

of a uniform distribution of Frenkel defects for bulk property studies without the limitation of sample dimensions by electron range. Kinchin and Pease¹ have suggested an additional process, namely, atomic displacement by recoil during photoelectron ejection. For photon energies involved here however, the electrons are ejected predominantly in the forward direction with respect to the absorbed photon¹⁰ and hence the momentum transferred to the emitting atom is usually so small that the recoil energy is less than the displacement energy in the case of Ge.

The necessary information for calculating the contributions of the Compton electrons and photoelectrons to σ_γ are summarized by Bethe and Ashkin.¹¹ Using the expression for the electron displacement cross section based on the theory of Mott¹² as modified by McKinley and Feshbach¹³ and Dugdale and Green,¹⁴ assuming an E_d of 25 ev, and integrating over both the energy

distribution and range of electrons, one obtains a total value of σ_γ for both processes of $\sim 1.3 \times 10^{-26}$ cm². In view of uncertainties in photon flux and the approximations in the calculation, this value is considered to be in satisfactory agreement with the observed σ_γ . A recent determination of E_d for Ge indicates that 23 ev is perhaps its upper limit.¹⁵ This smaller value of E_d would increase the calculated σ_γ by several percent.

An interesting consequence of the calculation is that, contrary to expectation, the contribution of the photoelectrons is found to be approximately the same as that of the Compton electrons. This results from the fact that the electron displacement cross section increases rapidly with energy and the energy of photoelectrons is essentially that of the absorbed photon whereas the effective Compton electrons have energies ranging from the threshold value to a maximum which is appreciably less than the photon energy (0.54 to 1.12 Mev).

ACKNOWLEDGMENTS

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¹⁵ J. J. Loferski and P. Rappaport, Phys. Rev. **98**, 1861 (1955).

¹⁰ A. Hedgran and S. Hultberg, Phys. Rev. **94**, 498 (1954).

¹¹ H. A. Bethe and J. Ashkin, *Experimental Nuclear Physics* edited by E. Segrè (John Wiley and Sons, Inc., New York, 1953), Vol. 1, p. 166.

¹² N. F. Mott, Proc. Roy. Soc. (London) **A124**, 425 (1929); **135**, 429 (1932).

¹³ W. A. McKinley and H. Feshbach, Phys. Rev. **74**, 1759 (1948).

¹⁴ R. A. Dugdale and A. Green, Phil. Mag. **45**, 163 (1954).

Free-Radical Quenching of Positron Lifetimes*

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The annihilation lifetime of positrons stopping in benzene has been measured as a function of the percentage of added free radical, diphenylpicrylhydrazyl. The long component of the complex annihilation curve quenches from 2.67×10^{-9} sec in pure benzene to 5.3×10^{-10} sec at a 3% free radical concentration. An annihilation model following Bell and Graham's assumptions is discussed, postulating the partial formation of bound positron states prior to annihilation. The long lifetime is regarded then as a measure of the conversion rate from triplet to singlet states due to collisions of the positron system with the unpaired electrons of the free radical. The experimental points yield, using such a model, a conversion cross section of $\sigma = 1.18 \times 10^{-17}$ cm².

INTRODUCTION

THE first detailed study of the lifetimes of positrons in solids and liquids was reported by Bell and Graham.¹ Their result can be summarized as follows:

In metals and crystalline solids, positrons annihilate with a single mean lifetime $\tau_1 = (1.5-2) \times 10^{-10}$ sec. This short lifetime seems to be almost independent of the particular material used. In some amorphous non-

metals, and in most liquids, about 70% of the two-photon annihilation proceeds via a short lifetime of the order of τ_1 in metals, and the rest via a longer "anomalous" component, τ_2 ($\tau_2 \cong 2 \times 10^{-9}$ sec). The τ_2 decay time is sensitive to the thermodynamical parameters of the solid material, such as temperature, phase, and order-disorder.

The exact nature of this anomalous lifetime is still not well understood.

Bell and Graham postulate the formation of bound states (similar to positronium in gases) in order to explain the behavior of the τ_2 component. This lifetime can be regarded then as a measure of the conversion

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‡ National Science Foundation Predoctoral Fellow, 1955-1956.

