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Formation of Quasi-Free and Bubble Positronium States in Water and Aqueous Solutions

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It is shown that in aqueous solutions a positronium atom is first formed in the quasi-free state, and, after 50–100 ps, becomes localized in a nanobubble. Analysis of the annihilation spectra of NaNO₃ aqueous solutions shows that the hydrated electron is not involved in the positronium (Ps) formation.

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1. Introduction

Most usually, the positron annihilation lifetime (LT) spectra in liquids (below we consider aqueous solutions) are well described in terms of three exponentials (3-E analysis). It is believed that this fact indicates that (1) Ps formation is a fast process, its duration does not exceed 10 ps, which is much shorter than the time resolution of a positron annihilation LT setup; and (2) the Ps atom is not involved in the non-homogeneous diffusion-controlled intratrack chemical reactions with radiolytic products. However, several facts plead against this conventional analysis, in particular:

- 1) The ratio of I_3 to I_1 (intensities of the *ortho*-Ps and *para*-Ps components) is not 3:1, as theoretically expected, but rather close to 2:1, Fig. 1 [1];
- 2) The 3-E analysis cannot describe the behaviour of the *S*-parameter (characterizing the shape of the Doppler spectrum) with time at short times, the so-called “juvenile broadening” effect, Fig. 2 [2] (one may find another data on $S(t)$ in pure H₂O obtained by conventional AMOC technique is in [3]). This effect consists in a decrease of the *S*-parameter when we go from “*para*-Ps times” (\approx 100–200 ps) to the negative times;
- 3) The lifetime of the short-lived component of the LT spectrum, τ_1 , the *para*-positronium (*p*-Ps) lifetime in a 3-E fit, comes out to be less than the *p*-Ps lifetime in vacuum (124 ps). However, as it follows from the magnetic quenching experiments, the Ps contact density in water is 0.75, so that the *p*-Ps lifetime should be 150–160 ps [1];
- 4) The lifetime of the long-lived component, τ_3 , ascribed to *ortho*-positronium (*o*-Ps), decreases with increasing temperature (Fig. 1). This is inconsistent with the in-

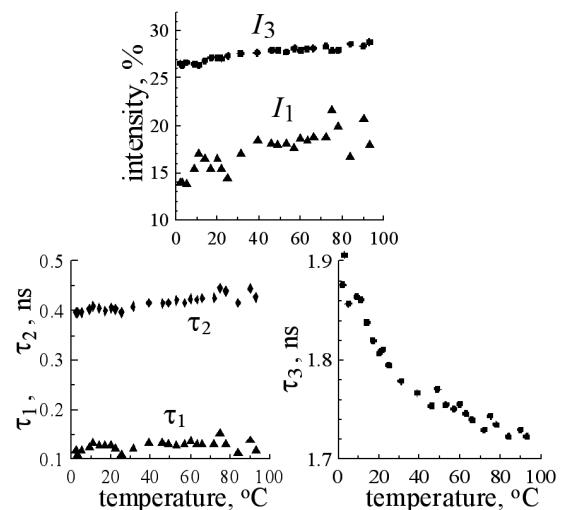


Fig. 1. Temperature dependence of the intensities of short-lived (I_1) and long-lived (I_3) components, and of the lifetimes τ_1 , τ_2 and τ_3 of LT spectrum of pure water [1].

crease of the size of the Ps bubble ensuing from the decrease of the surface tension of water.

What hints give us these features of the simplest exponential treatment of the LT spectrum of pure water and how to interpret them?

Explanation of the anomalies of τ_1 and τ_3 lifetimes was already given in [1]. The low value of τ_1 is simply an artifact in processing the LT spectrum. It is overcome by fixing τ_1 to the value expected from magnetic quenching experiments and subsequent correction (very slight broadening) of the time resolution function of the LT spectrometer.

