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Positronium formation in a liquid phase: Influence of intratrack reactions and temperature

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Received 2 February 2009, revised 27 February 2009, accepted 12 March 2009 Published online 5 October 2009

PACS 71.60.+z, 78.70.Bj, 82.33.-z, 82.40.-g

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This work clarifies some discrepancies between conventional models, used in positron annihilation lifetime (PAL) spectroscopy, and experimental data. The importance of taking into account Ps interactions with primary intratrack radiolytic products is demonstrated, for example, for PAL data in water. We examine the applicability of a nonhomogeneous chemical kinetics approach and of a well-known expression for the reaction rate constants

1 Introduction The basics of positron annihilation spectroscopy have been mainly worked out during the last half of the 20-th century. Many approaches have been elaborated to interpret the experimental data. However, there are some glaring contradictions in the description of the Ps dynamics which are still awaiting physical interpretation:

1) Attempts to recover the experimental values of the rate coefficients k(Ps + S) of Ps with various solutes, S, obtained from PAL data by means of conventional analysis,¹ implies the use of a very small Ps bubble radius (similar to that of Ps in vacuum), or, conversely, taking into account a realistic Ps bubble radius and the time dependence of the (Ps+S)-rate coefficient results in quite unrealistic solute radii [1,2].

2) An even simpler contradiction has to be mentioned. Figure 1 shows the *T*-dependence of the lifetime (τ_3) of the long-lived component of PAL spectra in pure water. Experimental data from different authors agree well, but to describe intratrack processes, and show that the prescribed diffusion approximation (PDA) is a reasonable model for this. Moreover, we have derived an analytical expression for the time-dependent reaction rate coefficient, which previously entered PDA as an external parameter. Preliminary fittings of the PAL spectra in H₂O over a wide temperature range indicate that Ps reactions in intratrack processes are diffusion controlled.

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considerably diverge from theoretical predictions based on any model of the Ps bubble state [3]: with increasing T, the surface tension coefficient decreases, so the size of the Ps bubble should increase, which should lead to increase of τ_3 with T, in drastic contradiction to the PAL data.

We suggest that these paradoxes are related with the interaction of the Ps atom with primary intratrack products, mainly with strong intratrack oxidizers (OH-radicals and H_3O^+ radical-cations). The initial concentration of



Figure 1 Temperature dependence of the lifetime, τ_3 , of the long-lived component in pure water: experimental data (derived from a 3-exponential analysis) and corresponding theoretical predictions (finite potential well, solid line; infinite potential well, dashed line).



¹ That is, analysing the PAL spectra in terms of 3 exponential components and applying the Smoluchowski equation to describe the reaction and recover the o-Ps lifetime.

these species in the terminal part of the positron track (e⁺ blob) is not small (up to 0.05 M), so the contribution of oxidation reactions and, probably, ortho-para conversion must be taken into account. Actually, Ps interaction with intratrack products is inherent to positron spectroscopy of any molecular medium. Radiolytic products are formed in the e⁺ tracks due to ionization slowing down of energetic positrons. One possible way to investigate Ps intratrack reactions is to study the changes in the PAL spectra with T.

We chose liquid water to initiate this investigation, because radiolytic chemical reactions in this medium have being studied for years and are now rather well known. In addition, the Ps bubble growth proceeds very fast in water (~ 10 ps, according to estimations based on the solution of the Navier-Stokes equation [4]) in comparison with the lifetime resolution of the experimental setup, so that it may be considered as an instantaneous process.

2 Effects of temperature on intratrack reactions Let us briefly outline some possible effects of temperature on intratrack reactions, including Ps formation.

1) It is commonly accepted that the reaction rate coefficients k_{ij} , which enter chemical kinetics equations, depend on T mainly through the diffusion coefficients

$$k_{ij}(T) = 4\pi D_{ij}(T)R_{ij},\tag{1}$$

where $D_{ij} = D_i + D_j$ is the sum of the diffusion coefficients of *i*-th and *j*-th species in a solvent, and $R_{ij} \approx R_i + R_j$ is the reaction radius, i.e., approximately the sum of the geometric radii of the reacting species.

2) According to the Einstein relationship and the Stokes law, a diffusion coefficient $D_i(T)$ of a spherical Brownian particle is expressed as:

$$D_i(T) = T/(6\pi\eta(T)R_i), \qquad (2)$$

where η is the viscosity of the medium and R_i is the hydrodynamic radius of the particle. Although the applicability of this expression on the atomic scale might be questionable, we have shown in preliminary studies in neat water [3] that it remains valid within a reasonable accuracy.