¹ R. E. Bell and R. L. Graham, Phys. Rev. **90**, 644 (1953).

rate from triplet to singlet spin states of the bound positron system due to collisions with the atoms (electrons) of the sample material. Dixon and Trainor² point out some difficulties with the above explanation, and interpret the experimental results in terms of annihilation from excited ($2S$) states of positronium. Since neither of these theories is quantitative, it is clear that there is a need for more experimental data pertaining to the exact parameters influencing the τ_2 component. If such experiments could distinguish between the above assumptions and could place one or the other on a firmer quantitative ground, lifetime measurements would form a useful tool in the study of the solid and liquid states.

The existence of some sort of bound state before annihilation has been substantiated by experiments^{3,4} correlating a higher 3γ annihilation rate with the appearance of the τ_2 component.

The recent experiments of Hereford and Wagner⁵ correlate the temperature dependence of the τ_2 component, as observed by Bell and Graham, with a nearly linear temperature dependence of the 3-photon rate down to liquid helium temperatures. Their results are also indicative of a strong phase dependence, the temperature effect, if any, being much weaker in the liquid state.

Complementary to an increase in the 3-photon rate, one expects a small decrease in the absolute 2γ rate. This effect has been observed by Pond,⁶ by comparing the total 2-photon rate in the material to be studied with the rate in a metal, known from Bell and Graham's results not to exhibit a τ_2 decay component. Since the resolving time of the coincidence circuit used was long compared to the annihilation lifetimes, Pond's data yields the integrals of the time delay curves as measured by the fast-coincidence method. Using the same technique of absolute 2γ rate comparison, Pond has observed the change of the annihilation rate in benzene as a function of an added organic free radical, diphenyl picryl hydrazyl (DPH) concentration. This effect ($\sim 0.6\%$) indicated a possible large quenching of the actual lifetime, recalling the triplet positronium quenching in gases due to NO addition.⁷ Since the addition of the free radical allows one to change the concentration of unpaired electrons in the medium, the detailed knowledge of the lifetime change *vs* DPH concentration can be of value in evaluating the possible annihilation models.

The present experiment,⁸ consisting of the direct measurement of τ_2 *vs* concentration of DPH, is part

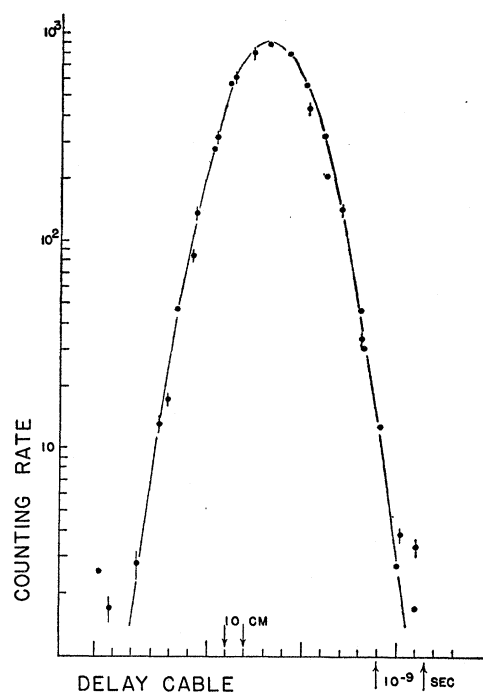


FIG. 1. Positron annihilation in aluminum. The solid line corresponds to the Gaussian $A \exp(-1.19 \times 10^{-3} L^2)$, where L is in cm of delay. This curve is used in the discussion of data as the resolution curve of the apparatus.

of a set of experiments designed to study independently the parameters influencing τ_2 . A detailed knowledge of these parameters might allow one to use the anomalous lifetime component as a tool in the study of the solid and liquid state of matter.

EXPERIMENTAL SETUP AND RESULTS

The experiment consisted of placing two thin-walled (0.0002 in.) aluminum containers around a Na^{22} source, and measuring the τ_2 annihilation lifetime of positrons in purified benzene with different DPH concentrations.

