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To the theory of Ps formation. New interpretation of the e^+ lifetime spectrum in water

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Abstract

A brief review of ideas behind the blob model is given. For the first time positron annihilation lifetime spectrum in liquid water is deconvoluted without a usage of the multi-exponential approach, but on the bases of the blob model, which suits well for description of the intratrack processes including positronium (Ps) formation in condensed molecular media. All adjustable parameters in the blob model have clear physical meaning. Excellent agreement with the experiment is obtained.

Keywords: Track structure; Radiolysis; Positron; Inhomogeneous kinetics

1. Introduction

Energetic positrons are usually born as a result of a β-decay of radioactive nuclei. Being implanted in condensed dielectric media, such a positron looses energy ($\sim$1 MeV) via ionizations of molecules. This process takes some tens of picoseconds. e^+ thermalization (loss of its energy from the ionization threshold down to a thermal one) lasts much shorter time (several tens of femtoseconds). Estimations of thermalization time and displacement (10–20 Å) are rather uncertain because we do not know the wave function of e^+ and the energy loss function of the medium within the needed frequency range (Stepanov and Byakov, 2004). Nevertheless, consideration of the kinetics of the Ps formation and accompanying intratrack processes becomes a topical task in view of a need of more accurate interpretation of the lifetime (LT) positron annihilation spectra. On one side experimental technique now becomes sensitive to the processes on a subnanosecond timescale, on the other side theoretical studies indicate that Ps formation may last up to nanoseconds.

Formation of the Ps atom in the bulk proceeds via *the recombination mechanism*, i.e. recombination of the thermalized e^+ with one of intratrack electrons knocked out by the positron at the end part of its track (Mogensen, 1995; Stepanov and Byakov, 2003). The Ps formation via the pickup abstraction of an electron from a molecule by a hot positron (the Ore process) seems unlikely. In fact, initially Ps emerges in a medium in the form of a weakly bound ($\sim$0.1 eV) e^-–e^+ pair, which is not localized in a certain position in the medium. It is obvious that the kinetic energies of particles that take part in the formation of the pair must be close to thermal energies. Otherwise, the pair just cannot exist as a single whole; the particles will fly off apart by overcoming their low bonding energy. Further this pair transforms into the quasi-free positronium (qf-Ps), which is the lowest energy state of the pair in the unperturbed medium (“unperturbed” means that the presence of the e^-–e^+ pair has not led yet to

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reorganization of the medium, i.e. to the displacement of molecules and the formation of a cavity) (Stepanov and Byakov, 2002). The binding energy of qf-Ps is approximately 0.5–1 eV at the most probable separation between e^+ and e^- (~5 Å).

There are two models which mathematically express the recombination mechanism, namely, the spur model (Tao, 1976; Mogensen, 1995) and the blob model (Stepanov and Byakov, 2003 and references therein). They differ in what is the terminal part of the e^+ track. The spur model is based on the Onsager theory of a geminate recombination and ignores competing intratrack reactions taking place in the terminal part of the e^+ track. On the contrary, the blob model assumes that this part of the track consists of several tens of the overlapped ion–electron pairs. So it is formulated with the help of chemical kinetics equations and better suited for consideration of the intratrack processes involving a large number of primary particles. The blob model was successfully applied for interpretation of the suppression of the Ps formation in electric fields (Stepanov and Byakov, 2002; Stepanov et al., 2005a), kinetics of accumulation of radiolytic products in aqueous solutions (Stepanov and Byakov, 2005) and explanation of the age–momentum correlation data in polymers (Dauwe et al., 2005).

High concentrations of chemically active particles (electrons, ions, radicals) in the e^+ blob are favorable for the Ps formation and further reactions of the Ps atom (ortho-para conversion, oxidation). All these processes, including out-diffusion of the blob species, affect the formation and decay kinetics of the e^+ states, which becomes essentially nonexponential. Obviously, it is inconsistent with conventional multi-exponential procedure of deconvolution of the LT spectra. We need new adequate approach for fitting raw experimental data. However, for this it is necessary to know the mechanism and parameters of intratrack chemical processes. Because the most detailed radiation-chemical data are available for aqueous media, we shall demonstrate here a new approach (based on the blob model) for the fitting the LT annihilation spectrum in pure water.

