Positronium as a Probe of Small Free Volumes

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The relation between free volume size and the lifetime of ortho-Ps trapped in that volume is usually described in the framework of simplified model, proposed by Tao and Eldrup et al. In that model the positronium trap has spherical shape and the potential is rectangular one with infinite depth. In spite of its simplicity in most cases the model gives proper values of o-Ps lifetime and its zero-point energy in the trap. It can be also easily extended toward nonspherical and large-size free volumes. In that last case the population of particle states lying above the zero-point energy has to be taken into account.

Positronium is a hydrogen-like structure, formed by an electron and positron. Owing to very low reduced mass the energies of all levels of that structure are scaled down by the factor of two comparing to hydrogen (e.g., the binding energy of the ground state is 6.8 eV). Positronium forms when it is energetically favorable, i.e., the energy of bound system is lower than sum of energies of quasi-free electron and positron in the medium. If a pair of electron and positron is on the surface of medium or close to that surface, it can escape to vacuum taking with it the energy gain in the form of kinetic energy of the bound system. When positronium is ejected not into an open space, but to a cavity (void) inside the medium, it is trapped, loosing the surplus of energy in the interactions with the bulk. The kinetic energy of positronium reaches finally the level of zero-point oscillations (Figure 1). Trapping of positronium has two important consequences:

- the uncertainty principle determines the momentum of particle as dependent on the trap size,

- interaction of positronium with surrounding bulk material gives additional possibility of annihilation and thus increases the decay rate (shortens the lifetime).
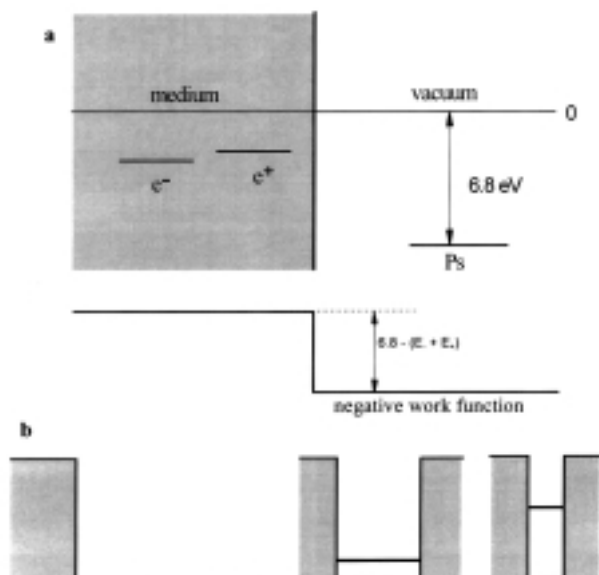

Figure 1. a) Energetic conditions of Ps formation; positronium work function is negative. b) Rectangular potential steps for Ps at the medium-vacuum boundary; from left to right: open space, broad void, narrow void. The narrower is the well, the higher zero-point energy.

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Positronium atom can exist in two hyperfine structure states: with antiparallel electron and positron spins (*para-positronium*, p-Ps) and with parallel ones (*ortho-positronium*, o-Ps), distinctly differing as to their annihilation properties.[1] *Para*-positronium annihilates in vacuum in a very short time 0.125 ns transforming into two gamma quanta, 511 keV each; *ortho*-positronium in vacuum decays via three quantum process (continuous energy spectrum) with the lifetime 142 ns. Due to very short lifetime *para*-Ps is weakly affected by surrounding medium, while it is very probable that *ortho*-Ps picks one of electrons of the medium with appropriate spin orientation (antiparallel one) and annihilates with it in a short time, via two quantum emission.

Trapped p-Ps annihilates as a whole entity and the width of its momentum distribution is simply related to the trap radius R by uncertainty principle[2]:

$$\Theta_{1/2} = 16.6/R \tag{1}$$

where $\Theta_{1/2}$ is half-width of angular distribution of annihilation quanta (in mrad, for R in angstroms). The deviation from colinearity of the quanta Θ is proportional to the transverse component of the momentum $p_\perp$ of annihilating system: $\Theta = p_\perp/mc$. Longitudinal p_{II} component of the momentum can be observed in Doppler broadening of the 511 keV annihilation gamma line. The Doppler shift in that case is $\Delta E = p_{II}c/2$. The lifetime of *ortho*-Ps annihilating by pick-off process is determined by the overlap of Ps wave function with bulk electrons of surrounding medium and the o-Ps lifetime becomes dependent on the trap size. Thus, positron annihilation methods (positron lifetime measurements PAL, or measurements of momentum distribution of annihilating pairs) can be used in the study of small free spaces in the structure of solids − defects in the crystals, free volumes in amorphous media. In the majority of practical applications of PAL method the relation between free volume size and *ortho*-positronium decay rate λ_{o-ps} is taken from Tao-Eldrup model,[3,4] assuming Ps as trapped in a spherical void representing for Ps a rectangular potential well. In order to simplify the calculations, in that model the penetration of Ps wave function outside the void is substituted by broadening the potential well by ΔR and assuming infinite height of that well (Figure 2). The value of ΔR was chosen to give the same probability to find the Ps atom in the range $(R, \Delta R)$ as outside the well in real finite potential. With these assumptions the model gives

