0(P/P_0)^{R_p/R_c}.$$

Since we can write

$$\lambda_p = \lambda_s G,$$

we have

$$\lambda_p = \lambda_s G_0 (1/P_0)^{R_p/R_c} (P)^{R_p/R_c}. \quad (10)$$

At equilibrium

$$P = P_{st}(\text{surface tension})$$

$$+ P_i(\text{Ps and surrounding molecules}).$$

We have

$$P_{st} = 2\gamma/r.$$

We can reasonably assume

$$P_i = k\gamma$$

with k a constant, provided the range of γ considered is small. Substituting these into (10) we obtain

$$\lambda_p = \lambda_s G_0 (1/P_0)^{R_p/R_c} (k + 2/r)^{R_p/R_c} (\gamma)^{R_p/R_c}.$$

Since λ_s , G_0 , P_0 , and k are constants and r varies slowly in the range considered, we obtain approximately

$$\lambda_p = \text{constant}(\gamma)^{R_p/R_c}. \quad (11)$$

From the Eq. (11) we are able to estimate the value of R_c by substituting the empirical values of the power in Formulas (6) and (7). For general hydrocarbons the value of R_c is calculated to be $1.1a_0$. From the curve shown in Fig. 2 where the slope of the curve is steeper for a large radius, obviously the Ps atom is less compressed in oxygenated short chain hydrocarbons than other general organic compounds.

B. A Simple Square Well Model

We shall again show that the relationship between pickoff rate and surface tension can be obtained by using an extra simple square well model. The square well used here will be the type shown in Fig. 3(c) in a spherical geometry. It is assumed that o-Ps is confined inside a rigid sphere of radius R_0 . On the wall of the sphere there is a layer of electron cloud of thickness $R_0 - R_1$, and the o-Ps annihilation rate in this electron cloud is 2.0 nsec^{-1} (one-fourth of p-Ps annihilation rate). Then the pickoff rate will be

$$\lambda_p = 2.0G,$$

where G is the fraction of the wavefunction inside the electron cloud. The values of G for various values of R_0 , R_1 can be calculated easily from the formula

$$G = R_1/R_0 - \sin(2\pi R_1/R_0)/4\pi \quad (12)$$

obtained by the standard methods of quantum mechanics.

The value of R_1 can be estimated by using the equilibrium radius between the pressure of the Ps atom and the pressure applied by the surface tension of the surrounding molecules as a basis. The attractive force between the Ps atom and the surrounding molecules will further reduce the radius of the cavity. We can reasonably assume the extent of the reduction of radius (ΔR) due to this effect is the same for similar compounds. The two best fit curves are obtained with $\Delta R = 1.70a_0$ and $R_0 - R_1 = 0.43a_0$ for general organic compounds and $R_0 - R_1 = 0.40a_0$ for oxygenated short chain hydrocarbons. They are also shown in Figs. 4(a) and 4(b) as the dashed lines. The closeness of these curves to the experimental data are quite encouraging. This implies that this crude model is actually not very far away from the exact model.

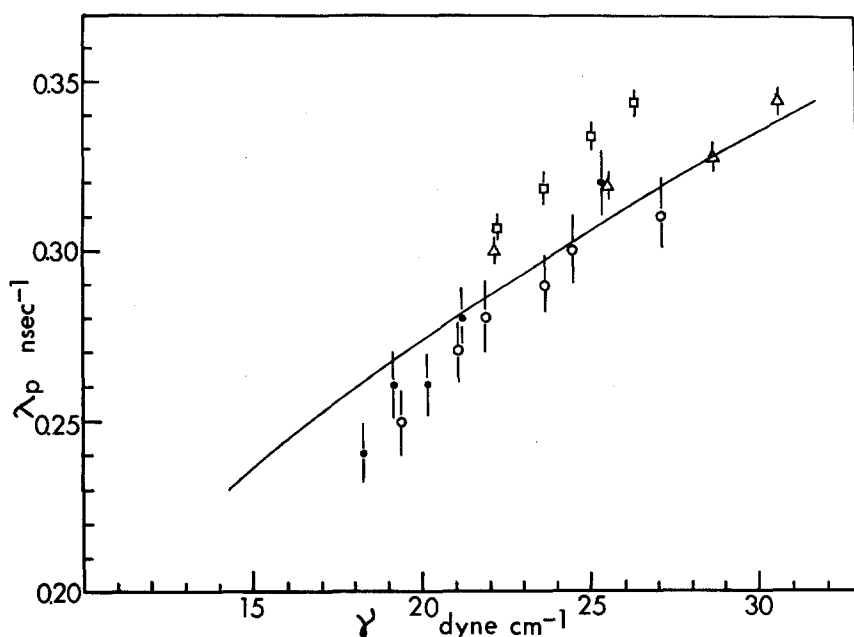


FIG. 5. The relationship between Ps pickoff rate and surface tension for several liquids at various temperatures (dot, *n*-octane; circle, *n*-hexadecane; triangle, benzene; square, cyclohexane).

