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CALCULATIONS OF ANNIHILATION RATE OF *o*-Ps IN PICK-OFF PROCESS

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In the paper we suggest the procedure of calculation of the *o*-Ps lifetime in the pick-off process. The procedure follows the scheme proposed by Tao but we employed the correct positron wave function. We extended our calculations for the case when the *o*-Ps is overlapping the core region of hydrogen and carbon atoms. The obtained dependence between the lifetime and the radius of the *o*-Ps fits much better to the experimental one observed in silica gel than the original Tao relation.

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Recently, there has been published a considerable amount of papers dealing with studies of the free volume in the microstructure of molecular solids deduced from the decay of the *orto*-positronium atom (*o*-Ps). The authors apply the relation between the radius of the free volume or empty cave and the annihilation rate in the pick-off process of the *o*-Ps suggested by Tao [1]. Besides of the interest the experimental and theoretical examination of this relation is still not conclusive enough. The aim of the paper is to present a critical view on this relation in order to find a better theoretical outline of the connection between the pick-off rate and the radii of the free volume.

It is well established that the annihilation rate of positron in matter can be expressed as follows:

$$\lambda = 1/\tau = \pi r_e^2 c \int\int\int_V \mathrm{d}r \psi_+^*(r)\psi_+(r)\psi_-^*(r)\psi_-(r)\gamma(r), \tag{1}$$

where r_e is the classical electron radius, c is the light velocity, ψ_+ and ψ_- are the positron and electron wave functions, respectively, γ is the enhancement factor (see e.g. [2]), τ is the corresponding positron lifetime and V is the volume element. If we wish to apply this relation to the calculation of the annihilation rate of *orto*-Ps in the pick-off process, ψ_+ should represent the wave function of the positron in the field of the electron to which it is bound creating the *o*-Ps as well as in the field of the surrounding medium molecules, ψ_- is the wave function of the electrons in the surrounding medium molecules under the same condition. Tao took into his calculations only a zero-velocity approximation as the positron wave function.

That means this wave function was equivalent to the wave function of the Ps treated as a particle with no structure in a spherical cave of radius r_0

$$\psi_+(r) \approx \psi_{\mathrm{Ps}}(r) = \frac{1}{\sqrt{2\pi r_0}} \frac{\sin\left(\frac{\pi r}{r_0}\right)}{r}, \tag{2}$$

only inside the cave and zero outside. He assumed that ψ_- is a constant value equal to zero inside the cave and non-zero only in the spherical layer of thickness $r_0 - r_1$ surrounding the cave. He assumed the annihilation rate of *orto*-Ps in this electron layer equal to 2.0 ns^{-1} (one-fourth of *p*-Ps annihilation rate). After integration of (1) with the additional assumption that $\gamma = 1$ we obtain the well-known formula

$$\lambda[\mathrm{ns}^{-1}] = 2\left[\frac{r_0 - r_1}{r_0} + \frac{1}{2\pi}\sin\left(\frac{2\pi r_1}{r_0}\right)\right]. \tag{3}$$

The coincidence of this relation with the experimental values of the annihilation rate was assured when $r_0 - r_1 = 0.1656$ nm. As we can see the theoretical background of the relation (3) is rather crude. First of all we should point out that we know the exact values of the wave function of positron bound with an electron when both are localized inside the spherical cave with infinite walls [3]. The Schrödinger equation for the positron under such a condition has the following form:

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{r} - W\right)\psi_+(r) = 0, \tag{4}$$

where $W < 0$ is the bounding energy of the positron and electron and μ is the reduced mass of the Ps which is exactly one-half of electron mass. The radial part of the equation can be rewritten in the following form:

$$\frac{\mathrm{d}^2R(r)}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}R(r)}{\mathrm{d}r} + \frac{2\mu}{\hbar^2}\left(W + \frac{e^2}{r}\right)R(r) - \frac{l(l+1)}{r^2}R(r) = 0, \tag{5}$$

where $l = 0, 1\ldots$ If we express W as equal to $-e^2/(2n^2a_{\mathrm{Ps}})$ where $n > 1$ is the parameter which we can deduce from the constraint $R(r_0) = 0$ and $a_{\mathrm{Ps}} = 0.1058$ nm is twice the Bohr radius. Finally, the positron wave function has the following form:

