

Effect of Temperature on Positronium Annihilation in Silica Gel

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A systematic temperature-dependent study of positronium annihilation rate within the void spaces (micro- and mesopores) of silica gel material has been performed through positronium annihilation spectroscopy. The results find their plausible interpretation through a novel theoretical explanation based on vibrational interaction of thermally energized atoms on the surface layer of the pores with positronium, which in fact justifies the observed increase in the annihilation rate of the latter, with the increase in temperature.

1. Introduction

The growing interest in the recent years in the positron annihilation studies on amorphous silica or silica gel material (not only bulk but also thin films)^{1–7} revealed that positronium (Ps) formation occurs with high efficiency in intrinsic microvoids of molecular network which was confirmed with several experimental techniques like positron annihilation lifetime spectroscopy (PALS),² angular correlation of annihilation radiation (ACAR),⁸ and age-momentum correlation spectroscopy (AMOC).⁹ Now that to these events the stimulating and contemplated effect of coherent emission of γ -rays via Bose–Einstein condensation¹⁰ has been added with a further motivation, which in fact beckons more intense investigations in the field.

From the material perspective, silica gel as reported by micromorphological study,¹ consists of an agglomerate of primary particles of nanometer size, rigidly joined together by fusion, with the entrapped voids between the particles forming the pore system, while the interior of each small particle is nearly completely linked with interlocking Si–O–Si chains forming the microvoids. Silica gel is widely known in technology for its versatile use^{2,11} due to its porous structure.

Ps formed in this molecular media is expelled from the matter due to exchange repulsion interaction and may exist in microvoids or free volume (a region of low electron density) from where it quickly diffuses into the region of pores.^{1,11} Parapositronium (p-Ps, the singlet spin state) has a short self-annihilation life span (0.125 ns in a vacuum) and is not significantly affected by molecular interaction, but orthopositronium (o-Ps in triplet state) survives long enough (140 ns in a vacuum) and can be trapped within the voids where its lifetime is markedly reduced by interaction with molecular electrons; i.e., its pick-off process could be suitably utilized to calibrate the pore size in the material. In a recent paper,¹ it has been argued precisely that the two distinct long-lived components (of o-Ps fraction) found experimentally (labeled by τ_3 and τ_4) are ascribable to microcavities within the grains and intergranular mesoscopic pores, respectively. In the latter type of void, a significant fraction decays via three-photon mode. Since the size

of the mesopore is quite large (radius > 10 Å), compared to the coherence length of the Ps wave function and more so, when the walls of the pores are considered to be composed of atoms at the thermal vibration state, then a statistical description of the Ps–atomic interaction seems to be more appropriate¹ rather than a quantal overlap effect in the case of the micropores¹² (cavity radius ≤ 10 Å).

The verification of the above ansatz has been sought through the temperature dependence of the observed annihilation rate in the pores through PALS studies in the silica gel medium. Finally, the interpretation of the results paves its righteous way through the interaction of Ps with the thermally energized atoms, ascribed to the surface layer of the cavities.

The paper is further divided into an experimental section followed by theoretical interpretation and a discussion based on the results.

2. Experimental Section

2.1. Chemical Aspects. The highly porous noncrystalline silica gel powder (polymerized silicic acid molecules, catalog no. 28861-6, mesh = 70–270, average pore diameter = 60 Å, and surface area = 500 m² g^{−1}) used for chromatographic purposes was purchased from Sigma Aldrich Chemical Co. The samples were baked at 473 K for about 12 h under constant evacuation to remove adsorbed air and moisture.

2.2. Positron Annihilation Lifetime Spectroscopy (PALS). The carrier-free positron source (²²Na in the form of NaCl) of strength ~ 15 μ Ci was deposited on a thin nickel foil and covered with another identical film and sealed. This source was placed within the silica gel sample, which was contained in a special vial maintained at the desired temperature using Leybold Cryogenic system with a temperature controller and under constant evacuation through a Turbo molecular pump. The system was placed between two BaF₂ scintillation detectors coupled to Philips XP2020Q photomultiplier tubes.

