

# Microstructural Study of Silica Gel by Positron Annihilation

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Microstructural studies of silica gel powder were carried out using positron annihilation lifetime spectroscopy (PALS) in conjunction with transmission electron microscopy (TEM). It is argued that the two distinct long-lived components found (labeled by  $\tau_3$  and  $\tau_4$ ) may be ascribed to ortho positronium annihilation in microcavities within the grains and intergranular mesoscopic pores, respectively. In the latter type of void, a significant fraction decays via the three-photon mode. A simple physical picture of positronium annihilation in the larger pores is put forward, while the situation vis-à-vis the smaller cavities is shown to be well described by a modification of the currently prevailing model for the pick-off process. The simple parametrization finally arrived at provides a sharpening of the use of the positron as a useful probe for microstructural study of porous substances. It is emphasized that two different positron annihilation mechanisms prevail in the microcavities and mesopores.

## 1. Introduction

The highly mesoporous nature of silica gel powder is extensively exploited in technology, through use as adsorbents, catalyst support, and chromatographic packings. These applications mainly result from their high surface area; tailored particle and pore size; and high thermal, mechanical, and chemical stability.<sup>1</sup> Due to the physical importance of microscopic hole properties in catalytic applications, there has been increased interest in obtaining information on size, distribution, and concentration of micro-cracks, nanocavities, pores, and surface chemical characteristics in these industrial materials. Positron annihilation spectroscopy being an in-situ and a non-invasive method<sup>2</sup> involves minimal interaction with the molecular material under study and yet probes the electronic micro-environment at the site. Positronium (bound state of an electron and a positron), which is formed in molecular substances after positrons impinge on the material, loses energy and is thermalized. Positronium (Ps) may exist in two states, viz., *para*-positronium (*p*-Ps) and *ortho*-positronium (*o*-Ps). Intrinsically (in a vacuum) *p*-Ps annihilates into two gammas with a lifetime of 0.125 ns, while *o*-Ps decays into three gammas with a much larger lifetime of 140 ns. However, in the presence of matter *o*-Ps can decay into two gammas through a process known as pick-off annihilation, whereby the positron in *o*-Ps seeks out electrons with opposite spin in the surrounding medium and annihilates through the two-gamma mode, a component of great utility, enabling its use as a microprobe in the study of molecular materials.<sup>2</sup> Most of these substances have a negative work function for positronium, a feature that is understandable from the repulsive exchange interaction between Ps and the surrounding atoms, which entitles Ps to be described as the “digger and seeker of holes” as it prefers to reside in a region of low

electron density. For this reason Ps has gained importance in the study of the average pore radii of porous substances such as zeolites,<sup>3</sup> porous glasses,<sup>4</sup> polymeric free volumes,<sup>5</sup> and particularly mesoporous<sup>6</sup> substances.

It has become a common practice to adopt the semiempirical model initially designed by Tao<sup>7</sup> and Eldrup et al.<sup>8</sup> to correlate the *o*-Ps lifetime with the average cavity size and microstructure of polymeric materials.<sup>9</sup> This relationship, however, is inadequate when the average life of the positronium is fairly long, i.e., greater than 20 ns.<sup>10</sup> Under such circumstances, the intrinsic three-gamma decay within the evacuated pore becomes significant. Though there have been several interesting studies of diffusion<sup>11</sup> of Ps across the silica gel surface, effects of incorporated interstitial helium gas<sup>12</sup> and angular correlation studies in the interstitial spaces,<sup>13</sup> which have provided information about annihilation characteristics in such materials, the present work aims at setting up a robust and reliable model enabling the simple correlation of average Ps lifetime with pore size. The pick-off annihilation of *o*-Ps in molecular substances with preexisting micro-cavities or the cavities created by positronium in liquids has been clearly described through a model<sup>14</sup> evolving a reliable calibration curve. In this study for mesoporous substances, a consistent picture is built for the concomitant process of pick-off and three-gamma annihilation, which describes a novel approach to handle the problem.

As a result, PALS is sharpened as an in-situ probe for the study of the porous materials, and this article, in general, evolves a microstructural view of the silica gel when taken together with the micro-morphological characteristics of the samples.