It should be mentioned that Ps formation models in liquids calculate kinetics and formation probability of qf-Ps only, leaving aside Ps localization in the bubble. Although in most liquids this process is much shorter than the para-Ps lifetime, in some cases (glycerol, water–glycerol mixtures, liquid helium) it could be experimentally observed (Mikhin et al., 2005).

2. Interpretation of the LT spectrum in water with a help of the blob model

We shall use here the original version of the blob model (white blob model, WBM), which neglects any interaction between e^+ and its blob (intuitively WBM means that the blob is "transparent" for the positron). WBM assumes that the distributions of all intrablob species, $c_j(r,t)$, can be described by means of the gaussian functions with according to the prescribed diffusion method (Stepanov and Byakov, 2005). In the similar way, we may write equation for the positron concentration, $c_p(r,t)$:

$$\frac{\partial c_j}{\partial t} = D_j(t)\Delta c_j - \sum_i k_{ij} c_i c_j - c_j/\tau_j,$$
$$c_j(t=0) \sim \frac{\exp(-r^2/a_{bl}^2)}{\pi^{3/2} a_{bl}^3}, \quad (1)$$

$$\frac{\partial c_p}{\partial t} = D_p(t)\Delta c_p - (k_{ep} c_e + k_{hp} c_h) c_p \cdot \vartheta(t > t_{th}) - c_p/\tau_p, \quad (2)$$

$$c_p(r,0) = \mathfrak{G}(r,0,a_{bl},D_p), \quad \mathfrak{G}(r,t=0,a_{bl}) = \frac{\exp(-r^2/a_{bl}^2)}{\pi^{3/2} a_{bl}^3}.$$

It takes into account e^+ diffusion ($D_p(t)\Delta c_p$), Ps formation process via recombination reactions with quasi-free ($k_{ep} c_e c_p$) and hydrated ($k_{eh} c_h c_p$) electrons and annihilation (c_p/τ_p) on molecular electrons. The terms describing Ps formation are "switched on" after the end of thermalization of e^+ and e^-, i.e. at $t > t_{th}$. a_{bl} is the initial size of the blob (≈ 40 Å). Transition from "hot" to localized (hydrated) e^+ state is described by time dependence of $D_p(t)$ only.[1] It should be mentioned that in water ambipolar expansion of the blob has a reversed character. Because H_3O^+ ions (but not hydrated electrons) are the most mobile species, local ambipolar electric field is directed to the center of the blob.[2] In this case the positron, being also a positively charged particle, cannot easily escape from the blob and has to obey ambipolar diffusion law. It implies that $D_p(t > \tau_{aq}) \approx D_{amb} \approx 10^{-4}\,cm^2/s$ (the ambipolar diffusion coefficient is approximately the double of the diffusion coefficient of hydrated electron, $D_{e_{aq}^-}$).

Equations, similar to (2), are written for concentrations $c_j(r,t)$ of the primary intratrack species, e^-, H_2O^+ (picosecond stage) as well as for all other radiolytic products: e_{aq}^-, H, OH, OH^-, H_2O_2, H_3O^+ (nanosecond–microsecond stage). In the WBM concentrations

[1] Hydrated states of the positron and electron could be rather different. e_{aq}^- resides in a small void because of spin-exchange repulsion on short distances (binding energy of e_{aq}^- is about 1–2 eV and hydration time $\tau_{aq} \approx 0.3$ ps). e^+ is not involved in spin-exchange and prefers to reside in a bulk because of polarization interaction. e^+ may be trapped by positive density fluctuations (aggregation of molecules) (Iakubov and Khrapak, 1982), but because of low compressibility of liquids creation of such agglomerates is unlikely.

[2] Opposite direction of the field is, for example, in hydrocarbons, where track electrons have the highest mobility.