The above calculation further indicates that the behavior of Ps atoms in liquids is highly dependent on the intermolecular forces; the repulsive exchange force, the attractive van der Waals force between the Ps atom and the surrounding molecules, and the pressure of the surrounding molecules applied to the Ps atom. The reduction in the amount of $\Delta R = 1.7a_0$ of radius of the cavity occupied by the Ps atom due to the effect of the attractive van der Waals force between the Ps atom and the surrounding molecules may be a little too large. If the effect of polarization is included, this amount is expected to be reduced. The penetration of the wave of the Ps atom into the surrounding molecules is not very deep. It is only $0.43a_0$ or 0.26 \AA in general organic compounds (liquids). The extent of the attractive van der Waals force between the Ps atom and the surrounding molecules of oxygenated hydrocarbons is smaller than that between the Ps atom and the surrounding molecules of simple hydrocarbons. It seems that because of the formation of hydrogen bonds the attractive interaction between the hydrogen atom in the surrounding molecules and the Ps atom is reduced.

C. Temperature Effect

In a short temperature range the surface tension of a liquid has a linear relationship with the temperature,²¹

$$\gamma = \gamma_0 + \epsilon(T_0 - T), \quad (13)$$

where γ_0 , T_0 , and ϵ are constants. Since in a short range of surface tension the relationship between the pickoff rate and surface tension can also be approximated as a simple linear dependence obviously we can write

$$\lambda_p(T) \simeq \lambda_i + \theta(T_0 - T), \quad (14)$$

where λ_i , T_0 , and θ are constants, provided there are no phase changes within the temperature range.

Alternatively, we can use Formula (6) or (7) if the values of the surface tension at various temperatures are known. Several examples are shown in Fig. 5 where the values of the pickoff rate of o-Ps in *n*-octane and *n*-hexadecane,²⁶ cyclohexane,²⁷ and benzene²⁸ measured at various temperatures are plotted against the surface tensions at these temperatures. The curve represents Formula (6). The departure of the data from Formula (6) is obviously due to the uncertainties involved in the accurate determinations of the pickoff rate. Thosar and his colleagues²⁶ tried to establish a relationship between the pick-off rate and viscosity of the medium. Two curves had to be used for two liquids, *n*-octane and *n*-hexadecane. If they had used surface tension instead of viscosity a simple relationship could be obtained.

D. Pressure

The dependence of pickoff rate of o-Ps in a liquid on external pressure can be obtained from Eq. (10) as

$$\lambda_p(P) = \lambda_0[1 + (P_e/P)]^n, \quad (15)$$

where P_e is the external pressure and $n = R_p/R_c$. Since at a constant temperature the compressibility coefficient is defined as

$$\kappa = (1/\Delta P)(\Delta V/V),$$

we obtain

$$\lambda_p = \lambda_0[1 + C(\Delta V/V)]^n \quad (16)$$

by substitution with C a constant. This formula is very similar to the one $\tau = \tau_0(1 - 5\Delta V/V)^{0.87}$ derived by

Wilson and his colleagues.²⁹ When the values P_e/P or $\Delta V/V$ is small, Eqs. (15) and (16) can be reduced to

$$\lambda_p = \lambda_0(1 + \text{const} P_e) \quad (17)$$

or

$$\lambda_p = \lambda_0(1 + \text{const} \Delta V/V). \quad (18)$$

Actually, Wilson and his colleagues²⁹ fit the experimental data in a formula

$$\tau = \tau_0 \exp(-\mu \Delta V/V).$$

This formula is as good an approximation as Formula (18) when the values of $\mu \Delta V/V$ is small.

E. Other Properties of the Liquid

1. Polarizability

Gray, Cook, and Sturm¹⁸ have related the pickoff cross sections to the polarizabilities of the liquids. The cross section is defined as

$$\langle \sigma v \rangle = (V_m/N_0)\lambda, \quad (19)$$

where N_0 is Avogadro's number. The pickoff cross section has been found to be a linear function of the electron polarizability P_e . Furthermore they have also found that the pickoff cross section of a molecule is a constitutive property of the radicals which form the whole molecule.