## 2. Experimental Methods and Results

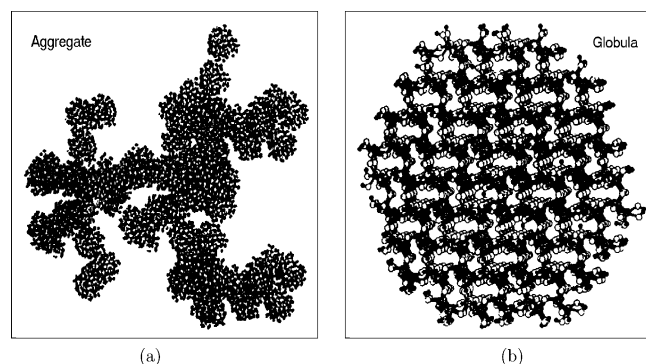
**2.1. Chemical Aspects.** The highly porous noncrystalline silica gel powders (polymerized silicic acid molecules) used for chromatographic purposes were purchased from Sigma Aldrich Chemical Company, SISCO Research Laboratory, and Spectrochem, India. The samples were baked at 200 °C under constant evacuation to remove adsorbed air and moisture.

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**Figure 1.** A schematic molecular model<sup>1</sup> of (a) the aggregated structure of silica gel composed of spherical globulae  $\text{Si}_{1705}\text{O}_{1560}\text{H}_{300}$ , each having a radius of nanometer size and (b) the globula having the structure of  $\beta$ -cristobalite.

**2.2. Micro-morphological Studies.** In most cases a porous solid such as silica gel can be represented by an agglomerate of primary particles, of nanometer size or less, rigidly joined together by fusion. A molecular model of such an agglomerate produced by irreversible random coagulation of a few primary spherical particles, each having the structure of high cristobalite, is schematically outlined in Figure 1.<sup>1</sup> The voids between the particles form a pore system, while the interior of each small particle is nearly completely cross linked with interlocking Si—O—Si chains. Transmission electron microscopic (TEM) studies of the silica gel powder samples under consideration were done using a Hitachi-H600 transmission electron microscope operating at 100 kV. The best resolution obtained was  $\sim 5$  Å. The samples were soaked in alcohol to make the silica grains swollen and then sonicated to separate the particles from each other to make them quite conspicuous when observed through TEM, which showed a spongy nature. The internal micro-morphology of the samples (Figure 2) indicates the resulting microstructure.

**2.3. Positron Annihilation Lifetime Spectroscopy (PALS).** The carrier-free positron source ( $^{22}\text{Na}$  in the form of  $\text{NaCl}$ ) of strength  $\sim 6$   $\mu\text{Ci}$  was deposited on a thin nickel foil and covered with another identical film, the edges of which were sealed. The source was put in a cylindrical glass container inside which the sample was baked and evacuated. After completing these steps the sample chamber was sealed and maintained at room temperature and placed between the scintillation detectors. The positron annihilation lifetimes were measured with a slow-fast coincidence system. The detectors used were truncated cone shaped (of dimension 25.4 mm diameter tapered to 12.7 mm diameter and of 25.4 mm height) spectroscopic quality  $\text{BaF}_2$  scintillators (optically polished on all sides) coupled to Philips XP2020Q photomultiplier tubes. The resolving time (fwhm) measured with a  $^{60}\text{Co}$  source was 200 ps, for the positron window settings, with a time constant of 50 ps per channel.

However, for the actual long lifetime measurements, the channel constant calibration was varied in steps of 200 ps, 400 ps, 800 ps, and 1 ns through the ORTEC TPHC electronic module. Also, the coincidence resolving time was kept as long as 200 ns using ORTEC Universal Coincidence electronic module before it is strobed to TAC, maintaining proper allowance for the lower level energy window to select pulses between 300 and 550 keV. However, we made observations by opening the lower level window further—but there was no special advantage as regards the *o*-Ps annihilation component detected above the background level. For each setting, a total of  $\sim 10^7$  counts (over a period of 24 h) were collected with peak-to-random ratio 5000:1. The lifetime spectra so obtained were analyzed with the PATFIT-88 program.<sup>15</sup> The resolution (fwhm)

obtained from the program RESOLUTION was used in the POSITRONFIT program, with a necessary source correction of  $\sim 5\%$  to get the final analysis of the data. A best fit could be obtained with four components taking the channel constant to be 200 or 400 ps. Although, the third component denoting the pure pick-off fraction ( $\tau_3$ ) could be emphatically analyzed from the data with channel constant 50 ps or 200 ps, the spectrum, however, contained insufficient information about the longest-lifetime component ( $\tau_4$ ). The latter could be resolved better with channel constant 400 ps or higher and the analysis showed a consistency for the longest lived component  $\tau_4$  with higher channel constant. The measurements were mainly focused on these two long-lived components ( $\tau_3$  and  $\tau_4$ ). The fitting errors in measuring the lifetime correspond to a standard deviation of  $\sim 1.5\%$ .