The positron annihilation lifetimes were measured with a slow–fast coincidence system. The resolving time (fwhm) of this experimental system measured for prompt γ -rays with a ⁶⁰Co source was 200 ps, at the positron window settings, with a time constant of 50 ps per channel. The actual details of the procedure of the measurement are described in ref 1.

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

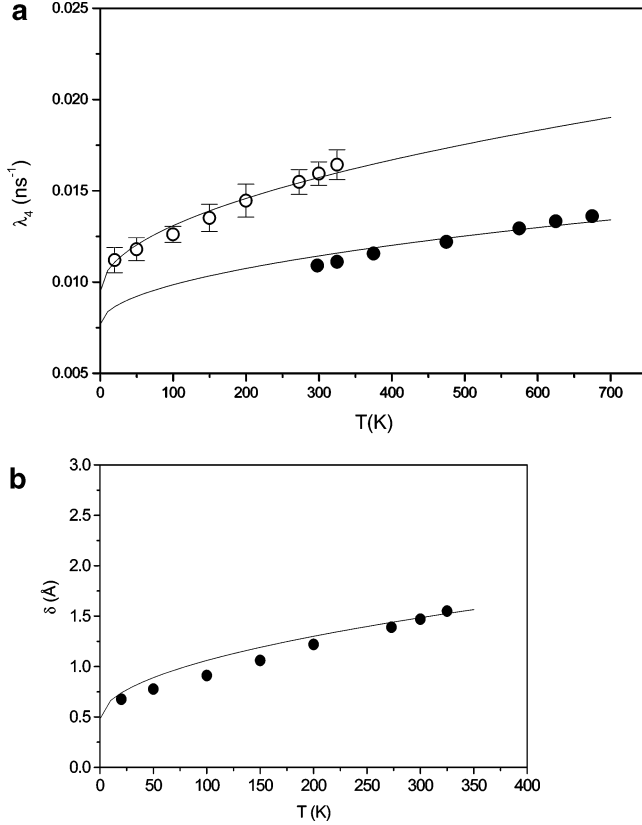
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TABLE 1: Changes in Long-Lived Orthopositronium Components in Silica Gel Sample with the Change in Temperature of the System and the Values of δ/\mathcal{R} (from Eq 4) of the Sample

T (K)	τ_1 (ns)	I_1 (%)	τ_2 (ns)	I_2 (%)	τ_3 (ns)	I_3 (%)	τ_4 (ns)	I_4 (%)	$I_3 + I_4$ (%)	δ/\mathcal{R}
20	0.25 ± 0.009	44.19 ± 2.03	0.69 ± 0.02	34.31 ± 1.99	9.99 ± 0.49	6.60 ± 0.22	89.28 ± 4.95	14.95 ± 0.2	21.33	2.2×10^{-2}
50	0.29 ± 0.008	49.83 ± 2.07	0.77 ± 0.03	31.04 ± 2.01	9.45 ± 0.46	6.38	84.76 ± 3.15	12.67 ± 0.20	19.27	2.6×10^{-2}
100	0.24 ± 0.009	45.3 ± 2.06	0.67 ± 0.02	36.76 ± 1.99	6.27 ± 0.84	3.23 ± 0.15	79.30 ± 3.10	14.71 ± 0.19	17.94	3×10^{-2}
150	0.23 ± 0.01	46.03 ± 2.00	0.66 ± 0.02	38.06 ± 2.8	6.10 ± 0.60	2.90 ± 0.13	74.00 ± 4.11	12.90 ± 0.41	15.80	3.5×10^{-2}
200	0.21 ± 0.01	40.43 ± 2.69	0.61 ± 0.02	44.50 ± 2.60	5.49 ± 0.48	2.84 ± 0.12	69.17 ± 4.32	12.23 ± 0.23	15.07	4.1×10^{-2}
273	0.20 ± 0.01	39.95 ± 2.49	0.55 ± 0.02	45.32 ± 3.29	3.72 ± 0.47	2.70 ± 0.29	64.59 ± 2.85	12.32 ± 0.21	14.73	4.6×10^{-2}
300	0.18 ± 0.006	38.96 ± 2.95	0.55 ± 0.02	45.7 ± 2.7	3.18 ± 0.52	2.41 ± 0.15	62.73 ± 2.53	12.97 ± 0.21	15.34	4.9×10^{-2}
325	0.19 ± 0.006	40.06 ± 2.69	0.59 ± 0.02	45.29 ± 3.43	3.10 ± 0.48	2.37 ± 0.38	60.88 ± 2.50	12.97 ± 0.32	15.67	5.2×10^{-2}