In the last section we mentioned the relationship between surface tension and internal pressure, latent heat of vaporization and the van der Waals constant a . Approximately we have

$$\Delta H_v/V_m = C(\gamma/V_m^{1/3}),$$

and

$$\Delta H_v = a/V_m,$$

with C a constant. Combining them we have

$$\gamma \propto a/V_m^{5/3}. \quad (20)$$

For simple liquids the van der Waals a is related to polarizability α by the formula²¹

$$a \propto \alpha^2 I/b, \quad (21)$$

where α is the polarizability, I is the ionization constant, and b the van der Waals constant b . Combining Formulas (20) and (21) we have

$$\gamma \propto \alpha^2 I/b V_m^{5/3}. \quad (22)$$

Replacing this in the Formula (6) we obtain

$$\lambda_p \propto \alpha(I/b) V_m^{5/6}.$$

Since the values I and b are slowly varying and $\frac{5}{6}$ is very close to 1 and $\alpha = P_e$, the above formula can be approximated as

$$\lambda_p/V_m \propto P_e. \quad (23)$$

Therefore, a linear relationship between the pickoff rate and polarizability of the liquid medium is expected,

particularly for a series of homologues of hydrocarbons. Since the electron polarizability of a compound is a constitutive property of simple compounds,³⁰ naturally the pickoff rate will be a constitutive property.

2. Cohesive Energy Density

As shown in the last section cohesive energy density is related to surface tension by the following empirical formula²²:

$$\delta = 4.1(\gamma/V_m^{1/3})^{0.43}$$

and

$$\text{CED} = \delta^2 = (\Delta H_v - RT)/V_m.$$

Substituting the above formula into Formula (6) we obtain approximately

$$\lambda_p \propto \delta V_m^{1/6}$$

and

$$\lambda_p \propto (\text{CED})^{1/2} V_m^{1/6}. \quad (24)$$

3. Free Volume

The relationship between the free volume v_f and surface tension γ of a liquid is not so direct as the parameters described before. In the Eyring equation of state,³¹

$$[P + (a/V_m^2)](1/2v_f^{1/3}v^{2/3}) = kT, \quad (25)$$

the free volume is given approximately by

$$v_f = 8(V^{1/3} - d)^3,$$

where d is the diameter of the assumed hard sphere molecules. Substituting Formula (20) into Formula (25) we obtain

$$\gamma v_f^{1/3} \propto RT/V_m^{1/3} \quad (26)$$

after some rearrangements. For ordinary liquids free volume v_f increases with, but surface tension γ decreases with, increasing of temperature. In practical application,^{12,31,32} free volume is correlated to the thermal expansion coefficient β of the substance by

$$V_m = V_m' + \beta T, \quad (27)$$

with

$$V_f = \beta T,$$

where V_m' is the molar volume at a specified temperature. Since both free volume and surface tension follow an approximately linear relationship with temperature, the pickoff rate of o-Ps in liquid media should bear a linear relationship to the free volume. However, since the value of V_m' is somewhat arbitrarily defined, the absolute values of the free volume of various liquids at a definite temperature and a definite pressure can not be obtained as easily and accurately as the surface tension. Therefore, free volume is only suitable to be used as a parameter in correlation with the pickoff rate of o-Ps in a single medium at various temperatures.

In the calculations described in Sec. III.B an increase in free volume corresponds to an increase of R_0 of the

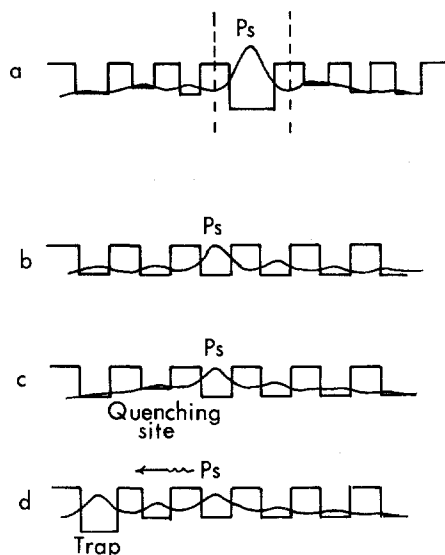


FIG. 6. Schematics of various possible square well type potential barriers.

cavity. This corresponds to a decrease of internal pressure applied to the cavity occupied by the Ps atom and a decrease of surface tension. Hence, free volume has been used in the past with some theoretical success in explaining the pickoff quenching of o-Ps in molecular substances.^{10,12}

IV. DIFFUSION

In the last section it has been shown that there exist intermolecular forces between the Ps atom and the surrounding molecules. The "pickoff" is principally an outcome of the dispersion force. This explains why the pickoff rate of o-Ps is highly related to the surface tension instead of viscosity of the liquids. Since the Ps atom is a very light particle, the association of the Ps atom to its surrounding molecules is not as tight as other free radicals, atoms, or molecules in liquids. Nevertheless, this type of association is there. Therefore, we can consider the Ps atom is at least loosely "caged" in molecular liquids. The motion of Ps atoms in liquids should be more or less controlled by the motion of the surrounding molecules. If there is a quenching agent in the liquid medium the Ps reaction will be "diffusion" controlled.