A graphical representation of the data showing the unusually long lifetime in the spectrum in the representative samples of silica gel powder with known pore characteristics (Table 1) are shown in Figure 3, and further the evaluated results are shown in Table 2.

### 3. Theoretical Analysis

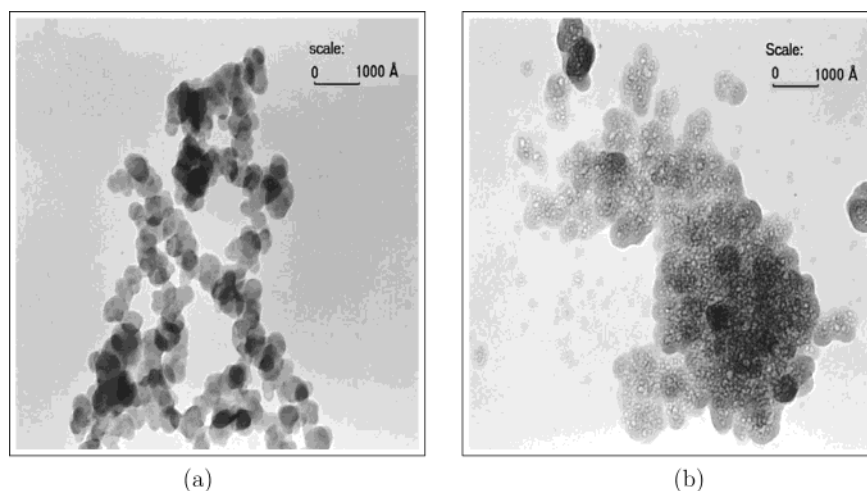
Since we specifically aim at probing the empty regions (free volumes) and void spaces in the silica gel, we are mainly concerned with the study of the decay modes of long-lived positronium states (*o*-Ps state) in the positron annihilation spectra.

The origin and mode of *o*-Ps formation in the solid material is presumed to be initiated either before trapping<sup>16</sup> of the bare positron or after trapping of the same in free space.<sup>17</sup> However, a certain contribution of Ps may exist<sup>18</sup> in the micro voids or free volume of bulk material, and the other fraction sensitively depends on the surface-to-pore volume ratio<sup>19</sup> owing to the energetically strained surface group of the silica gel material. The ultimate segregation of *o*-Ps into the vacant space is aided by the repulsive electron exchange interaction between *o*-Ps and the atoms of the medium (which is responsible for the negative work-function for Ps).<sup>14</sup> Thus, once formed it is considered to diffuse out quickly<sup>11</sup> and is expelled from the high-density regions into the cavities and pores of the porous substances. Accordingly, we concentrate our attention on *o*-Ps in the microcavities and mesopores.

The *o*-Ps in the microcavity (parametrized on the average as a spherical hollow region of radius  $R$ ) gets trapped in a manner describable, in an approximate sense, as a particle of mass  $2m$  ( $m$  = electron mass) confined in a spherical well potential with repulsive walls (of height  $U_0$  which is related to the work function taking into account modifications due to curvature, etc). This trapped *o*-Ps has a probability of being found in and about the cavity given by the square modulus of its wave function  $\psi_{\text{Ps}}(r)$  with  $r$  measured from the center of the hollow region. The lifetime for pick-off annihilation in this situation can be estimated by multiplying the basic rate for  $e^+e^- \rightarrow 2\gamma$  at low energies (namely,  $4\pi r_0^2 c$  where  $r_0 = e^2/mc^2$  is the classical electron radius,  $e$  being the electronic charge and  $c$  the velocity of light) by the probability for the positron in the positronium for finding an electron with opposite spin in the surrounding matter. This leads to a pick-off rate given by

$$\lambda_p = 4\pi r_0^2 c \int_0^\infty \rho(r) Z_{\text{eff}} |\psi_{\text{Ps}}(r)|^2 d^3r \quad (1)$$

where  $\rho(r)$  is the number density of atoms around the cavity, and  $Z_{\text{eff}}$  is the available number of valence electrons per atom contributing to the process. The model so defined (originally



**Figure 2.** Electron micrograph of silica gel powder (with the magnification of 80 000) (a) after sonication in alcohol, (b) after soaking in alcohol overnight and sonication.