Two stilbene crystals mounted on RCA 6342 type photomultiplier tubes faced the benzene containers. The fast-coincidence circuit was of a modified Bell and Graham type design; distributed Hewlett-Packard wide-band amplifiers cut off 404A type pentodes. The photomultipliers also had side channels with integral discriminators biased to accept only a narrow upper range of the 1.28-Mev and 0.51-Mev γ rays, respectively. The resolving time of the circuit was approximately 2.3×10^{-9} sec with a drop-off rate for coincidence pulses of 2.2×10^{-10} sec. The lifetime curve for positron annihilation in aluminum indicated that the drop-off rate due to the intrinsic resolution of the crystals and counters of our circuit was larger than the corresponding lifetime of 1.5×10^{-10} sec as measured by Bell and Graham¹ by their beta-ray spectrometer method. We have therefore assumed throughout our discussion that the resolution of the apparatus is identical to the delay

² W. R. Dixon and L. E. H. Trainor, Phys. Rev. **97**, 733 (1955).

³ S. De Benedetti and R. T. Siegel, Phys. Rev. **94**, 955 (1954).

⁴ R. L. Graham and A. T. Stewart, Can. J. Phys. **32**, 1678 (1954).

⁵ R. T. Wagner and F. L. Hereford, Phys. Rev. **99**, 593 (1955).

⁶ T. A. Pond, Phys. Rev. **93**, 478 (1954).

⁷ M. Deutsch and E. Dulit, Phys. Rev. **84**, 601 (1951).

⁸ Preliminary results of this experiment were reported at the Toronto Meeting of the American Physical Society, 1955 [S. Berko and A. J. Zuchelli, Phys. Rev. **99**, 1652(A) (1955)].

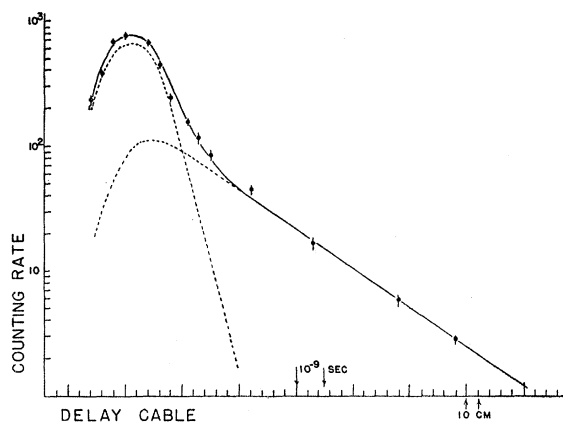


FIG. 2. Experimental points for annihilation in pure benzene. The theoretical curve corresponds to 31% of all positrons annihilating from bound states.

curve obtained using annihilation in aluminum (properly displaced of course to take into account the centroid shift corresponding to τ_1 in aluminum). Figure 1 shows this aluminum curve and a Gaussian fit to the experimental points. The fit is fairly good, within our experimental precision, and we shall use it for the discussion of the delay curves, thereby avoiding the necessity of numerical integrations. The Gaussian is given by

$$R(L) = A \exp(-1.19 \times 10^{-3} L^2),$$

where L is the time delay as measured in cm of delay cable with a signal velocity $= 2.52 \times 10^{10}$ cm/sec.

The delay curve, as obtained for pure benzene, is plotted in Fig. 2. The measurement yields a τ_2 lifetime ($1/e$ value) of $(2.67 \pm 0.08) \times 10^{-9}$ sec. We shall discuss the percentage of all positrons decaying via τ_2 and the theoretical curve of Fig. 2 in Sec. III.

The result of the addition of the free radical is plotted in terms of a set of decay curves with varying DPH concentrations in Fig. 3. For sake of clarity, only part of all measured curves has been plotted. It can be seen that τ_2 quenches quite rapidly, leaving the total area under the delay curves the same within experimental accuracy, thereby confirming Pond's results. The exact variation of τ_2 vs DPH concentration is seen in Fig. 4. The theoretical curve plotted on the graph will be discussed in the next section.

III. INTERPRETATION OF RESULTS

Dixon and Trainor² point out that if one assumes a fast capture rate into bound states, resulting in annihilation solely from bound states, the experimental percentage of the number of positrons decaying with τ_2 is in contradiction with the percentage as derived from such a model (see appendix and table in reference 2). It is mainly on this contradiction that they base their criticism of the Bell and Graham triplet-singlet conversion model. They then proceed to assume a model whereby the τ_2 component is due to annihilation from

the $2S$ excited states of positronium. [The probability for annihilation depending on $\bar{\psi}(0)\psi(0)$ which decreases as the cube of the principal quantum number for S states.] This assumption however, seems to necessitate infinitely fast conversion rate between the spin triplet and spin singlet states; one would otherwise observe four, instead of two lifetimes, corresponding to the finite conversion rates between the triplet and singlet states.