3) Numerous data from the literature show that the viscosity $\eta(T)$ drops down approximately exponentially with T, whereas the surface tension coefficient $\sigma(T)$ weakly decreases with T in most liquids.

4) The surface tension allows one to estimate the equilibrium size of the Ps bubble R(T) (free volume radius) and, with the help of a Ps bubble model, to calculate the pick-off annihilation rate $\lambda_{po}(t,T)$, which is of utmost importance to interpret PAL spectra:

$$\lambda_{po}(t,T) = \lambda_p \cdot P(R(t,T)). \tag{3}$$

Here λ_p is the "free" positron annihilation rate and P(R) is the penetration probability of e⁺ into the space containing outer electrons.



Figure 2 Mechanism of the Ps formation: ${\rm e_{th}^+}+{\rm e_{blob}^-}\to quasi-free-Ps\to Ps$ in the bubble.

5) Recently, we have found that the temperature in the e^+ blob is higher than the bulk temperature, due to the ionizations promoted by the slowing down energetic positron and subsequent ion-electron recombinations: e^{+*} releases up to 1 keV in the terminal blob, an energy which finally converts into heat; we have termed this *local heating effect*. This transient temperature regime may strongly affect, for example, the Ps bubble growth through the viscosity [5]. This effect may also influence the mobility of intratrack species and their reaction rates coefficients.

Thus, it is seen than developing a comprehensive model, which would take into account all *T*-dependent effects, appears as a very difficult task.

3 Water radiolysis and Ps formation The scheme of water radiolysis is well known. A list of the most important primary reactions has been given in a number of previous publications [3,6,7]. The values of the diffusion coefficients D_i and reaction rate coefficients, k_{ij} , between species of *i*- and *j*-types are known at the nanosecond stage. For a picosecond range we have considered them as adjustable parameters, and thus succeeded into fitting the accumulation kinetics of the major radiolytic products.

Ps is formed through the reaction of the thermalized e_{th}^+ with one of the knocked out intratrack electrons within or close to the terminal e^+ blob. Initially, Ps appears in a medium as a weakly bound ($\sim 0.1 \text{ eV}$) stretched $e^+ \cdot e^-$ pair (Fig. 2). Then this pair transforms into the quasi-free Ps, qf-Ps, the ground state of a nonlocalized e^+e^- pair in an unperturbed medium. Further energy gain is related with rearrangement of the surrounding molecules and formation of the Ps bubble state.

For a correct interpretation of PAL spectra it is necessary to take into account the Ps interaction with intrablob oxidizers and radicals (OH, H_3O^+ , e_{aq}^- , H_2O^+ , H). Preliminary attempts have shown that contribution from oxidation reactions is the most important:

$$Ps + OH \to e^+ + OH^-, \tag{4}$$

$$\mathrm{Ps} + \mathrm{H}_3\mathrm{O}^+ \rightarrow \mathrm{e}^+ + \mathrm{H} + \mathrm{H}_2\mathrm{O}.$$

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In the following, we restrict ourselves to these Ps reactions only, assuming, in addition, that their rate coefficients are the same. We will consider these reactions in an "independent pair approximation", which means that the probability of the Ps reaction with a given oxidizer does not depend on arrangement (positions) of other oxidizers.

4 Conventional approach to the description of intratrack reactions A nonhomogeneous chemical kinetics approach (as well as the blob model [3]) starts with the following equations on concentrations of different intratrack species:

$$\frac{\partial c_i(r,t)}{\partial t} = D_i \Delta c_i - k_{ij} c_i c_j - \lambda_i c_i, \qquad (5)$$
$$c_i(t=0) = c_i^0 \frac{\exp(-r^2/a_i^2)}{\pi^{3/2} a_i^3}.$$

Actually, these equations are rather phenomenological: they take into account the diffusion redistribution of the reagents, their reactions when they meet each other at the same point of space, and decay process, $-\lambda_i c_i$. But this approach does not answer to the question: what is k_{ij} here? It appears here as an empirical parameter.

