

Positronium lifetimes in porous Vycor glass

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Received 2 March 1998; in final form 7 April 1998

Abstract

The ortho-positronium lifetimes in porous Vycor glass were measured in a wide range of pore radii. A good correlation of the most probable lifetime with the model accounting for the population of upper levels of a particle in the potential well was observed. For channel-like voids (capillaries in porous media) a new value of the empirical parameter, ΔR , entering in the semi-empirical Eldrup equation, is proposed: $\Delta R = (0.191 \pm 0.007)$ nm; it explains some of the discrepancies previously found in crystalline solids. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

A positronium (Ps), the bound state of a positron and an electron, formed in the solid is usually trapped in ‘free volumes’ (voids), i.e. the regions of negligible electron density [1]. Its singlet sub-state, para-Ps (*p*-Ps) decays in a short time (≈ 120 ps) while the triplet sub-state (ortho-Ps, *o*-Ps) lives much longer. Its mean lifetime depends on the overlap of *o*-Ps wavefunction with the electron cloud around the void; thus it depends on the void size. For small voids one can describe the relation between the *o*-Ps lifetime τ_3 and the void radius R using the popular Eldrup equation [2], which is well tested on liquids, zeolites and molecular crystals with vacancies. The equation is commonly used for the determination of free volumes in polymers [3]. The radii of free volumes in the media listed above do not exceed 1 nm; for large voids a deviation from the Eldrup equation was observed and some modifications pro-

posed [4,5]. In our previous study of porous media [6,7] we pointed to the necessity of accounting for the *o*-Ps annihilation from excited states of the particle in the potential well, if the energy of these states is comparable to or smaller than the thermal energy kT . The pores are irregular in shape; we will approximate them using idealized geometries: spherical and cylindrical. Thus the radii R discussed below are only ‘the equivalent ones’ from the viewpoint of annihilation processes and are not necessarily identical with those commonly used in physical chemistry. In an infinite rectangular potential the energies of the states are:

$$E_{nl}^{\text{sph}} = 1.90 \times 10^{-2} \frac{X_{nl}^2}{R_0^2}$$

$$E_{nm}^{\text{cyl}} = 1.90 \times 10^{-2} \frac{X_{nm}^2}{R_0^2} + E_{II} \quad (1)$$

where E_{nl} is given in eV for a potential well radius R_0 in nanometers. X_{nl} , X_{nm} stand for the nodes of the radial wavefunction — a Bessel function j_l for

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spherical voids, and J_m for cylindrical ones, E_{II} is the energy related to the axial motion of the particle in the well. At room temperature and $R_0 \geq 1.5$ nm the population of the excited levels cannot be neglected (RT equilibrium population of the 1p state for $R_0 = 1.5$ nm is 9%).

2. Experimental

Vycor glass composed of 7% Na_2O , 23% B_2O_3 and 70% SiO_2 was used as the starting material. Portions of this glass (35–75 μm fraction) were heated at 800 K during various times in order to ensure different liquation processes [8] in the initial glass. The thermally treated samples of glass were next converted into porous ones by proper leaching with 3 N H_2SO_4 solution according to the procedure described in Refs. [8] and [9]. Before the measurements, the samples were carefully washed with water to neutrality and dried at 470 K for 24 h. Some samples with large pores were of commercially available Vycor glass CPG-10; the silica gel samples were from Merck.

The positron source, ^{22}Na , in a Kapton foil envelope was placed between two layers of grains pressed together in a copper container fixed inside the chamber in which a pressure of ≈ 0.5 Pa was maintained.

The samples were viewed by two counters with BaF_2 scintillators coupled to a standard fast–slow lifetime spectrometer. In order to assure a high efficiency of registration of the continuous 3γ annihilation spectrum the ‘stop’ window of the spectrometer was widely opened to 80% of the energy range. The resolution of the spectrometer was 0.28 ns, and the channel definition 0.26 ns, the total area of each spectrum was about 2×10^6 coincidences.

The average pore radius in Vycor glass was measured using the nitrogen method in the CLAU laboratory at the Faculty of Chemistry; the pore radii of silica gels quoted here were taken from the literature (LN method [10]).

The Ps atoms formed in the bulk are ejected to the pores owing to their negative work function [11], only a small fraction of them annihilate outside the grains, giving the long-lived component with the lifetime close to 140 ns, as for *o*-Ps in a vacuum. The intensity of that component was determined by

us as about 0.6% of the total. In further analysis of the spectra the 140 ns component was taken into account.