**TABLE 1: Known Characteristics of the Silica Gel Samples (Aldrich Chemical Co. supplied data)**

sample	mesh	average grain size	pore size (diameter) (Å)	surface area (m <sup>2</sup> g <sup>-1</sup> )
1. Silicagel/Aldrich (28861-6)	70-270		60	500
2. Silicagel/Aldrich (40360-1)	70-230	63–200 μ	100	300
3. Silicagel/Aldrich (40356-3)	70-230	63–200 μ	40	750
4. Silicagel/Aldrich (24217-9)	35-70		40	675

proposed by Ferrell<sup>20</sup>) to account for positron annihilation in liquid helium has been further revisited and modified by us<sup>21–23</sup> and applied to different molecular substances. In the present context, however, the *o*-Ps atom gets confined in the preexisting cavities in the material. Taking, moreover, into account the fact that the positronium itself has a finite size,<sup>24</sup> the model has been improved through the introduction of a transition layer or diffuseness (or roughness) of the cavity boundary parametrized by a “skin” of thickness  $\delta$ . This has led,<sup>14</sup> taking into consideration all available data on pick-off lifetimes in liquids as well as micro-cavities [sizes ( $2R$ )  $\leq 20$  Å] in solid molecular substances, to a very simple fit described by

$$\tau_3 = 1.88R - 5.07 \quad (2)$$

with  $\tau_3$  measured in ns and  $R$  in Å. The magnitude of  $\delta$  turns out to be of the order of 0.2 Å. This relationship provides us with a calibration for the average size of microcavities (perforations in Figure 2b), from the measured lifetime data  $\sim 2$ –3 ns as also reported by Brandt et al.<sup>11</sup> [see the fitting for the smaller cavities ( $R < 10$  Å) in Figure 4].

For pore sizes greater than of the order of a nanometer (mesopores) the mechanism for *o*-Ps annihilation is not properly described by the model set out in the previous paragraph. One source for this deviation is the contribution from the intrinsic *o*-Ps annihilation process (*o*-Ps  $\rightarrow 3\gamma$ ) which becomes significant as the pore size is large and hence lifetime becomes longer. However, this by itself is unable to account for the data. A literature account in this context presents more sophisticated potential wells,<sup>18,25–27</sup> and of contributions to the annihilation rate from excited states.<sup>28</sup> In this paper, however, we present a simple different physical approach to the problem.

In the present study, we have developed the basic notion of *o*-Ps annihilation characteristics in large voids, resulting in an extremely simple description of the underlying process which also fits the trend of the existing data rather well. In the

mesopores and microcavities which may be inter-connected, the mobile Ps-atom may be sampling these regions with equal a priori probability. It is likely that the sizes of these pores are large compared to the coherence length of the positronium wave function, particularly in view of the fact that the walls of the pore which are rough at the microscopic scale are composed of atoms in a state of thermal agitation. Thus the approach to the problem is in conformity with that followed in case of microcavities except that in the latter situation the cavity radius is very small ( $< 10$  Å) and a quantal description is necessitated while here for mesopores with much larger radii the statistical description seems more appropriate. Thus, the pick-off rate will be given by an expression which is analogous to eq 1 wherein the integral involving the quantum mechanical probability will be replaced by the corresponding statistical probability, namely,  $\lambda_p = 4\pi r_0^2 c \rho Z_{\text{eff}} / V \int_{\mathcal{R}}^{\mathcal{R}+\delta} d^3r$ , where,  $V$  is the volume of the mesopore, which when taken spherical (as here) has a radius say  $\mathcal{R}$  and the process of pick-off annihilation occurs in a layer of thickness  $\delta$ . Thus adopting a statistical point of view, one would be led to surmise that the relative probability for pick-off annihilation would be proportional to the ratio of the volume of the surface layer of thickness  $\delta$  (found to be  $\sim 1.7$  Å for spherical pores) and the total volume of the pore, because the process can only happen in this region, while the  $3\gamma$  decay should be omnipresent. Accordingly one expects, on the basis of our simple picture, that the rate for annihilation in the large pores be given by