To get an idea on what is k_{ij} in Eq. (5), one usually solves the Smoluchowski problem for the concentration $c_i(r,t)$ of *i*-species around a given *j*-particle, placed at the origin, r = 0:

$$\frac{\partial c_i(r,t)}{\partial t} = D\Delta c_i, \qquad c_i(r > R, 0) = c_i^0, \qquad (6)$$
$$c_i(r \to \infty, t) = c_i^0, \qquad c_i(R, t) = 0,$$

where $D = D_i + D_j$ is the sum of the diffusion coefficients of the species, $R \approx R_i + R_j$ is the radius of the reaction sphere, R_i and R_j are geometric radii of the species. The reaction rate coefficient k_{ij} is defined as a total inward flow rate of *i*-species across the reaction surface, divided by c_i^0 :

$$k_{ij}(t) = \frac{4\pi R^2 D}{c_i^0} \left. \frac{\partial c_i(r,t)}{\partial r} \right|_{r=R},\tag{7}$$

which leads to the known Smoluchowski formula [8]:²

$$k_{ij}(T,t) = 4\pi D_{ij}(T) R_{ij} \left(1 + R_{ij} / \sqrt{\pi D_{ij} t} \right).$$
 (8)

This approach has been criticized on several aspects: 1) not all *i*-particles that flow across the reaction surface, but only that *i*, which comes first, contributes to the i + j-reaction; 2) how can *j* react with *i*, if there are no *i* on the reaction surface: $n_i(R, t) = 0$?

Moreover, in the case of intratrack reactions we have to deal with the Gaussian distributions of intratrack products, but not with the stepwise (uniform) distribution.



Obviously the fluxes through the reaction sphere and, therefore, the reaction rate coefficients will be very different in these cases. Our aim below will be to calculate $k_{ij}(t)$ in case of Gaussian distributions of the intrablob reagents (Ps and its oxidizers).

5 Pair survival probability Formally, the problem is reduced to the calculation of the survival probability of a particle A (=Ps) surrounded by many other intratrack reactive species B (=oxidizers) in the case when the initial distribution of B's is Gaussian.

In the 70-80's M.Tachiya [9] developed the theory of the diffusion-controlled reactions and treated similar problems in a general way. He derived an equation for the pair survival probability (the adjoint Fokker-Planck equation) and solved it when many B's are uniformly distributed around one A (but did not consider the case of the Gaussian distribution). His method is rather complicated, so we chose to follow a simpler approach suggested by A.Pontryagin et al. and A.Kolmogorov et al. (1933) [10]: this is sufficient for our needs and allows one to obtain the equation we need.

The starting point of the analysis is the conditional probability density $w(\mathbf{r}, t | \mathbf{r_0})$, which describes the probability to find a particle at \mathbf{r} at time t, if at t = 0 it was at $\mathbf{r_0}$. This function obeys the integral Smoluchowski equation. If the particle moves in a diffusion way³ this equation can be rewritten in a differential form, which is called the Fokker-Planck equation or the differential Smoluchowski equation. In case of a homogeneous medium (\mathbf{v} and D are constants) it comes as follows:

$$\frac{\partial w(\mathbf{r},t|\mathbf{r}_0)}{\partial t} = -\mathbf{v} \cdot \nabla_{\mathbf{r}} w + D\Delta_{\mathbf{r}} w, \qquad (9)$$
$$w(\mathbf{r},t|\mathbf{r}_0)dx = 1, \qquad w(\mathbf{r},t=0|\mathbf{r}_0) = \delta(\mathbf{r}-\mathbf{r}_0).$$

It reduces to the usual diffusion equation in the absence of interaction between particles and in the absence of an external field ($\mathbf{v} = 0$).

However, the solution of this equation, i.e. $w(\mathbf{r}, t|\mathbf{r}_0)$, contains a wealth of experimentally unobservable informa-

 $^{^2\,}$ the applicability of this relationship in the case of Gaussian initial distribution of reacting species in the terminal part of the e^+ track is discussed below

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³ Mathematically it implies that there exist two following limits ($\tau \rightarrow 0$), expressing "continuity" of the diffusion motion: 1) $\frac{\langle \mathbf{r}-\mathbf{r}_1 \rangle}{\tau} = \int \frac{\mathbf{r}-\mathbf{r}_1}{\tau} w(\mathbf{r},\tau | \mathbf{r}_1) d\mathbf{r} \equiv \mathbf{v}(\mathbf{r}_1)$ – the drift velocity; 2) $\frac{\langle (\mathbf{r}-\mathbf{r}_1)^2 \rangle}{2\tau} = \frac{1}{2\tau} \int (\mathbf{r}-\mathbf{r}_1)^2 w(\mathbf{r},\tau | \mathbf{r}_1) d\mathbf{r} \equiv D(\mathbf{r}_1)$ – the diffusion coefficient (here we consider the spherically symmetric case); all higher moments are zero.