This has been found to be the case for Ps reactions with oxygen or iodine in various organic liquids.^{33,34} If we disregard the various interactions involved in Ps-oxygen or Ps-iodine reactions and consider Ps moving much faster than oxygen or iodine in these organic liquids we obtain the diffusion coefficient D of the Ps atom in ordinary organic liquids as roughly

$$D \approx 1 \times 10^4 (1/\eta) \text{ cm}^2 \text{ sec}^{-1}, \quad (28)$$

where η is the viscosity in poise.

The above argument is further supported by the evidence that the activation energies of these Ps reactions are of the order of those of the viscosities of the solvents.^{33,35}

The diffusion coefficients of the Ps atom in most liquids are of the order of $10^5 \text{ cm}^2 \text{ sec}^{-1}$, which is much greater than that in solids, for example, about $10^{-4} \text{ cm}^2 \text{ sec}^{-1}$ in silica. This explains why many powerful o-Ps quenching agents in gaseous or liquid media, such as oxygen, iodine, and others become ineffective when the medium is solidified. The reaction rate is reduced more than 10^5 times. This is one of the effects which must be taken into consideration in the investigation of positron or positronium annihilation in solids. In solids, because of the immobility of the molecules, the diffusion of the Ps atom is quite different from the diffusion of the Ps atom in liquids. This phenomenon will be further discussed in the next section.

V. MOLECULAR SOLIDS

Many of the above arguments and results can be applied to molecular solids with minor modifications; but there is a major distinction between molecular liquids and molecular crystalline solids. In molecular liquids the Ps atom is localized in the occupied cavity created by the balance of various molecular forces. The Ps wave and the potential barrier around the Ps atom can be illustrated schematically as in Figure 6(a). The localized Ps atom is not stationary. It moves very fast. However, when it moves the potential well or the cavity also moves with it. This motion is "diffusion" controlled, or it is controlled by the viscosity of the liquid. Therefore, if only the Ps atom is concerned, it can be treated as if it is stationary. One must bear in mind, though, that if a simple type of potential well is used in treating the behavior of the Ps atoms in condensed molecular media, the type of potential used for pickoff is different from the type of potential used for diffusion.

In pure crystalline molecular solids, the Ps wave and the potential barrier around the Ps atom can be illustrated schematically as in Fig. 6(b). If the Ps atom still does exist in the interstitial site of the lattice, under favorable conditions the Ps atom is only localized to a certain extent. The appearance of the Ps atom at the interstitial site does not change the potential profile substantially. The motion of the Ps atom in the lattice is just diffusion.

If a quenching site for Ps atoms does exist in the lattice near the location where the Ps atom is temporarily localized, the effect is not significant. As shown in Fig. 6(c) a quenching site is represented by a smaller potential well. The Ps atom tends to avoid instead of occupy the quenching site.

If a trap site for Ps atoms does exist in the lattice near the location where the Ps atom is temporarily localized, the effect can be significant. As shown in Fig. 6(d) the trap site is represented by a larger potential well. First, the Ps atom may be tunneling through the other barriers

and fall into the trap. Secondly, once the Ps atom is in the trap it will be highly localized there. This can explain why a small amount of certain types of defects in solids will give a long lifetime component for Ps annihilation which does not appear in pure crystalline solids.

In many pure crystalline molecular solids, such as anthracene, there exists no long lifetime component in positron annihilation lifetime spectra.²⁸ It seems that in these media the high lattice energy of the molecules in the lattice excludes the possible formation of Ps atoms.

However, in almost all molecular solids in glass form, such as various polymers, there exists a long lifetime component. This can be explained as follows: The chains of the polymers are flexible enough to allow the Ps atom to force out a cavity for itself to occupy. Therefore, the pickoff rates of o-Ps in these glass solids are more like those in liquids than those in crystalline solids.

VI. ANGULAR CORRELATION

In the method of angular correlation the appearance of a narrow component in the angular correlation curve has been generally attributed to the annihilation of p-Ps. The reason is very simple. The positron-electron pair in the p-Ps atom in free space possesses no momentum with respect to its center of mass. The annihilation of p-Ps atoms will give an angular distribution in respect to a momentum distribution corresponding to their translational energy distribution. If the p-Ps atoms are thermalized the angular deviation of the two quanta from the colinear line will be small.

