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Lifetimes of o-Ps in the Pores of Silica Gel

T. Goworek, K. Ciesielski, B. Jasińska and J. Wawryszczuk

Institute of Physics, Maria Curie-Sklodowska University, PL-20-031 Lublin, Poland

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Abstract

An attempt to extend the popular Tao-Eldrup model (TEM) toward large voids is presented. The lifetimes of o-Ps in various states of the particle in the spherical and cylindrical wells have been calculated. The existence of o-Ps in excited well state („1p-like" state) is demonstrated.

The popular formula describing the pick-off rate λ_{po} as a function of free volume radius R [1,2] was derived, assuming that the void represents a rectangular infinite potential well for Ps atom; the well radius R_0 is assumed larger than that of the void; between R and R_0 an electron layer, into which the Ps wavefunction penetrates, is located. In molecular crystals these assumptions are not fulfilled exactly: the potential barrier is not infinite and not rectangular. It seems that the media closest to the TEM assumptions are porous materials, like silica gels. The Ps formed in the bulk is ejected to the pore, the height of the potential barrier is equal to the negative work function of Ps, in silica - 3,3 eV [3]. The pore radii are at least by one order of magnitude larger than the voids in nonporous solids, the spacing of levels in the well, decreasing like $1/R^2$, become smaller than 0,1 eV, thus infinite barrier is rather a good approximation.

The energies of a particle in the spherical and infinite cylindrical wells of radii R_0 are

$$E_{nl}^{sph} = \frac{\hbar^2}{2m_{Ps}} \frac{X_{nl}^2}{R_0^2} \quad ; \quad E_{nm}^{cyl} = \frac{\hbar^2}{2m_{Ps}} \frac{Z_{nm}^2}{R_0^2} \tag{1}$$

where X_{nl} and Z_{nm} are the nodes of Bessel functions $j_l(r)$ and $J_m(r)$, respectively, n=1,2,...; l=0,1,2...; m=0,±1,±2 etc. The o-Ps lifetimes can be calculated the same way as in TEM model

$$\tau_{nl}^{sph} = \left[\lambda_a N_s \int_{X_{nl}R/R_0}^{X_{nl}} j_l^2(r) r^2 dr + \lambda_T \right]^{-1} \quad ; \quad \tau_{nm}^{cyl} = \left[\lambda_a N_c \int_{Z_{nm}R/R_0}^{Z_{nm}} J_m^2(r) r dr + \lambda_T \right]^{-1} \tag{2}$$

where the normalizing factors are $N_s = [\int_0^{X_{nl}} j_l^2(r) r^2 dr]^{-1}$ and $N_c = [\int_0^{Z_{nm}} J_m^2(r) r dr]^{-1}$ and λ_T is the intrinsic o-Ps decay rate, $\lambda_T = 7.04\ 10^{-3}$ ns^{-1}. Figs.1 and 2 show the o-Ps lifetime as a function of pore radius for both discussed geometries. It is seen that distinct differences of lifetimes for various states can be observed for R≤3 nm; for larger R the term λ_T becomes dominant, thus as an object of study we have chosen the Silicagel Si40 (Merck) with average pore radii 2.0 nm, auxiliary measurements were performed for EUSI144 (R = 1.42 nm).

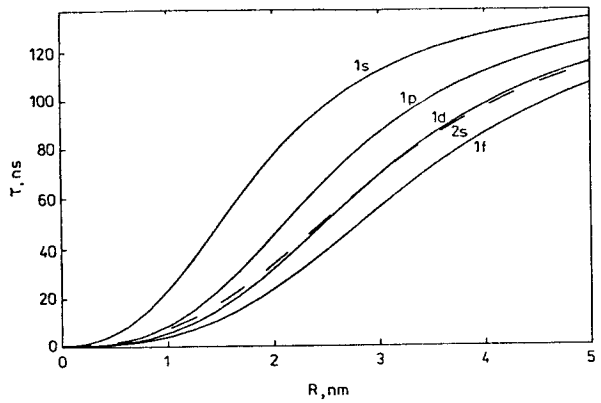

Fig.1 Ortho-Ps lifetime as a function of pore radius R for lowest (nl) states in the spherical well

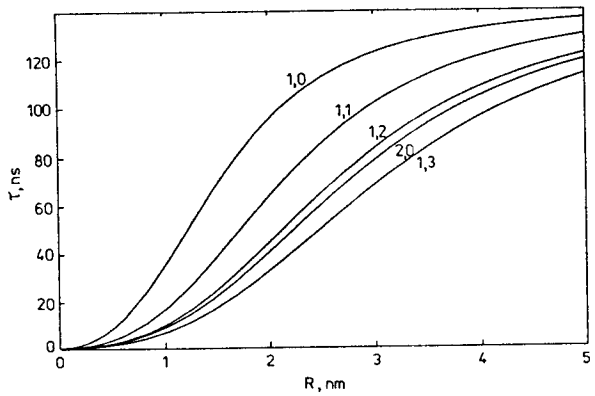

Fig.2 Ortho-Ps lifetime as a function of radius R for the states (n,±m) in the of infinitely long cylindrical well

In silica gels we have no single pore size, but a bell-shaped distribution of them; thus we should observe also similar distribution of lifetimes. For this reason an analysis of lifetime spectra was performed using LT program [4] allowing us to fit the sum of discrete λ components or continuous distributions of Gaussian shape in logarithmic λ scale.