tion. From a physical viewpoint the most important quantity is the *survival probability*, $\int w(\mathbf{r}, t|\mathbf{r}_0) d\mathbf{r}$.⁴ Let us consider the *pair survival probability* $W(t|\mathbf{r}_0)$, the probability that an A–B-pair, having the initial separation \mathbf{r}_0 , will survive against reaction A + B \rightarrow Products by the time t:

$$W(t|\mathbf{r}_0) = \int \tilde{w}(\mathbf{r}, t|\mathbf{r}_0) d\mathbf{r}.$$
 (10)

We assume that A (=Ps) is fixed at the origin of coordinates and B (= oxidizer) moves around with diffusion coefficient $D = D_A + D_B$. The conditional probability density $\tilde{w}(\mathbf{r}, t | \mathbf{r}_0)$ differs from the $w(\mathbf{r}, t | \mathbf{r}_0)$, which enters the Fokker-Planck equation because of the difference in the boundary conditions (presence of the reaction surface at $R \approx R_A + R_B$ significantly affects the solution).

The integral equation, which governs the pair survival probability, is as follows:

$$W(t+\tau|\mathbf{r}_0) = \int_{>R}^{\infty} W(t|\mathbf{r}) \tilde{w}(\mathbf{r},\tau|\mathbf{r}_0) d\mathbf{r}.$$
 (11)

where the boundary conditions are (fully absorbing sphere)

$$W(t|r_0 = R) = 0, \qquad W(t|r_0 \to \infty) = 1,$$
 (12)

and the initial condition is $W(0|r_0 > R) = 1$. Eq. (11) can be derived as follows. In its R.H.S. $W(t + \tau | \mathbf{r}_0)$ is represented as a product of probabilities of two independent events: $\tilde{w}(\mathbf{r}, \tau | \mathbf{r}_0) d\mathbf{r}$, the probability of propagation of



the particle B from \mathbf{r}_0 to \mathbf{r} during τ without touching the reaction sphere, and $W(t|\mathbf{r})$, the probability to avoid reaction during t, if the particle B starts from \mathbf{r} . Let τ be very small ($\tau \rightarrow 0$), so \mathbf{r} is close to \mathbf{r}_0 . In this case $\tilde{w}(\mathbf{r}, \tau | \mathbf{r}_0)$ is strongly

localized at $\mathbf{r} \approx \mathbf{r}_0$. So we may expand the integration range over \mathbf{r} to infinity and adopt that $\tilde{w}(\mathbf{r}, \tau | \mathbf{r}_0)$ is the same function as in the Fokker-Planck equation (9):

$$W(t+\tau|\mathbf{r}_0) = \int W(t|\mathbf{r})w(\mathbf{r},\tau|\mathbf{r}_0)d\mathbf{r}.$$
 (13)

Now let expand $W(t|\mathbf{r}) \approx W(t|\mathbf{r}_0) + \nabla_{\mathbf{r}_0} W(t|\mathbf{r}_0) \cdot (\mathbf{r} - \mathbf{r}_0) + \dots$ in a series over $\mathbf{r} - \mathbf{r}_0$, move the first term to the L.H.S., divide all by τ , integrate over \mathbf{r} and obtain that $W(t|_0)$ satisfies the *adjoint* Fokker-Planck equation:

$$\frac{\partial W(t|\mathbf{r}_0)}{\partial t} = \mathbf{v} \cdot \nabla_{\mathbf{r}_0} W(t|\mathbf{r}_0) + D\Delta_{\mathbf{r}_0} W(t|\mathbf{r}_0). \quad (14)$$

As before, we assume that $\mathbf{v} = 0$ and D = const, so the solution of Eq. (14) is well-known

$$W(t|\mathbf{r}_0) = 1 - \frac{R}{r_0} \left[1 - \operatorname{erf}\left(\frac{r_0 - R}{\sqrt{4Dt}}\right) \right].$$
(15)

Actually, it is the survival probability of Ps to escape oxidation by a given oxidizer, if their initial intrapair separation (at t = 0) was \mathbf{r}_0 .

$$\int w(\mathbf{r}, t \to \infty | \mathbf{r}_0) d\mathbf{r}$$
 is the escape probability.