In a condensed molecular medium the above situation may be modified by other effects. First, the energy of the Ps atoms in there is not really at the level of the ground state in a free space. The confinement of the Ps atom reduces its ionization potential. This amount of the reduced potential energy can be interpreted as having been changed into the vibrational energy of the Ps atom, or the positron-electron pairs with respect to its average position. Therefore, in molecular liquids the energy distribution corresponding to the narrow component should be higher than the thermal energy even though p-Ps atoms have been thermalized before its annihilation. This broadening effect is greater for p-Ps atoms in a liquid of higher surface tension than in a liquid of lower surface tension. A similar theory has been suggested for Ps atoms in solids.³⁶

The above theory has been found to be in agreement with the experimental results.^{37,38} Trumpy³⁷ has mentioned that the sharpness of the narrow component varies from one water solution to another water solution. The Ps atoms that give rise to this "narrow" component in water have been found to possess energies of about 0.3 eV.^{36,38} The Ps atoms that give rise to the narrow component in *n*-alkanes have also been found to possess energies of about 0.3 eV.³⁹

There is another effect which must be taken into consideration. This is the reaction or interaction, other than the pickoff, between p-Ps atoms and the medium molecules. This effect has also been pointed out by Trumpy.³⁷

In molecular solids, particularly the crystalline solids, the situation certainly will be different. As a whole the pickoff effect will broaden the narrow component somewhat. Under certain conditions, as mentioned before, Ps atoms may not be formed. However, if defects exist in the solid, the entire picture may be altered. This is particularly so for p-Ps atoms because of their short mean life of 0.125 nsec. The motion of the Ps atom in the lattice can create defects, particularly temporary defects.⁴⁰ Any short lived defect sites, either already in existence or created by the presence of the Ps atom with a mean life of about 0.1 nsec, will not affect the annihilation of o-Ps to a great extent but will affect the annihilation of p-Ps. If the defect sites are sufficiently large to accommodate p-Ps atoms, under very little pressure p-Ps atoms may annihilate in a condition very close to that in a free space. The result is a very narrow component if the p-Ps atoms are thermalized. This can happen particularly at low temperatures where the recombination rates of the defects are slower. Certainly, these defects created in various media are not all expected to be large vacancies for p-Ps atoms. This may well be the reason for many seemingly hard to explain experimental results.^{36,38,41}

VII. SUMMARY

The behavior of the Ps atom in molecular liquids is investigated. The Ps atom is highly localized in a cavity created by the balance of various intermolecular forces inside the liquid. Since the cavity moves with the Ps atom, the Ps atom can be treated as being stationary in the potential well of the cavity if only the interactions between the Ps atom and the medium molecules are considered. A potential well which is suitable for a highly localized particle will be a good choice in the calculation of the pickoff rate of o-Ps.

The pickoff rates of o-Ps in various organic liquid compounds are found to have a very simple empirical relationship with the values of the surface tension of the liquids. An investigation has found that the empirical relationship between the pickoff rate and surface tension of the liquids has, indeed, a theoretical foundation. Another theoretical calculation using an extra simple square well model has also produced a relationship very close to the empirical one. Here, surface tension represents a form of pressure exerted onto the Ps atoms directly and indirectly by the surrounding molecules. The dependence of the pickoff rate in molecular liquids to temperature or pressure change can also be explained by the above theory.

From the relationships between surface tension and other properties of the liquids, unexplained relationships between the pickoff rate and polarizability,

cohesive energy density, free volume, and others have also been explained satisfactorily.

The diffusion rates of the Ps atom in liquids are very fast. The Ps reactions with a quenching agent in an inert solvent are "diffusion" controlled.

In molecular glass solids the behavior of the pickoff rate of the o-Ps atom will be very similar to that in liquids. In crystalline molecular solids the situation will be quite different. The existence of a Ps trap site in crystalline molecular solids will be noticed more significantly than the existence of a Ps quenching site.

It is hoped that this report will serve as an interesting stimulant for further research work. There are still many unanswered questions. We will raise a few of them as examples. What is the exact nature of the intermolecular force between the Ps atom and its surrounding molecules? Which type of the more complicated potential well is the best or better one in the calculation of pickoff rate of o-Ps in liquids? How can we find the exact reaction rates of various Ps or positron reactions in liquids? What is the exact condition for the formation of Ps atoms in solids? And last, there is a strong need for more precise and reliable experimental data. Without the experimental work done by Gray, Cook, and Sturm,¹⁷ it would have been extremely difficult for us to make this systematic analysis.

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