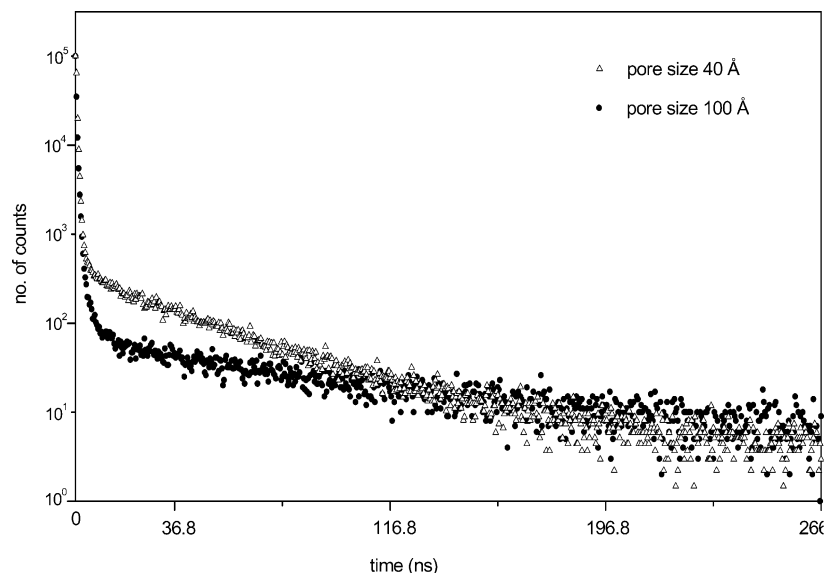
$$\lambda_4 = \frac{1}{\tau_4} = \lambda_p + \lambda_{3\gamma} = \zeta \left( \frac{\delta}{\mathcal{R}} \right) + \lambda_{3\gamma} \quad (3)$$

where,  $\zeta (= 12\pi r_0^2 c \rho Z_{\text{eff}}) = 0.18 \text{ ns}^{-1}$  as calculated using eq 1 taking the effective density of porous silica to be 0.05 g/cc.<sup>11,25</sup> The value of  $\zeta$  depends on the value of  $Z_{\text{eff}}$  (for silica,  $Z_{\text{eff}} = 4$  as calculated using the methodology described in ref 2) and the density ( $\rho$ ) of the porous material.  $R$  is the size parameter for the large pore here and  $\lambda_{3\gamma} (= 1/140 \text{ ns}^{-1})$  is the intrinsic  $3\gamma$  annihilation rate for *o*-Ps. It can be shown that the total annihilation rate ( $\lambda_4$ ) in this case is only mildly dependent on any type of geometric shape of the pore.

#### 4. Discussion

Since porous silica gel has been of wide interest in chemical industries as supporting catalysts and absorbing material, there are standard conventional methods of determining the pore





**Figure 3.** Positronium lifetime spectra for the silica gel powder samples depicting the noticeable change in slope for long lifetime component ( $x$  axis channel constant = 400 ps).

**TABLE 2: Characteristics of the Silica Gel Samples Studied along with the Evaluated Results**

sample	application	PALS data		cavity size ( $2R$ ) from eq 2 (Å)	PALS data		pore size ( $2R$ ) from the calibration (using eq 3) (Å)
		$\tau_3$ (ns)	$I_3$ (%)		$\tau_4$ (ns)	$I_4$ (%)	
1. Silicagel/Aldrich <sup>a</sup> (28861-6)	column chromatography	2.90	2.40	8.48	60.62	12.83	64.12
2. Silicagel/Aldrich <sup>a</sup> (40360-1)	column chromatography	2.53	3.20	8.08	75.19	7.06	97.48
3. Silicagel/Aldrich <sup>a</sup> (40356-3)	column chromatography	3.20	2.40	8.80	44.65	12.7	39.34
4. Silicagel/Aldrich <sup>a</sup> (24217-9)	column chromatography	2.75	2.32	8.32	41.22	15.14	35.10
5. Silicagel/SISCO	flash chromatography	2.79	4.75	8.36	73.79	19.79	93.62
6. Silicagel/SPECTROCHEM	lipid chromatography	2.00	5.30	7.52	36.10	14.28	29.18
7. Silicagel/SPECTROCHEM	column chromatography	2.25	7.08	7.78	32.35	13.97	25.24