Lifetime spectra of silica gels.

Each lifetime spectrum in Si40 contained 2.2 10^6 coincidences, including ≈ 15 % of the background. At the channel definition of 256 ps it was not possible to resolve p-Ps and free annnihilation components giving one averaged lifetime of 0.57 ns. The spectrum contained also a weak (2.4%) component with τ_2=1.9 ns and a long-lived part with the intensity exceeding 30%. This part, beginning from the delay 10 ns was analysed separately using LT program.

At very low temperatures only the *1s* ground state in the well should be populated, and the long-lived part of the spectrum should be described by one component with the distribution of λ, i.e. by two parameters: λ value at maximum of distribution λ_{3p} and the width of distribution σ_3. The spectrum registered at 110 K contained at the beginning of the time scale a certain amount of short-lived species, leading in one-component fit to anomalous broadening of σ_3. The values λ_{3p} and σ_3 stabilized at the delays over 50 ns. This 50 ns delay can be the measure of thermalization time. Stable values of parameters were found: τ_{3p} = (83±1) ns, σ_3 = 0.22. In the case of spherical free volumes the TEM model gives a lifetime of 77.5 ns, thus quite close to the experimental value. The pores can be of various shapes, cavities and "ink-pot" pores can be approximated by spheres; there are also capillary pores, and for them the approximation by cylinders (Eq.5) gives at R = 2 nm the lifetime of 95 ns. The experimental value suggests predomination of sphere-like pores. The width of τ_3 distribution is larger than expected; according to the porometric data we

should expect $\sigma_3 = 0.16$.

Silica gel EUSI144 has smaller pore radii and their structure is cylindrical. At the radius 1.42 nm the spacing of levels is increased twice compared to R = 2.0 nm, thus the population of the levels lying above the lowest one is small; in the low temperature limit (T = 104 K) we received the lifetime τ_{3p} = (67±1) ns, which corresponds rather well to the calculated value 64 ns. However, the width of distribution σ_3 is very big, contrary to the expectations for the medium with a very narrow distribution of pore radii [5]. The positron measurements with EUSI144 are much more difficult than with Si40 due to a very low intensity of the long-lived part of spectrum (7%).

In the case of Si60 with R = 3.0 nm even at 113 K the second level in the spherical well is populated; according to Boltzmann distribution ≈25% of o-Ps atoms annihilate from that state; the average lifetime calculated from Eq.2 for spheres is 107 ns, while the experimental value is (103.8±0.8) ns.

These results indicate that at sufficiently low temperature, when only the ground sate in the well is populated, the TEM model describes quite well the lifetime of o-Ps, despite of doubts if the value $\Delta R = R_0 - R$, determined empirically for small voids in molecular crystals and liquids, can be applied to the case of silica.

Temperature variations of lifetime spectra.

The lifetime spectra in Si40 were measured in a broad range of temperatures. In one component fit the lifetime τ_{3p} shortens with temperature increase, while the width of distribution σ_3 became larger. This effect can be the result of growing intensity of the fourth component related to annihilation from "1p-like" state. Thus, the long-lived part of the spectra was assumed to consist of two components. The parameters of one of them were fixed τ_{3p} = 83 ns, σ_3 = 0.22, as they were found at 113 K, the parameters of the other were left free (or σ_4 fixed also at 0.22, which gave the fitted values changed less than the experimental error). It was found that in the range of temperatures up to 240 K the lifetime τ_4 was constant, (43±1) ns; the calculated value for *1p* state in spherical well was 45.2 ns. At temperatures above 250 K τ_4 began to shorten slowly, which can be explained by growing admixture of next states lying above *1p*. The shape of lifetime distributions for several temperatures is shown in Fig.3. The intensity of the fourth component was

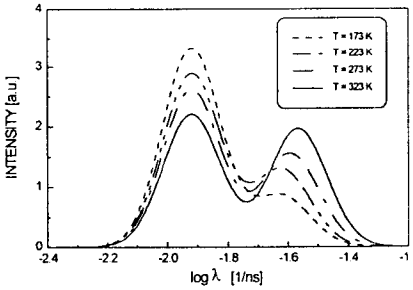

Fig.3 The distribution of long lifetimes in silica gel Si40 for several temperatures.

growing with the temperature, but remained always higher (by ≈7%) than expected from Boltzmann law. This can be an indication that thermalization of Ps was still incomplete.

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Positron Annihilation - ICPA-11
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