$$\psi_+(r) = C_{nl}\exp\left(-\frac{r}{na_{\mathrm{Ps}}}\right)\left(\frac{2r}{na_{\mathrm{Ps}}}\right)^l F\left(l-n+1, 2l+2, \frac{2r}{na_{\mathrm{Ps}}}\right)Y_{lm}(\theta,\phi), \tag{6}$$

inside the cave and zero outside. F is the hypergeometrical function and C_{nl} is the normalization constant. Note that the wave function (6) differs from the wave function considered by Tao (2). From (5) and (6) one can deduce also that for the radius r_0 below a critical value $W > 0$ a bound state between electron and positron is not possible, so the *o*-Ps does not exist. For $l = 0$ that critical radius is equal to $1.835a_{\mathrm{Ps}}$ (0.1942 nm) and for $l = 1$, $5.070a_{\mathrm{Ps}}$ (0.5366 nm). The destruction of the Ps in the cave whose radius is below the critical value arises from the fact that the attractive Coulomb force between electron and positron is pressed by the interaction with the potential of the cave. Figure 1 presents the dependence of the binding energy on the radius of the cave. When the radius of the cave increases to infinity this energy tends to the asymptotic value $-e^2/(2a_{\mathrm{Ps}})$ (−6.803 eV) and

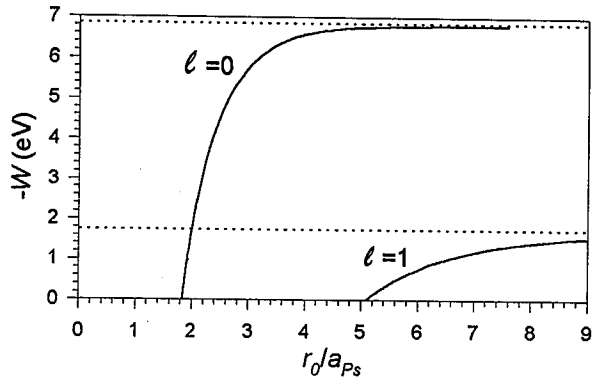

Fig. 1. The values of the binding energy of the Ps atom as a function of the radius of the cave with infinite wall for two values of the orbital quantum number l.

$-e^2/(8a_{\mathrm{Ps}})$ (1.701 eV) for $l = 0$ and $l = 1$, respectively. This fact was not taken into account in the relation (3) which does not have any limitation for the value r_0.

Nevertheless, we can try to apply Tao's consideration taking into account the correct positron wave function (4). Still we assume that the spherical cave is surrounded by the uniform layer of electrons where the positron annihilates and $\gamma = 1$, then the annihilation rate equals to

$$\lambda = 1/\tau = A \int_{r_1}^{r_0} \psi_+^2(r) r^2 \mathrm{d}r. \tag{7}$$

Note that in such an approach we have still two parameters A and $r_0 - r_1$, which should be treated as fitting parameters for obtaining a good agreement of relation (7) with experimental values. In our case we took the values of these parameters in such a way as to obtain a good coincidence of (5) with the relation (3) for r_0 close to the critical value and to get a realistic value of the annihilation rate for large cave radii. In our calculations we assumed that $A = 0.05$ ns^{-1} and $r_0 - r_1 = 0.5a_{\mathrm{Ps}} = 0.0529$ nm. Figure 2 presents the plot of obtained dependence, the dashed line presents the τ value versus the radius r_0 for $l = 0$ and $l = 1$. The lifetime of the o-Ps increases almost parabolic with the radius of the cave and very soon it is able to reach the value of the lifetime in the vacuum (141.880 ± 0.032 ns [4]). We should remember that the o-Ps can decay in pick-off process or the decay in the self-annihilation of the o-Ps. The second process is getting significant when the first one is slower. In such a case the observed annihilation rate will be a sum of the annihilation rates of two processes as follows:

$$\frac{1}{\tau} = \frac{1}{\tau_{\mathrm{pick-off}}} + \frac{1}{\tau_{\mathrm{self}}}, \tag{8}$$

where $\tau_{\mathrm{pick-off}}$ is expressed by the relation (7). In our calculation we assumed that $\tau_{\mathrm{self}} = 100$ ns which corresponds to the value obtained in pores materials [5]. Figure 2 presents the calculations of the lifetime of the o-Ps, the solid line corresponds to the relations (7) and (8) as the function of the cave radius. The obtained dependence has the sigmoidal shape with saturation at high values of the cave radius, which should be expected. For comparison, in Fig. 2, one can find the plot of the Tao relation (3) which does not saturate. The interesting feature