$$\lambda_{o-Ps} = \lambda_b[1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi} \sin(2\pi \frac{R}{R+\Delta R})] + \lambda_t \tag{2}$$

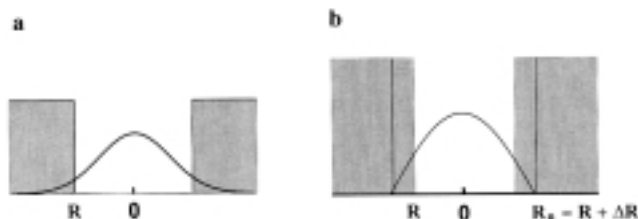where λ_b, R, λ_t are o-Ps annihilation rate in the bulk, sphere

Figure 2. Tao-Eldrup model. Finite depth well with penetration of the wave function to outside (a) is substituted by infinite well broadened by ΔR (b); the wave function does not extend behind $R+\Delta R$.

Figure 3. The o-Ps lifetime as a function of void volume for several void shapes: a) sphere; b) ellipsoid with the eccentricity $\varepsilon = 0.2$; c) cube; d) cuboid with constant square cross section 0.5×0.5 nm. In all cases ΔR is assumed 0.166 nm.

radius, intrinsic decay rate of o-Ps in vacuum, respectively. There is to note, that at very small R no energy levels in the well, thus positronium cannot be bound. The minimal radius at which the energy level for Ps exists is $\approx 0.216/\sqrt{V_0}$, where V_0, the depth of potential well, is in eV for R in nanometers. Thus, probing the distribution of free volumes in the medium by positron methods, we do not see the smallest objects with R below ≈ 0.12 nm. The equation (2) was applied to the free volume holes from 0.15 nm (e.g., Ref. 5) to 0.60 nm (zeolites[6]) and in that range of R the last term in eq 2 can be neglected.

The equation eq 2 contains in fact a set of empirical parameters. The value of λ_b is usually assumed as weighted average of p-Ps and o-Ps intrinsic decay rates

$$\lambda_b = \frac{1}{4}\lambda_s + \frac{3}{4}\lambda_t \qquad (3)$$

In that approach λ_b looks independent on electron density of the medium surrounding the free volume hole. In earlier models of the pick-off annihilation[7] the λ_b was assumed proportional to the medium density and effective number of electrons per molecule Z_{eff} participating in that process:

$$\lambda_b = \pi r_0^2 cn Z_{eff} \qquad (4)$$

where r_0 is the classic electron radius and n is the number of molecules per volume unit. Z_{eff} is also an empirical parameter, related to some extent to the number of outer electrons in the molecule, but leaving certain freedom in fitting λ_b to the experimental data. Thus, λ_b vs. electron density dependence in one model (eq 3) is contrasting to that in other one (eq 4). The annihilation rate is determined by the electron density at the site of positron. This density is created partly by o-Ps own electron, partly by the electrons of surrounding medium. However, owing to the Pauli principle only one of these electrons can found itself in the nearest vicinity of e^+ (that one with the spin opposite to o-Ps electron), repulsion between o-Ps and other electrons reduces their influence on the annihilation rate. Thus, the configuration giving maximal electron density is similar to that in Ps^- ion and Ps^- decay rate is known to be the same as that given by eq 3[8]: $\lambda (Ps^-) = 2ns^{-1}$. The λ_b value equal 2 ns^{-1} is thus rather the maximal expected rate, the real ones can be lower and dependent on n. If the Tao-Eldrup model works (as we observe in polymers, molecular crystals, liquids) it means that we are in the range of high densities and λ_b approaching its maximum; the dependence of λ_b on n and Z_{eff} is thus weakened.