The free radical used in the experiment, diphenyl picryl hydrazyl, has been extensively studied⁹; it exhibits the sharpest paramagnetic resonance curve, yielding a g value of $g=2.004$. Negligible energies are required to invert the spin of the odd electron. It is unusually stable because of electron resonance. The strong quenching of τ_2 due to these unpaired electrons seems to contradict the necessary assumption of infinite triplet-singlet conversion rate of the $2S$ model. This model would require a strong $2S-1S$ conversion in order to explain the experimental result; it becomes, however, hard to understand why a spin-unpaired electron should be necessary for such a process. We conclude, therefore, that the Bell and Graham model yields a more natural explanation of the quenching process.

In the following, we would like to point out how such a model could yield quantitative results, and how Dixon and Trainor's objection to the I_1/I_2 ratio can be resolved by assuming that the main part of τ_1 is due to annihilation of free rather than bound positrons. Following Dixon and Trainor's notation, let $P_f(t)$ be the probability of finding a free positron, at time t , in the solid; $P_s(t)$ and $P_T(t)$ the probability of finding singlet and triplet "positronium" states. Let λ_f , λ_s , λ_T be the annihilation rates of free positrons and singlet and triplet positronium; let γ_c be the capture rate into bound states, and γ the conversion rate.

In order to formulate such a model, one has the following choices: (1) The capture rate, γ_c is constant in time, and of the same order of magnitude as the

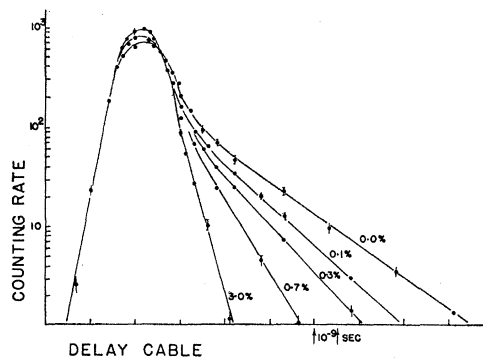


FIG. 3. Representative set of experimental delay curves as a function of free radical concentration.

⁹ Hutchison, Pastor, and Kowalsky, J. Chem. Phys. 20, 534 (1952).

annihilation rate λ_f . Capture and annihilation are therefore competing processes. (2) The capture rate is very fast but strongly velocity-dependent, the capture process reaching a maximum when the positrons are unable to ionize the atoms (molecules), but still can capture (similar to the Ore region in gases). Assuming that the slowing down process of positrons is fast (10^{-12} – 10^{-11} sec), one can then say that the fate of a positron (whether it will annihilate via a free state or form positronium) is decided within these times, capture and annihilation being subsequent and not competing processes.

Although one has good theoretical reasons for believing that the second assumption approximates closer to reality, we shall follow up both possibilities. Using assumption (1), the differential equations governing P_f , P_s , and P_T are

$$\begin{aligned}\dot{P}_f &= -(\lambda_f + 4\gamma_e)P_f, \\ \dot{P}_s &= \gamma_e P_f - (3\gamma + \lambda_s)P_s + \gamma P_T, \\ \dot{P}_T &= 3\gamma_e P_f + 3\gamma P_s - (\gamma + \lambda_T)P_T.\end{aligned}\quad (\text{A})$$

The reasonable assumption has been made that the dissociation rate of positronium (into free particles) is negligible compared to the annihilation rates. The second assumption, neglecting annihilation during slow-down, yields two separate systems of equations:

$$\begin{aligned}\dot{P}_f &= -\lambda_f P_f, \quad \text{and} \quad \dot{P}_s = -(3\gamma + \lambda_s)P_s + \gamma P_T, \\ \dot{P}_T &= 3\gamma P_s - (\gamma + \lambda_T)P_T.\end{aligned}\quad (\text{B})$$