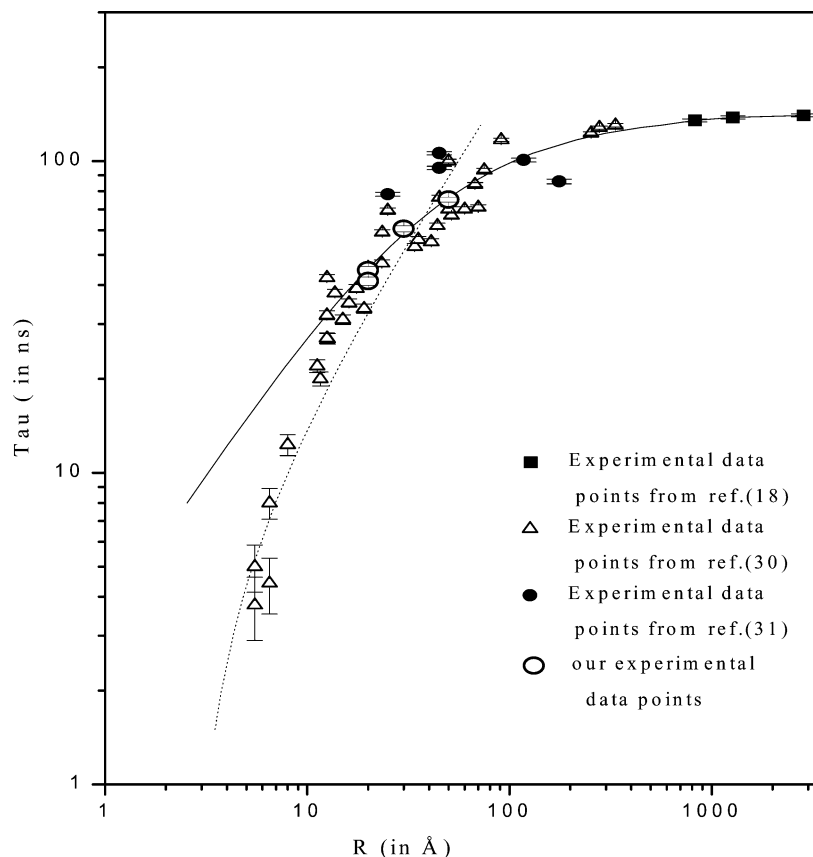
<sup>a</sup> The evaluated pore size characteristics for these samples from eq 3 provide a means of verification with the supplied data and hence the validity of calibration.

volume and surface area such as nitrogen absorption at 77 K by the Brunauer-Emmett Teller (BET) method or mercury porosimetry method. But each method has its own limitation as to the application and sensitivity toward the elucidation of the hidden crevices or pore structures.<sup>1,29</sup> Also, these methods make use of an idealized cylindrical model which may deviate from what occurs in a natural setting. To this purpose, positron annihilation spectroscopy is expected to serve in a better way, although this is also model-based. It is now understood<sup>30</sup> that Ps trapped in microcavity will have shorter lifetimes than in mesopores where the lifetime ( $\tau$ ) should asymptotically approach the vacuum value ( $o$ -Ps, 140 ns). To handle a large number of experimental data, the most common trend has been to use (for small cavity) Tao-Eldrup model<sup>7,8</sup> based on spherical well potential with infinite walls, and a virtual electron layer of fixed thickness was somewhat empirically added to the inside wall of the well to make the possibility of overlap of the positronium wave function. This needed further improvement, as in these kinds of models the cavity as well as the confining potential are taken to have sharp boundaries. In a series of papers, the present authors<sup>21–24</sup> have shown that this is not only artificial but also leads to systematic discrepancies which become evident wherever additional data on the angular correlation of decay gammas is also available. As an improvement to this description, it may be claimed that the simpler relation found by using a finite potential well with diffused boundary<sup>14</sup> not only appears to be more realistic but fits faithfully both lifetime and angular correlation data and is therefore better suited for the purpose at hand.