The equation 2 is valid for spherical voids. The real free volume holes are irregular, the lifetime depends on their shapes. Figure 3 shows the o-Ps lifetime as a function of void volume for several simple shapes. It is seen that the positron lifetime experiments bring no information strictly about the volume; all what we determine is an equivalent radius of a hypothetical sphere, giving the same lifetime as that observed experimentally. Note, that in the case of elongated free volume holes the lifetime stops to be dependent on volume (length) if the hole cross section remains constant. Depending on the crystalline structure or polymer chain arrangement we can
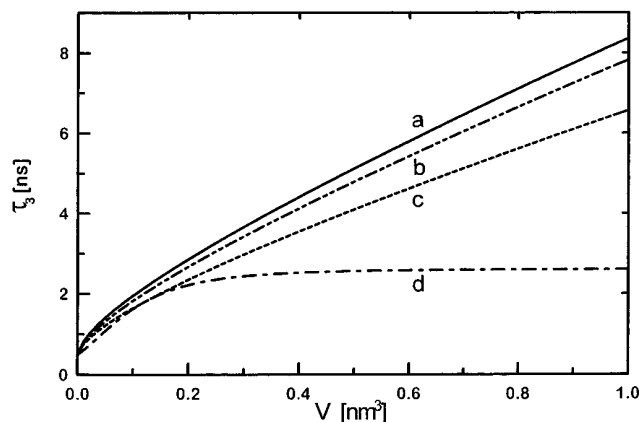
make the choice between the idealized bodies (sphere, cuboid, ellipsoid, cylinder) most suitable for description of particular medium, but always we receive equivalent cylinder radii, equivalent cuboid sides etc. The "equivalent" dimensions should be compared with these obtained using other methods, expecting they are identical (or at least close to each other).

The parameter ΔR is introduced as a means to simplify the calculations. The ΔR value is chosen to receive the probability to find Ps between R and $R+\Delta R$, equal to the probability to find Ps outside the real well, i.e., between R and ∞ (Figure 2). The value of $\Delta R = 0.17$ nm was proposed by Eldrup et al. for plastic crystals investigated by them.[4] In liquids it was noticed that ΔR can vary in certain limits.[9] Almost all the data, on which the estimation of ΔR was based, relate to narrow class of media, organic solids and liquids, composed of similar atoms. It cannot be excluded that for other compounds different values of ΔR would be needed. The ΔR is not an universal number fitting to all cases, thus, giving too many digits in its value (e.g., ΔR=0.1656… etc.) has no physical meaning. By the way, even the value of R is not too precisely defined: the boundaries of such a small hole are not a stepwise function of r and the electron density changes from the bulk value to zero in certain range of r. For large R this transition region can be neglected, but not for smallest holes.

In some cases, e.g., interpretation of the results of momentum distribution measurements we need to know the zero point energy of Ps particle in the well. Comparing to real well (finite depth V_0, radius R), the transition to infinite well shifts the zero point energy upwards, while substitution of R by $R+\Delta R$ shifts it down. However, for $\Delta R = 0.166$ nm these two shifts do not compensate exactly. Figure 4 shows the energies for real void radius R and $V_0 = 1$ eV or 1.5 eV (exact solution in rectangular potential) and for $R+\Delta R$, $V_0 = \infty$ (Tao-Eldrup model) in the units of zero point energy for the radius R and infinite potential V_0, i.e., in the units of $\frac{\hbar^2}{2m_{Ps}}\frac{1}{R^2}$. It is seen that the application of $R+\Delta R$ instead of R gives acceptable energy values for 0.30 nm $< R < 0.55$ nm if $V_0 \approx 1$ eV, but for larger R or deeper potential the shift to lower energies, following from Tao-Eldrup model, is exaggerated. The misfitting is not too large, but should be taken into account. With the rise of R the role of potential depth reduces.

The Tao-Eldrup model gives to us relatively good estimate of free volume size and Ps zero-point energy for definite kind of that volume. It is enough when the structure of free volume in a solid is simple, like in crystals: one dominant type of defects (e.g., vacancies), or several well defined ones (divacancies, free spaces in the vicinity of impurities *a.s.o.*). In the amorphous structures, like polymers, we have rather continuous spectrum of free volume sizes which produces a continu-
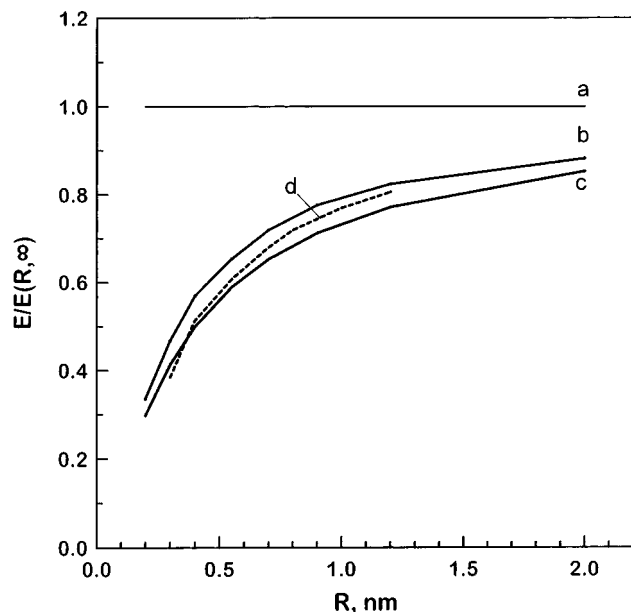
Figure 4. Zero point energy in spherical well in the units of $\hbar^2\pi^2/2m_{Ps}R^2$: a) infinitely deep well, radius R; b) finite potential depth $V_0 = 1.5$ eV and radius R; c) infinite potential depth and radius $R+\Delta R$ (ΔR assumed 0.166 nm); d) finite potential depth $V_0 = 1.0$ eV and radius R. Cases b) and d) represent real situations, case c) - the Tao-Eldrup model.