Equations (B) are identical to those of Dixon and Trainor.² One can solve the system (A) with the initial conditions $P_f(0)=1$, $P_s(0)=0$, $P_T(0)=0$, and the system (B) with $P_f(0)=I_1$ and $P_s(0)=\frac{1}{4}I_2$, $P_T(0)=\frac{3}{4}I_2$, where $I_2=1-I_1$. The solutions are

$$\begin{aligned}P_f(t) &= A_f e^{-\lambda_1 t}, \\ P_s(t) &= A_s e^{-\lambda_1 t} + B_s e^{-\lambda' t} + C_s e^{-\lambda_2 t}, \\ P_T(t) &= A_T e^{-\lambda_1 t} + B_T e^{-\lambda' t} + C_T e^{-\lambda_2 t},\end{aligned}\quad (\text{A}')$$

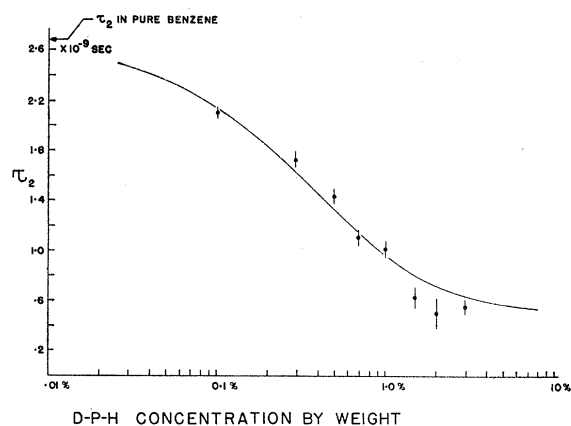


FIG. 4. Variation of the long-lifetime component with concentration of DPH free radical. The theoretical curve has been fitted by $\gamma_f = N\sigma v$, yielding $\sigma v = 9.7 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$.

and

$$\begin{aligned}P_f(t) &= A_f' e^{-\lambda_1 t}, \\ P_s(t) &= B_s' e^{-\lambda' t} + C_s' e^{-\lambda_2 t}, \\ P_T(t) &= B_T' e^{-\lambda' t} + C_T' e^{-\lambda_2 t}.\end{aligned}\quad (\text{B}')$$

Elementary computations yield all coefficients as functions of $(\gamma_e, \gamma, \lambda_s, \lambda_T)$ and $(I_1, \gamma, \lambda_s, \lambda_T)$, respectively. The system (A) contains three rates, although they cannot be called 3 independent "lifetimes," since not all coefficients A, B, C are positive. Both models lead to the same λ' and λ_2 . We identify λ_2 with the reciprocal of the long-lifetime component τ_2 .

If one assumes λ_s and λ_T to be the annihilation rates as computed for positronium in vacuum, one can match $\lambda_2(\lambda_s, \lambda_T, \gamma)$ to the experimental λ_2 in benzene; solving then for γ one obtains a conversion rate of $\gamma = 4.3 \times 10^8 \text{ sec}^{-1}$. It is questionable whether the λ_2 rate in pure benzene is due to a genuine triplet-singlet conversion. Since one does not have spin-unpaired electrons, the effect might rather be due to the annihilation of positrons in collisions between positronium and electrons of appropriate spin direction in benzene (see Garwin's¹⁰ suggestion).

By introducing, however, the free radical, the genuine triplet-singlet conversion can take place via the unpaired DPH electrons. One can write $\gamma = \gamma_0$ for benzene and attribute the DPH effect to γ_f by setting $\gamma = \gamma_0 + \gamma_f$.

The theoretical τ_2 vs γ_f curve can be fitted to the experimental τ_2 vs DPH concentration points by setting $\gamma_f = N\sigma v$; N is the number of unpaired electrons per cm^3 introduced by the free radical, σ is the conversion cross section, and v is the relative velocity of the positron system and the DPH molecules. This fit has been plotted in Fig. 4. It yields $\sigma v = 9.7 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$. If one assumes that the positron system is a genuine positronium atom moving with thermal velocity, one obtains $\sigma = 1.18 \times 10^{-17} \text{ cm}^2$ for the triplet-singlet conversion cross section. This value is in good agreement with Pond's results, after correcting for the difference in the experimental τ_2 for pure benzene and his assumed value for τ_2 . σ is of the same order of magnitude as the conversion cross section of positronium in gases due to the addition of NO. The large value of σ indicates that the effect is due to a spin exchange during Coulomb collisions, rather than to a paramagnetic quenching process. More detailed computations would be needed, however, to completely rule out the latter effect.