All measurements were performed at room temperature.

3. Results and discussion

The decay rate of *o*-Ps in the void is

$$\lambda_3 = \frac{1}{\tau_3} = \lambda_t + \lambda_{\text{po}} \quad (2)$$

where λ_t is the intrinsic decay constant, λ_{po} is the pick-off process rate $\lambda_{\text{po}} = \lambda_b P$, with λ_b representing the *o*-Ps decay rate in the bulk, i.e. the spin averaged annihilation rate or decay rate of the Ps^- ion, both equal to 2 ns^{-1} ; P is the probability of finding a Ps outside the void. In the commonly used model [2] the penetration of the Ps wavefunction outside the void of the radius R and finite depth of potential is substituted by broadening the well by ΔR and assuming it is infinitely deep. Then for the spherical geometry

$$\lambda_{\text{po}}^{nl} = \lambda_b \int_{X_{nl}R/R_0}^{X_{nl}} j_l^2(r) r^2 dr / \int_0^{X_{nl}} j_l^2(r) r^2 dr, \quad (3)$$

while for infinitely long cylinders (capillaries):

$$\lambda_{\text{po}}^{nm} = \lambda_b \int_{X_{nm}R/R_0}^{X_{nm}} J_m^2(r) r dr / \int_0^{X_{nm}} J_m^2(r) r dr, \quad (4)$$

where $R_0 = R + \Delta R$.

When the population of states above 1s cannot be neglected, the shape of the long-lived part of the lifetime spectrum depends on the average dwell time of the Ps in definite state t_d :

(a) if $\tau_3 \ll t_d$ the spectrum contains a separate exponential component for each state;

(b) if $t_d \ll \tau_3$ there should be one averaged component with the pick-off decay constant $\lambda_{\text{po}} = \sum \lambda_i P_i$, where P_i is the probability of finding *o*-Ps in the i th state.

The thermalization time is shorter than the lifetime [12] indicating the effective interaction of the Ps with the pore walls, thus variant (b) seems to be more probable, although there are also data [7] suggesting incomplete thermalization and the existence

of separate components. In porous media we have no single R , but rather a continuous distribution around the average R , thus the o -Ps decay curve is not exponential, making the distinction of cases (a) or (b) difficult.

The distribution of pore radii in Vycor glass is relatively narrow, usually $\pm 5\%$; thus in the estimates of λ_{po} we assumed discrete decay rates $\lambda_{po}^{(nl)}$ for each quantum state, corresponding to the average radius. Thus, in thermal equilibrium, we obtain for the spherical geometry:

$$\lambda_{po} = \sum_{i=1}^N \lambda_{po}^{(i)}(R) g_i \exp\left[-\frac{E_i(R)}{kT}\right] \Bigg/ \sum_{i=1}^N g_i \exp\left[-\frac{E_i(R)}{kT}\right], \quad (5)$$

where g_i is the statistical weight of the i th state, N is the number of levels taken into account (in our calculations $N=7$), i numerates the states from the lowest upwards. The curve representing $\tau_3 = [\lambda_{po} + \lambda_1]^{-1}$ as a function of R for the spherical geometry and at room temperature is shown in Fig. 1. (ΔR is the same as that used in the literature, 0.166 nm.) It is drawn to $R = 8$ nm only, for larger R the number

of involved states rises rapidly and summing over seven states is not sufficient.

In the case of cylindrical channels the axial part of the energy E_{II} is not quantized, but its average value for a given temperature is constant. In Eq. (5) the energies are given relative to the ground state, thus if we assume the energies E_i in Eq. (5) as average ones for each (n,m) state, the E_{II} part cancels out and Eq. (5) can be used with E_i equal to 'radial' part of energy.

In variant (a) one can calculate $\bar{\tau} = \sum \tau_i P_i$; the difference between $\bar{\tau}$ and τ_3 (variant b, Eq. (5)) largest near $R = 2.66$ nm, is insignificant not exceeding 4.2 ns. One can determine the experimental $\bar{\tau}$ directly (after background subtraction): $\bar{\tau}_{exp} = \sum n_i m_i D / N$, where n_i , m_i , D and N are the channel content, channel number, definition and total number of counts, respectively. However, the existence of the short-lived components in the spectrum (p -Ps, free annihilation) forces the summing to begin ($m_i = 1$) at a delay of ≈ 10 ns. If all components of ' o -Ps in the pore' origin are very long-lived, the $\bar{\tau}_{exp}$ determined from 10 ns onwards is not measurably distorted. In the presence of the components living shorter than 70 ns, that 10 ns delay cuts a substantial part of their intensity and distorts (increases) $\bar{\tau}_{exp}$. Thus we decided to use the most probable lifetime τ_p instead of the average one. The