Thus in the present context, comparing the microscopic evidence (Figures 1,2) with the PALS analysis, the pure pick-off component  $\tau_3$  has been clearly assigned for the description of the sub-nanometer spaces (Figure 4, dotted line) within the material (sponge-like) while, another component  $\tau_4$  with relatively much longer life is attributed to the large void space (Figure 4, solid line).

The model proposed by Ito et al.<sup>30</sup> introduces the novel idea of the positronium in a large pore bouncing around as a wave packet. However, since a hybrid description is used involving the wave function of a trapped particle, the interpretation of the parameters becomes overly involved and the resulting expressions are very complicated. Our model on the other hand relies on a simple physical picture for the mesopores as described above and yields excellent results fitting all the available data in the region of large pores.

An important development for the discussion of Ps annihilation in large pores is represented by the work of Dull et al.<sup>18</sup> Here it is recognized that with the increasing size of the pore the energy levels corresponding to the center-of-mass motion of the positronium come closer and closer to each other and the thermal mixing between the levels becomes appreciable so that the wave function description must, in their view, give way to the density operator approach. The net effect of this mixing is in essence to homogenize the probability of finding the positronium in different regions of the pore. We have adopted a highly simplified approach to this situation through our model of equal a priori probability. This is particularly suitable since



**Figure 4.** Calibration curve showing the fit for small cavities (dotted line,  $\tau = 1.88R - 5.07$ ) and large pores (solid line,  $1/\tau = 0.3/R + 1/140$ ) for all the calculable data, where  $R$  denotes the mesopore radius. The experimental data points of silica gel samples have been taken from Dull et al.,<sup>18</sup> Ito et al.,<sup>30</sup> and Venkateswaran et al.,<sup>31</sup> which contains the details of the silica gel samples concerned.

the implementation of the density operator approach becomes impracticable for realistic wells with diffuse boundaries.

It is important to note that our contention to have an estimation of the pore size of the silica gel samples with respect to the average particle size (actually dependent on the mesh of the sample grade) is satisfactorily met (samples with given pore size in Table 1) as found from the calibration curve (Figure 4 and Table 2). The detailed pore structure in general is not known from PALS data and is probably quite complicated. In fact, Ps lifetime is strongly dependent on the measure of the pore size and it is more or less independent of any particular type of geometry of the pore.<sup>18</sup> The size of the small cavities, however, is of the order of  $\sim 8$  Å and is in accordance with the spongy nature of the substance (Figure 2).<sup>11</sup> The respective intensities  $I_3$  and  $I_4$  under the lifetime components  $\tau_3$  and  $\tau_4$  correspond to the surface area of the annihilation site.<sup>31</sup> It is possible that a significant contribution (as is envisaged from eq 3) from three-gamma annihilation add on to  $I_4$ %.

## 5. Conclusion

Summarizing, the paper explains the interaction of Ps within porous silica gel material providing insight through micro-morphological study of the samples and accounts for the origin of the long lifetime within the pores. It is realized that in order for PALS to be a useful probe, Ps needs to be formed in the molecular material and which subsequently diffuses into free space by virtue of the negative work function. It is this fundamental property which is in turn calibrated to gauge the pore size. This study reflects two different types of mechanisms to assay the microcavities and mesopores in silica gel samples through PALS.

While going through the complementary nature of the various techniques<sup>32</sup> for characterization, PALS has been shown to be sensitive to cavities much smaller than those that could be approached by small-angle neutron scattering spectroscopy (SANS),<sup>33</sup> and to a porosity range inaccessible by the nitrogen gas absorption methods.<sup>1</sup> Last, the merits of the method were found to lie on its in-situ nature of the probe to approach the hidden areas (both sub-nano as well as meso-porous) and unfold the electronic microenvironment simply through positronium interactions, the information being inscribed in the annihilation gammas.

It is important to envisage that an appreciable fraction of thermal *o*-Ps (annihilating with intrinsic life of 140 ns) concentrate in the interior of the pore rendered incapable to escape by the barrier heights and may thus serve as a source for important experimental applications.

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