**Figure 1.** (a) Variation of the observed decay rate (λ_4) of o-Ps with temperature (T) of the silica gel samples. Data points “O” represent our experimental data (with known value of $\mathcal{R} = 30$ Å), and data points “●” are taken from ref 19 (with $\mathcal{R} \sim 80$ Å as considered from our method¹); solid line represents the fitting curve using eq 6. (b) Variation of the parameter δ (as per eq 4, observed through λ_4 with temperature T); the solid line represents eq 5.

measurements were mainly focused on the two long-lived components (τ_3 and τ_4) with a channel constant 400 ps; the criterion set for analysis was the best chi square fit with corresponding variance of fit ~ 1 . The fitting errors in measuring the lifetime correspond to a standard deviation of $\sim 1.5\%$. The evaluated results are shown in Table 1, and the annihilation rate dependence on temperature of the system is shown in Figure 1a.

3. Theoretical Analysis

3.1. For Microcavities. For very small cavities (parametrized on the average as a spherical hollow region of radius $R \leq 10$ Å), o-Ps gets trapped in a manner describable 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 the modifications due to curvature, etc.).¹² 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, $4\pi r_0^2 c \rho$, where r_0 is the classical electron radius, c is the velocity of light, and ρ is surrounding electron density) 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

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

where Z_{eff} is the available number of valence electrons per atom contributing to the process and $\rho(r)$ is the number density of atoms around the cavity. This initial form of model¹⁴ was further improved by taking into account the fact that the positronium itself has a finite size,¹² through the introduction of a transition layer or diffuseness (or roughness) of the cavity boundary employing a Woods–Saxon potential description. This has evolved,¹² taking into consideration all available data on various molecular substances (from liquids to solids), to a very simple fit described by

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

with τ_3 measured in nanoseconds and R in angstroms for the microcavities ($R \leq 10$ Å). This model calibration thus provides us with a methodology to gauge the minute pore structure in spongy silica gel material.¹

3.2. For Mesopores. However, for the pores having size greater than of the order of a nanometer (radius $\mathcal{R} > 10$ Å), the contribution of intrinsic o-Ps annihilation process (o-Ps $\rightarrow 3\gamma$) becomes significant in addition to the pick-off rate; hence, the lifetime becomes longer. As the pore sizes could be large compared to the coherence length of the positronium wave function, and also may be interconnected, a statistical description with equal a priori probability (at any given temperature) here seems to be more appropriate, and the pick-off rate is given by an expression that is analogous to eq 1, wherein the integral involving the quantum mechanical probability will be replaced by the corresponding statistical probability, namely

$$\lambda_p = 4\pi r_0^2 c Z_{\text{eff}} \rho \left(\frac{1}{V} \right) \int_{\mathcal{R}-\delta/2}^{\mathcal{R}+\delta/2} d^3r \quad (3)$$

where V is the volume of the mesopore, assumed as spherical, with a radius \mathcal{R} , and the pick-off annihilation occurs in the thin active surface layer of thickness δ . Thus, adopting this very simple picture, the relative probability for pick-off annihilation would be proportional to the ratio of the volume of the surface layer to the total volume of the mesopore, while the intrinsic 3γ decay is omnipresent and cannot be neglected for a mesopore as opposed to the situation in micropores. According to this

picture, the observed annihilation rate in the mesopores would be given as¹

$$\lambda_4 = \lambda_p + \lambda_{3\gamma} = \varsigma \left(\frac{\delta}{\mathcal{R}} \right) + \lambda_{3\gamma} \quad (4)$$