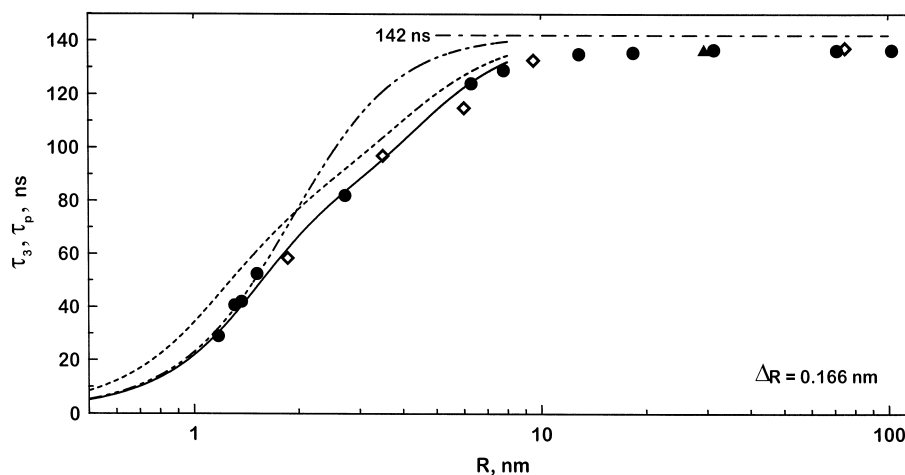


Fig. 1. Ortho-Ps lifetime as a function of pore radius in Vycor glass and silica gels for $\Delta R = 0.166$ nm. The solid curve (—) is drawn for spherical pores at room temperature, the dash-dot curve (— · —) at 0 K (1s state only), the dotted curve (----) is for a cylindrical geometry. Circles (●) denote Vycor glass, diamonds (◇) silica gels; the triangle (▲) is for Vycor glass with a 2 nm polymer surface coverage. The uncertainty of R determination is estimated as about 5%.

whole spectrum was analysed by the LT program [13], which fits to the experimental data the function

$$C(t) = \sum_{i=1}^2 I_i \lambda_i \exp(-\lambda_i t) + \frac{I_3}{\sigma\sqrt{2\pi}} \times \int_0^\infty \exp\left[\frac{\ln^2(\tau_p \lambda)}{2\sigma^2}\right] \exp(-\lambda t) d\lambda \quad (6)$$

where $\lambda_1 \approx 2.1 \text{ ns}^{-1}$ represents the free annihilation and unresolved *p*-Ps decay, $\lambda_2 \approx 0.8 \text{ ns}^{-1}$ *o*-Ps annihilation inside the glass. The long-lived part of the spectrum is approximated by continuous log-Gaussian distribution of λ with the most probable lifetime τ_p (due to the distribution of R the width σ cannot be zero). The lifetimes τ_p and $\overline{\tau_{\text{exp}}}$ are not identical; however, the difference between them observed for $R > 3.5 \text{ nm}$ is negligible. The experimental points on Fig. 1 show τ_p . The data for Vycor glass are supplemented by those for silica gels [7]; one point is for glass with the pore surface covered by a 2 nm layer of polymer.

As a measure of pore size ('equivalent R ') we have accepted the radius determined by classic nitrogen or mercury methods and this value is used in the figures as the abscissa. All experimental points run along the curve calculated for spherical voids, except the range of the largest R , where the saturation value of τ_p is $\approx 137 \text{ ns}$, slightly less than the theoretical limit 142 ns. This is partly due to the presence of high (nl) levels always lowering the average, but also to the fact that the spectrum of lifetimes is asymmetric, cut at 142 ns, while LT program fits to a symmetric log-Gaussian distribution. The difference of τ_p and $\overline{\tau_{\text{exp}}}$ for a large R is estimated by us as $\leq 1.5 \text{ ns}$. There may also be an inaccuracy of time calibration, which was not higher than 1%.