6 Reaction rate in terms of the pair survival probability Let us average the pair survival probability over \mathbf{r}_0 . For a uniform distribution we have

$$\langle W(t|\mathbf{r}_0)\rangle_{\mathbf{r}_0} \equiv n_A(t), \quad \langle \dots \rangle_{\mathbf{r}_0} = \int_{>R}^{V \to \infty} \frac{d^3 r_0}{V}.$$
 (16)

By definition, the *reaction rate* is the probability for the A-B pair to react per unit time. It is given by the time derivative:

$$K(t) \equiv -\frac{d\langle W(t|\mathbf{r}_0)\rangle_{\mathbf{r}_0}}{dt} = -\left\langle \frac{dW(t|\mathbf{r}_0)}{dt} \right\rangle_{\mathbf{r}_0}, \quad (17)$$

$$-\frac{dW(t|\mathbf{r}_0)}{dt} = \frac{R(r_0 - R)}{r_0} \cdot \frac{\exp[-(r_0 - R)^2/4Dt]}{\sqrt{4\pi D}t^{3/2}}.$$
(18)

Now, let us consider the case of many B particles $(n_B \gg 1)$ being uniformly distributed within V. Because we consider all A-B pairs independently, the survival probability for A, $n_A(t)$, is just a product of the pair survival probabilities for each pair:

$$n_A(t) = [\langle W(t|\mathbf{r}_0) \rangle_{\mathbf{r}_0}]^{n_B} = [1 - (1 - \langle W \rangle_{\mathbf{r}_0})]^{n_B} \rightarrow$$
$$\rightarrow \exp\left[-n_B \cdot (1 - \langle W(t|\mathbf{r}_0) \rangle_{\mathbf{r}_0})\right],$$

because $1 - \langle W(t|\mathbf{r}_0) \rangle_{\mathbf{r}_0}$ is small when $V \to \infty$. Then

$$\dot{n}_A(t) = \langle \dot{W}(t|\mathbf{r}_0) \rangle_{\mathbf{r}_0} \cdot n_B n_A(t).$$
(19)

Taking the average of Eq. (18) for the uniform distribution of B's and substituting $\langle \dot{W}(t|\mathbf{r}_0) \rangle_{\mathbf{r}_0}$ here

$$\langle \dot{W}(t|\mathbf{r}_0) \rangle_{\mathbf{r}_0} = -\frac{4\pi DR}{V} \left(1 + \frac{R}{\sqrt{\pi Dt}} \right)$$

we arrive to the well known Smoluchowski result ($c_B = n_B/V$):

$$\dot{n}_A(t) = -4\pi DRc_B n_A \cdot (1 + R/\sqrt{\pi Dt}), \qquad (20)$$

In case of an initial Gaussian distribution of species B with respect to A, which should hold for Ps reactions with intratrack species, the average comes:

$$\langle \dots \rangle_{\mathbf{r}_0} = \int_{>R}^{\infty} e^{-r_0^2/a^2} d^3 r_0 \dots \bigg/ \int_{>R}^{\infty} e^{-r_0^2/a^2} d^3 r_0,$$
(21)

where $a^2 = a_{blob}^2 + a_{Ps}^2 \approx 2a_{blob}^2$. Assuming that the reaction radius R is much less than the width a of the Gaussian distribution, one obtains

$$\langle \dot{W}(t|\mathbf{r}_0) \rangle_{\mathbf{r}_0} = -\frac{4\pi DR}{V_0 (1+4Dt/a^2)^{3/2}} \left(1 + \frac{R}{\sqrt{\pi Dt}}\right),$$
(22)

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where $V_0 = \pi^{3/2} a^3$. To calculate the total reaction rate of Ps with n_B intrablob oxidizers (generally $n_B(t)$ may vary with time due to other intrablob reactions) we should substitute Eq. (22) into Eq. (19). Therefore, the decay kinetics (Ps survival probability) obeys the following equation:

$$\dot{n}_{\rm Ps}(t) \stackrel{R \ll a}{=} -\frac{4\pi D R n_B(t) n_{\rm Ps}(t)}{V_0 (1+4Dt/a^2)^{3/2}} \left(1 + \frac{R}{\sqrt{\pi Dt}}\right).$$
(23)

We see that this equation differs from what was obtained for the homogeneous case. However, some similarity may be established with the prescribed diffusion approximation (PDA), which "prescribes" to look for an approximate solution of Eq. (5) in a Gaussian form:

$$c_i(r,t) = n_i(t)G_i(r,t), \quad G_i(r,t) = \frac{e^{-r^2/(a_i^2 + 4D_it)}}{\pi (a_i^2 + 4D_it)^{3/2}}.$$
(24)