It is however imperative that ς ($= 0.18 \text{ ns}^{-1}$)¹ includes the parameters such as Z_{eff} as well as the density ($\rho \sim 0.05 \text{ g/cm}^3$) of the dry (evacuated) porous silica material^{11,15} and $\lambda_{3\gamma}$ ($= 1/140 \text{ ns}^{-1}$) is the intrinsic 3γ annihilation rate for o-Ps. The total annihilation rate λ_4 is however only mildly dependent on the geometric shape of the pore.^{1,2}

3.3. Temperature Dependence. To discuss the temperature dependence of annihilation rate of Ps entrapped within micropores, it is pertinent to adopt the methodology^{12,17} followed by the “scaling of the cavity size” wherein the overlap integral of Ps wave function with the electrons has been discussed in the context of the model (represented by eq 2, which is actually based on the available temperature-dependent data of liquids and room temperature solids). This could relate the pick-off lifetime (τ_3) to the effective microcavity or the free volume radius (R) at any given temperature. But this is true only in the absence of any other chemical reaction (oxidation, spin exchange, complex formation, etc.) at the microcavity surfaces of the sample. At the lower temperature regime (where the other reaction channels are negligible), the results from eq 2 may show a release in the effective free volume in the molecular lattice. However, it needs to be remarked that since the pores (micro and meso) are interconnected,¹ there is reason for o-Ps to diffuse to the larger cavity,¹¹ and at higher temperatures the probability of diffusion for o-Ps increases, which may be reflected in τ_3 and I_3 (as shown in Table 1).

In the case of the mesopores, as already stated, the interaction of Ps and the surface atoms of the cavity can be treated statistically, in terms of thermal energy possessed by the system. The motivation of our present work is to study the temperature dependence of positronium annihilation characteristics in the mesopores. Keeping in mind that the pores may be interconnected and the Ps atom may be sampling these pores with equal a priori probability at all temperatures, and also the fact that the surface atoms are at the state of thermal agitation and the pick-off annihilation can only occur in the region of the surface layer of thickness δ , we proceed further to show the small change in the surface layer thickness due to the thermal vibration^{16,21} of the surface atoms, which in turn causes the change in pick-off annihilation rate in mesopores. If the average root-mean-square amplitude of thermal vibration of surface atoms is represented by a small length scale $\langle \delta' \rangle$, then we can correlate the thermal energy possessed by the surface atoms to the energy due to oscillation, i.e.

$$\frac{1}{2}\chi\langle\delta'\rangle^2 = \frac{3}{2}k_B T \quad (5)$$

where k_B is the Boltzmann constant, T is the absolute temperature, and χ is the force constant of surface molecular atoms for thermal vibration. Thus, the average active layer thickness at any given temperature is $\delta = \delta_0 + \delta'$, where δ_0 ($\leq 1 \text{ \AA}$) is the layer thickness for very cold lattice. This simple picture finally gives the expression for the temperature-dependent annihilation rate (from eqs 4 and 5)

$$\lambda_4 = \frac{1}{\tau_4} = \frac{\varsigma}{\mathcal{R}} \left(\delta_0 + \sqrt{\frac{3k_B}{\chi}} \sqrt{T} \right) + \lambda_{3\gamma} \quad (6)$$

At extremely low temperature, the pick-off annihilation rate is completely negligible.¹⁸ The value of χ can be found from the fitting of experimental data (Figure 1a) and can be verified with the deduced value from eq 5.

4. Discussion

Our main contention in this experiment with the silica gel sample in a temperature regime of 20–325 K has been focused on the dependence of the annihilation rates, viz. λ_3 and λ_4 , with temperature. While λ_3 in this case depends on the free volume of the system along with the diffusion of o-Ps at a given temperature, the changes in λ_4 are ascribable to the thermal energy state of the surface atoms at a given temperature.