The results are rather surprising, the experimental points locate neatly near the model curve for spheres, while the radii R obtained from nitrogen desorption relate to the capillary geometry. The equation for capillaries (Eqs. (4) and (5)) gives higher values of τ_3 than the experimental ones, for an arbitrary R . Thus, we have several possibilities:

(1) Ps in porous medium locates in definite place in the channel, feeling the sphere-like surroundings, but, in that case, one would expect a lengthening, not shortening, of the lifetime;

(2) The capillary model should be consequently used, but with the modified ΔR value. The ΔR is an empirical parameter fitted to the set of experimental data for nearly spherical structures (bubbles in liquid, zeolite cages, vacancies in plastic crystals) in a narrow range of $R < 1 \text{ nm}$, it does not need to have a universal value for all structures and sizes. Fig. 2 shows the model curves for cylindrical channels at several values of ΔR , together with 10 experimental points. It can be seen that these points are distributed near the curve with $\Delta R = 0.190 \text{ nm}$; the best fit is obtained for $(0.191 \pm 0.007) \text{ nm}$. The cylindrical model with $\Delta R = 0.191 \text{ nm}$ gives a similar τ_3 vs. R dependence to that of the spherical model with $\Delta R = 0.166 \text{ nm}$.

(3) The capillary model does not need the change of ΔR , but then one has to assume that the Ps in pores is not thermalized; the increased participation of upper levels shifts the lifetimes below the equilibrium value. However, for the smallest pores in our Vycor glass the lifetime τ_p is 27 ns, thus close to that in largest bubbles observed in liquids (20 ns in SF_6 ; see Ref. [14]) where the effects of non-thermalization were not seen. Thus case (2) seems to be more probable.

Note that the characteristic bending of model curves near $R = 2 \text{ nm}$ produced by the increasing population of excited levels with larger decay rates is

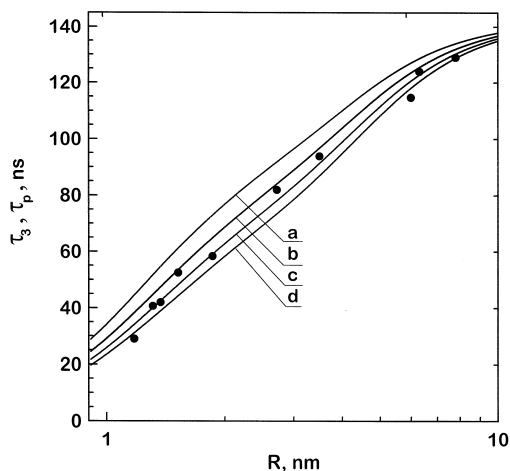


Fig. 2. Ortho-Ps lifetime in the cylindrical channel for several values of ΔR : (a) 0.166, (b) 0.180, (c) 0.190 and (d) 0.200 nm. The experimental points are the same as in Fig. 1.

Table 1

Experimental and calculated values of *o*-Ps lifetime in channel-like intermolecular free volumes at room temperature

Crystal	τ_3 (ns)		
	Experimental	$\Delta R = 0.166$ nm	$\Delta R = 0.190$ nm
phenanthrene	1.08 ± 0.02	1.18	1.05
biphenyl	1.14 ± 0.01	1.32	1.14
catechol	0.98 ± 0.02	1.24	1.08
hydroquinone	1.08 ± 0.01	1.26	1.10

visible in the experiment. As seen in Fig. 1, the states above 1s play an important role in the range of radii (2–8) nm. For smaller *R*, excited levels are not populated at room temperature; for large *R* the dominant decay mode is the intrinsic one, independent of *R*.

A discrepancy between the lifetime in channel-like voids and respective model was observed by us earlier in the case of small intermolecular free volumes in crystalline solids [15]. When these voids have the form of channels running through the crystal, the equation for a channel with a rectangular cross-section (≈ 0.1 nm²) gives systematically higher values of τ_3 than those which are observed. Increase of the penetration depth of the wavefunction from 0.166 to 0.190, adopted from the model above, greatly improves the consistency of the model and the experiment (Table 1).

4. Conclusions

The model of Eldrup has never pretended to give a quantitative measure of the lifetime in the void; however, in spite of the model approximations, the non-identity of τ_3 , $\bar{\tau}$ and τ_p , the correlation between the experimental data and the model curves is good if the excited states of the particle in the well are taken into account.

In the case of channel-like free volumes we propose a new value of the parameter ΔR equal to 0.19 nm.

The experimental points for silica gel locate on the same curve as those for Vycor glasses (different pore structures).

The lifetime versus radius dependence is particularly steep in the range of 0.5–4 nm; thus it seems that the positron annihilation can be used as a tool in the estimation of the average radii in porous media. This method has no limitation on the side of small *R* as in the case of the nitrogen method.

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