As a result, Eqs.(5) convert into a simpler set of ordinary differential equations on $n_i(t)$.

$$\dot{n}_i(t) = -\frac{k_{ij}n_in_j}{V_0(1+4Dt/a^2)^{3/2}} - \lambda_i n_i, \qquad (25)$$

where $D = D_i + D_j$, $a^2 = a_i^2 + a_j^2$. So PDA reproduces correctly only the main structure of the equations, but does not allow one to calculate the reaction rate coefficient.

The approach described above proves that PDA provides a good description of intratrack processes; moreover, it suggests a theoretical expression for k_{ij} , namely, k_{ij} in Eq. (25) should be replaced by the Smoluchowski relationship (8).

Further calculation of the theoretical prediction for the PAL spectrum shape and fitting PAL experimental data can be made straightforwardly, if $n_{\rm pPs}(t)$, $n_{\rm oPs}(t)$ and $n_{\rm pPs}(t)$ are known (solving equations like Eq. (23), see [3]).

7 Estimation of the parameters involved Before taking a look on the results of fitting of the experimental data in water, let us estimate the expected value of the Ps oxidation reaction rate coefficient with intrablob OH radicals. In water at room T (20 °C) we have $\eta = 0.01$ P, $R_{\rm Ps} \approx 0.3$ nm, $R_{\rm OH} \approx 0.14$ nm, so, by using the Einstein relation and the Stokes law, one obtains

$$D_{\rm OH} \approx \frac{T_{room}}{6\pi\eta R_{\rm OH}} \approx 1.5 \cdot 10^{-5} \, \frac{\rm cm^2}{\rm s}, \quad \text{exp. val.=} 2.8 \cdot 10^{-5}.$$
$$D_{\rm Ps} \approx \frac{T_{room}}{4\pi\eta R_{\rm Ps}} \approx 10^{-5} \, \frac{\rm cm^2}{\rm s},$$

Here, we used the Rybchinski formula for the Ps bubble diffusion coefficient ⁵. If the initial number of ion-electron

pairs in the blob is about 30 and a is about 4 nm, we obtain

$$c_{ox}(0) = \frac{n_B(0)}{V_0} \approx \frac{30 \text{ [OH \& H_3O^+]}}{(2\pi)^{3/2} (4 \text{ nm})^3} = 0.05 \text{ M},$$

therefore at 20 °C

$$k_{ox}c_{ox}(0) \approx 4\pi (D_{\rm Ps} + D_{\rm OH})(R_{\rm Ps} + R_{\rm OH})c_{ox}(0) \approx 0.4 {\rm ns}^{-1}.$$
(26)

In Fig.3 we presented the *T*-dependence of $k_{ox}(T)c_{ox}(0)$ in H₂O, when the *t*-dependence of k_{ox} is neglected. The solid line fits the data by the Stokes-Einstein law, $\propto T/\eta(T)$. It is seen that the numerical estimation (26) agrees well with the experimental value.



Figure 3 Temperature dependence of the product $k_{ox}(T)c_{ox}(0)$ in pure water (the time dependence of k_{ox} is neglected).

8 Conclusions

1) When interpreting PAL spectra it is important to take into account the chemical reactions of Ps with intratrack products (essentially, the oxidation reactions (4) in water). Otherwise, one may meet paradoxes.

2) We have derived a master equation for the pair survival probability of Ps against intratrack chemical reactions (oxidation) and solved it in the independent pair approximation. We have found that the prescribed diffusion approximation is a reasonable model to describe intratrack processes. Moreover, we have obtained a time-dependent expression for the reaction rate coefficient, which previously entered PDA as an external parameter;

3) Fitting the PALS spectra in H_2O in a wide *T*-range taking into account the time dependence of the reaction rate coefficient is in progress; preliminary results indicate a good agreement with data known from radiation chemistry;

4) The *T*-dependence of $k_{ox}(T)$ agrees well with the Stokes-Einstein law, which implies that intratrack reactions of Ps are diffusion controlled.

This work is supported by the Russian Foundation of Basic Researches (Grant 08-03-01105) and RosAtom.

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⁵ On the surface of the Ps bubble there is no sticking boundary condition, as there is for a solid sphere in the Stokes law.

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