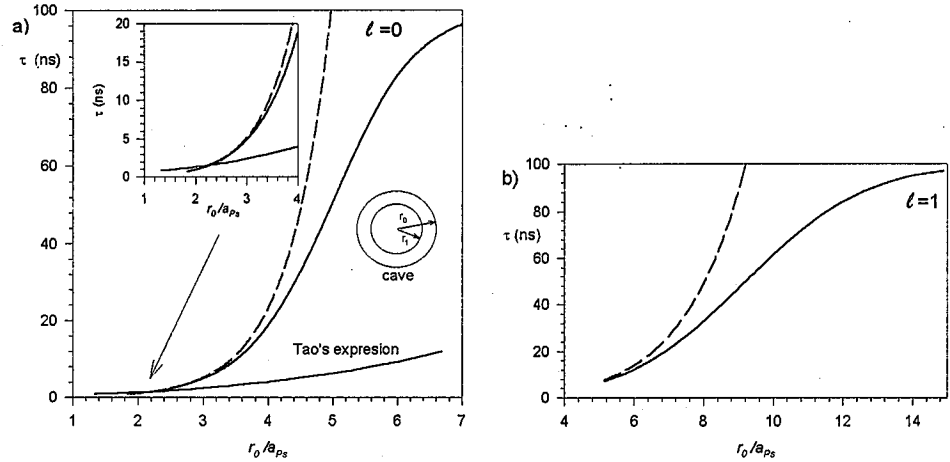

Fig. 2. The lifetime of o-Ps located inside a cave with infinite wall as a function of the cave radii. The dashed line represents the case with no self-annihilation of the o-Ps (7) and the solid line with self-annihilation (8). For comparison the o-Ps lifetime evaluated from the Tao expression (3) is drawn as well. The calculations were performed for two values of the orbital quantum number equal to 0 (a) and 1 (b), respectively.

of the obtained dependence is that the positron lifetime increases fast in rather narrow range of the cave radius: from $3a_{\mathrm{Ps}}$ to $6a_{\mathrm{Ps}}$. This indicates the region of the maximum sensitivity of the positron measurements in determination of this radius.

The unclear point in the Tao consideration lies in the origin of the electron layer which surrounds the cave. In molecular solids or polymers where the relation (3) is applied, voids or caves are surrounded by atoms instead of a uniform electron gel. The positron wave function may penetrate the core region of these atoms where the concentration of electrons is significant. Let us consider that the o-Ps of radius r_0 is located close to the hydrogen and carbon atoms and the annihilation of the positron will take place with core electrons. We neglect the influence of the atom with the o-Ps on the wave functions and for the positron we use the relation (6). From the solution of the Dirac–Slater equation we were able to find the density of electron in the core region of these atoms and then use it in further calculations. In any case we can also use the atomic orbitals suggested by Clementi [6] which are presented in the analytical form. From this we can calculate the density of electrons in any point. If we neglect any correlation effect we can rewrite the relation (1) in the following form:

$$\lambda = \pi r_{\mathrm{e}}^2 c \int\int\int_V \mathrm{d}r \psi_+^*(r)\psi_+(r)\gamma(\mathrm{n}_-(r)), \tag{9}$$

where n_- is the electron density at the point r and as the enhancement factor we employed the interpolation formula suggested by Boroński and Nieminen [7]:

$$\gamma = n_-(1 + 1.23r_{\mathrm{s}} + 0.8295r_{\mathrm{s}}^{3/2} - 1.26r_{\mathrm{s}}^2 + 0.3286r_{\mathrm{s}}^{5/2} + r_{\mathrm{s}}^3/6), \tag{10}$$

where $r_{\mathrm{s}} = \sqrt[3]{3/(4\pi n_-)}$ is the electron density parameter. In our calculations we assumed that at the distance $r_{\mathrm{at}} = 0.746a_{\mathrm{Ps}}$ and $0.860a_{\mathrm{Ps}}$ from the center of