Once σ has been determined, the remaining parameters γ_e or I_1 in the respective models can be obtained by the following process: The pure benzene curve yields $\lambda_1 = 2.7 \times 10^9 \text{ sec}^{-1}$ for the fast annihilation rate. In the lifetime experiment, one observes the composite theoretical curve $\lambda_f P_f(t) + \lambda_s P_s(t)$ properly folded into the resolution curve of the apparatus. One can find explicit expressions for this folded curve in terms of

¹⁰ R. L. Garwin, Phys. Rev. **91**, 1571 (1953).

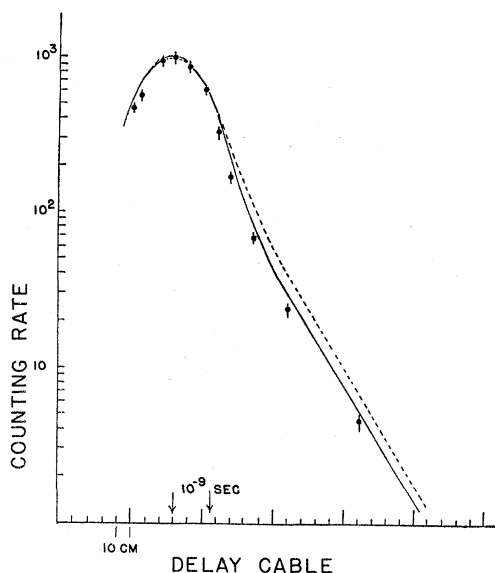


FIG. 5. Delay points for the 0.7% DPH concentration. The solid and broken curves correspond to the two different annihilation models discussed in the text.

error integrals, by using the Gaussian fit to the delay curve in aluminum as the resolution curve. The delay curve for benzene can then be fitted by adjustment of the parameter γ_e or I_1 . This fit yields $\gamma_e = 0.18 \times 10^9 \text{ sec}^{-1}$ for model (A) and $I_2 = 0.31$ (31%) for model (B).

The curve plotted in Fig. 2 is such a fit for $I_2 = 31\%$. This value of I_2 leads to 25% of all positrons annihilating with the τ_2 lifetime, $I_1 = 69\%$ annihilating with the τ_1 lifetime from the free state, and about 6% decaying from the singlet state of the bound positron system with a lifetime $(\lambda')^{-1}$. Once I_2 is found, the theory actually predicts that 0.6% of all positrons forming bound states decay via three photons directly from the triplet state, but the precision with which the magnitude of I_2 is determined ($\sim 10\%$) does not allow us a direct comparison of this percentage with Pond's data. The percentage of positrons decaying via the τ_2 component remains constant within the experimental precision of 10%. The ratio of fast to slow component should

be actually corrected, taking into account the percentage of positrons decaying in the vessel walls. This effect is estimated to be, however, less than $\sim 4\%$.

The exact shapes of the experimental curves could decide quantitatively between model (A) and model (B). The lifetime $(\lambda')^{-1}$ is not, however, exhibited directly in these curves, because of the too wide resolution curve of the apparatus; the positrons decaying via λ' add only to the total area under λ_1 .

A comparison of the experimental curves for different DPH concentration with the shapes of the theoretical composite curves for different conversion rates indicates, at least qualitatively, that the results of model (B) fit the experiment better. Figure 5 demonstrates this qualitative fit, by presenting the experimental points together with the theoretical curves as predicted by the two models and folded into the Gaussian resolution, for the 0.7% concentration. These theoretical curves were obtained after determining the parameters of both models by matching to the pure benzene curve. The same qualitative result is obtained by a comparison of the total two-photon rate vs γ_f curve with Pond's experimental points.

We conclude therefore, that a Bell and Graham type triplet-singlet conversion picture, assuming rapid but velocity-dependent capture rates, and only partial positronium formation, can account for the experimental results. It is well understood that the above description is a purely phenomenological one. Theory is needed to account for the magnitude of the experimental rates. The assumption that λ_s and λ_T are, in benzene, identical with the vacuum values for positronium is a questionable one, since they depend on the extent of the ψ function of the system. Even if real positronium is formed in molecular liquids, one expects a different size for the wave function because of the influence of neighboring molecules.

Other experiments, designed to study the parameters influencing the magnitude of the τ_2 component in liquids and solids, and the exact nature of the bound positron system, are being presently performed, and will be reported in a subsequent paper.