ous spectrum of decay rates $S(\lambda)$. Fitting programs like CONTIN[10] or MELT[11] allow to determine that $S(\lambda)$ spectrum. However, can the λ spectrum be directly "translated" into void radii spectrum, is still an open question. In the experiment we observe not the radii distribution $V(R)$, but the product $V(R)T(R)$, where $T(R)$ describes the dependence of Ps trapping probability on R. From eq 2 we have[12]:

$$V(R)T(R) = \lambda_b \Delta R \frac{1 - \cos(2\pi \frac{R}{R+\Delta R})}{(R+\Delta R)^2} S(\lambda) \quad (5)$$

The $T(R)$ function is not well determined yet. Moreover, the transformation from $S(\lambda)$ to $V(R)$ as in eq 5 needs to assume that positronium once trapped does not change its location up to the decay, i.e., the processes like tunneling from void to void, averaging the lifetime (with preference to larger voids), are neglected.

The Tao-Eldrup model describes the ground state of a particle in the potential well. In deep or broad wells we should expect the existence of excited levels. However, if the free volume holes are of the sizes not exceeding (0.3–0.4) nm, like usually in polymers or crystals, the spacing of second state in the well from the ground one is much larger than thermal energy at the temperatures usually applied. If the thermal equilibrium is achieved, we can neglect the population of excited states.

In spite of all limitations, created by approximate character of the model, rough agreement of model and experiment is observed. The model is well tested in the case of plastic crystals,[4,13] however the range of free volumes equivalent to vacancies cover a very narrow range, from 0.10 to 0.25 nm³, several points for zeolites[6] also fit well to the expectations from the Tao-Eldrup model. In principle, the data for liquids cannot be the test of our model, for the sizes of zero-point bubbles are calculated ones, basing on the macroscopic surface tension, which need not be true in *micro* scale. One can compare the positron data on free volumes with similar data obtained by other methods; as an example of such a comparison can serve the Reference 14, where the free volumes were independently estimated from gas diffusivity measurements.

In our recent papers (e.g., Ref. 15) we have tried to extend this model to the case of large R and cylindrical free volumes, e.g., to the pores, without introducing too radical changes in order to retain smooth transition from small to large radii within one model. The only change was the increase of ΔR to 0.19 nm; it has proven necessary to match the annihilation radii to those determined by classic chemical methods: LN desorption, thermogravimetry etc.). This extended model (i.e., accounting the annihilation from excited levels in the well) explains e.g., the decrease of o-Ps lifetime with the rise of temperature, commonly observed in porous media.

At low temperature limit, like for small R, only the ground level in the well is populated and the o-Ps lifetime is determined by classic eq 2, i.e., at T→0 the o-Ps lifetime should tend to the constant value. This "saturation" value was observed in some cases, however, in others more complex behavior appears. If we assume, as in the model presented above, that the overlap of Ps wave function with the bulk is determined only by the size and shape of the void and there are no other factors influencing the Ps decay beside pick-off, the deviation from expected lifetime value needs to accept the possibility of λ_b variation.

There is to note that in standard applications of positron lifetime technique to the determination of free volume holes, only the term λ_{po} relating to pick off process is taken into account, the intrinsic decay rate λ_T is usually neglected as a small contribution. In the case of large voids, already at R = 2 nm the pick-off rate is smaller than intrinsic decay one. The pick-off process, which is the subject of Tao-Eldrup and similar models, is no longer the dominant one. Various factors which in usual case are of secondary importance for annihilation rate can begin to play substantial role, e.g., chemical effects, sorption processes. The lifetime is reciprocal of λ, thus if λ decreases, the lifetime should lengthen.

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