hydrogen and carbon atoms, respectively, the electron density is equal to zero and the positron wave function is equal to zero at the nucleus of atoms (Fig. 3). Only the region where two spheres of the radii r_0 and r_{at} are overlapping contributes to the integral (9). Figure 3 presents the results of the calculation of the o-Ps lifetime in such an approach for hydrogen and carbon as the function of the radius r_0. As above, the increase in the o-Ps radius causes a very fast increase in its lifetime shown by the dashed lines. The solid lines in Fig. 3 present the results when the self-annihilation of the o-Ps is included according to the relation (8). Now, after very fast increase the lifetime saturates at the assumed value 100 ns at certain radius of the o-Ps. The character of the dependence is not related much to the kind of atom. Note that if the o-Ps is surrounded by e.g., two atoms the lifetime from Fig. 3 (dashed line) is reduced twice and finally the solid line is shifted down. We can see that type of dependence obtained using the Tao approach and the approach when the positron from the o-Ps annihilates with the electron from core region of the atoms are very similar (compare Fig. 2a and Fig. 3). It shows that the shape of the positron wave function has rather a more important influence on the annihilation rate of the o-Ps in the pick-off process than the electron cloud.

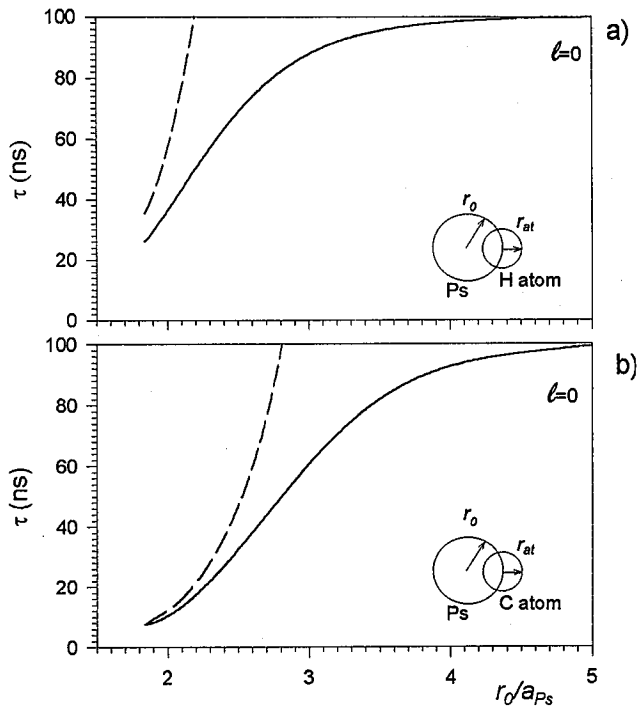

Fig. 3. The o-Ps lifetime when the o-Ps overlaps the core region of the hydrogen (a) and carbon (b) atom as a function of the o-Ps radii. The dashed line represents the case with no self-annihilation of the o-Ps (9) and the solid line with self-annihilation (8).

The relationship between the o-Ps lifetime and its radius from Fig. 3 is observed experimentally in the prepared silica gels where one can measure the size of pore with other experimental methods. For this material the observed o-Ps lifetime ranged from 1.5 ns to 100 ns and strongly depends on the radius of pores in the range from 0.3 nm to 1 nm. The Tao relation (3) failed in this case.

The calculations presented above may be an instruction how to calculate the o-Ps lifetime in the solid or pores material. First we should find the free spaces in the structure where the o-Ps could be located (see e.g. [8]). The average radius must be larger than the critical radius mentioned above. Then we should look at the atoms which surround the place and their coordinates. After that we sum the annihilation rates originated from electrons at different atoms, the relation (9) and the self-annihilation rate. The procedure presented above could help to identify the structure of the space in well defined systems where the o-Ps annihilates. In rough estimations it could give us information how many atoms surround the free space and the size of the o-Ps before annihilation. In more detailed calculations instead of the Boroński and Nieminen enhancement factor (10) we can use another one where the gradient of the electron density is taken into account [9].

In conclusion we can note that application of the more accurate positron wave function to the o-Ps lifetime calculation shows a different type of dependence on the cave radius than the one predicted by the Tao expression. The obtained lifetime exhibited a sigmoidal shape. A similar type of dependence arises from calculations when o-Ps overlaps the core region of hydrogen and carbon atoms. The results obtained are in qualitative agreement with the results in the silica gels observed experimentally.

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