Microscopically, surface activity of the mesoporous cavities of this catalytic material is in fact represented through the ensemble of dangling atoms and is considered to have only vibrational motion, which in turn reflects upon the energy possessed by each individual constituent atom due to the attendant temperature of the system.

Therefore, the statistical probability for the pick-off process in eq 3 can be shown to be dependent on the temperature of the system, as has been perceived through the vibrational fluctuation of the atoms as seen in Figure 1a,b as per the proposed theory. It is seen that this simple relationship gives an excellent fitting of the experimental data with the values of $\chi \sim 0.5 \times 10^4 \text{ dyn/cm}$, which can also be verified to obtain the thermal energy from eq 5 at a given temperature. Further, when the data from Dull² et al. and Gidley et al.¹⁹ (RET model) are plotted (Figure 1a) through the same relationship, it also shows the same dependency, thus agreeing well with the simple thermal fluctuation model, the essence of which is already present in refs 2 and 21 although in a different manner. There also the effective inner surface layer of the pore with some thickness has been invoked through an analogous free parameter “ δ ”.

Quite importantly, Dull et al.² have taken recourse to the density operator approach, in the case of large pores, where the energy levels corresponding to center-of-mass motion of Ps in their wave function description come closer and closer to each other so that thermal mixing between the levels become plausible. The net effect of this mixing is in essence to homogenize the probability of finding the Ps in different regions of large pore. There have been other views also by Gidley et al.^{19,20} concerning the temperature dependence on the collision rate of Ps atom with the pore surface. Our approach in the similar situation is however different, which is highly simplified because of equal a priori probability for realistic wells¹ with diffuse boundaries.

Further, it remains to say that the temperature-dependent study of Ps annihilation rate on silica gel powder is of paramount importance for it not only depicts the augmentation of surface activity of the atoms but also probes the other shorter reaction channels. Our experience with the percentage intensities of the long-lived o-Ps components, namely I_3 and I_4 , correspond to the contributions of the surface layer²⁴ of the micro- and mesopores together. It is seen in Table 1 that I_3 decreases with the increase in temperature; this could be due to the escape of o-Ps from the micropore followed by enhanced annihilation rate at higher temperature. A careful observation from our data toward the higher temperatures shows a discrepancy of about $\sim 5\%$ in the total long-lived components ($I_3 + I_4$) when compared to the lowest temperature regime, and this is shifted to the lower lifetime components. Chuang and Tao²¹ have discussed a similar possibility taking recourse through chemical rout. If an unpaired electron (local paramagnetic center) exists

at the activated surface as a defect or the strained surface groups ($\text{Si}-\text{O}^\bullet$),²² created due to irradiation with about 10–15 μCi positron source under high vacuum ($\sim 10^{-6}$ Torr), a lifetime quenching effect can be observed.^{21,23}

Also, from the reports of Van Veen et al.,⁸ we find there is ample possibility of observing p-Ps component in the various silica gel samples. It is shown in the concerned reference²¹ that in silica gel samples with smaller pore size there is considerable increase in shorter component intensities with temperature as there the volume of surface layer is considerably large compared to void volume.

5. Conclusion

In this study, the surface activity of porous silica gel sample has been expressed through positronium annihilation characteristics. The decay rates of the two long-lived components of o-Ps, namely λ_3 and λ_4 corresponding to micro- and mesopore, respectively, of the silica gel sample show an enhancement with the increase of temperature in the system. While the changes of λ_3 are attributed to the free volume of the substance at a given temperature (considered in the absence of any other chemical reaction channels) and overlap integral of positronium–electron wave functions, the increased decay rate λ_4 is due to the enhanced probability of Ps interaction with the thermal fluctuation of the atoms in the surface layer δ of the meso pore. The percentage intensities associated with the long-lived components depend on the surface interaction of the pores.

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