The decrease in τ_3 with increasing T occurs due to the exponential increase of the reaction rate constant of the oxidation reactions of Ps by intratrack species

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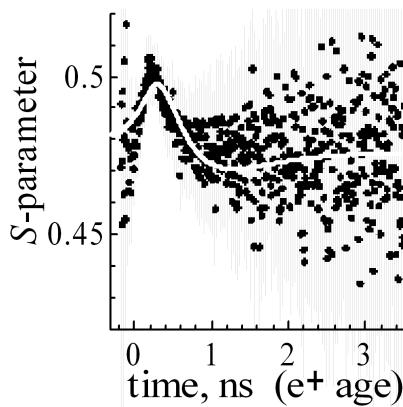


Fig. 2. Time dependence of the S-parameter in water at room temperature (recalculated from a GiPS-AMOC spectrum [2]). The solid line represents the fit of the AMOC spectrum, which takes into account appearance of the quasi-free positronium (see below). S-parameter is defined as the ratio of counts of annihilation photons within the energy 511 ± 0.7 keV to that of 511 ± 3 keV for each e^+ age.

(OH radicals, H_3O^+ ions). These reactions are diffusion-controlled and their rate constants increase exponentially with temperature. As a result, in spite of the drop in the pick-off annihilation rate (due to increase of the radius of the Ps bubble with increasing T), parameter τ_3 decreases with temperature.

Discussion of the reasons for the first two anomalies (violation of the $I_3 : I_1 = 3 : 1$ relationship and the maximum of $S(t)$ at short times in water) as well as interpretation of the LT spectra of $NaNO_3$ aqueous solutions is the subject of this communication.

2. General consideration

The basic hypothesis we have used to interpret the experimental data is that localization of Ps (in a bubble) does not occur immediately. It has a relatively long-lived precursor (intermediate transient state): quasi-free positronium (qf-Ps). Confidence in this assumption about qf-Ps in water has become possible after measuring AMOC spectra with high statistics [2].

Qualitatively, the picture is as follows. After ^{22}Na beta-plus decay, a fast positron (e^{+*}) enters a medium and loses energy through ionization. After thermalizing, it becomes solvated (or hydrated) similarly as does a quasi-free electron (the electron hydration time is 0.3 ps). All in all, it takes up to 10 ps [4]. The thermalized quasi-free (presolvated) positron can react with one of the quasi-free electrons in the terminal part of the e^+ track (e^+ blob). This is the essence of the recombination mechanism of Ps formation (also called the blob or spur model). As a result a quasi-free Ps, not yet localized in a bubble, is formed [5]. It is a loosely coupled (swollen) state of the e^+e^- pair, located in a dielectric continuum undisturbed by the presence of the qf-Ps it-

self. The binding energy of qf-Ps in water is $\varepsilon^2 \approx 4$ times less ($\varepsilon \approx n^2 \approx 2$ is the high-frequency dielectric constant of water; n is the refractive index) than that in vacuum (approximately it is 1.7 eV, i.e. 5 eV less than in vacuum). In qf-Ps e^+ and e^- are separated by a distance ε times larger than in a vacuum. Consequently, the qf-Ps contact density in water is $\varepsilon^3 \approx 8$ times less [6]. This means that the annihilation rate of qf-Ps only slightly exceeds the annihilation rate of “free” e^+ (strictly speaking, hydrated e^+). For this reason we do not subdivide qf-Ps into *ortho*- and *para*-states, because both of them annihilate on outer molecular electrons within approximately the same time. The contribution to the $S(t)$ -parameter from qf-Ps is approximately equal to that of free e^+ , since the latter also annihilates with the same electrons.

Processing of the GiPS-AMOC spectrum of pure water at room T [2] in terms of S -parameter clearly shows (Fig. 2) that the transformation of qf-Ps into the bubble state lasts $t_{loc} \approx 50-100$ ps since the e^+ birth (in the bubble state because of p -Ps self-annihilation S -parameter gets larger value). This value far exceeds the duration of the Ps bubble growth (≤ 10 ps, derived on the basis of a solution of the Navier-Stokes equation) [7]. This fact implies that the bottleneck of the formation of the Ps bubble state is not the growth of the bubble, but its initial stage — search for a preexisting trap (density fluctuation) by qf-Ps. It is well known that qf-Ps cannot be trapped in a fairly small/shallow trap, because there is no bound state of Ps therein. The search for a deeper/larger trap requires longer time. This is the reason for some delay in formation of the equilibrium Ps bubble state [5].

The notion of a quasi-free Ps state, preceding the Ps bubble state, is not new. A similar approach was used in [8] to explain the juvenile broadening of the Doppler spectrum in some substances. The authors suggested that a “hot” positron knocks out an electron from a molecule in a medium and with a noticeable probability forms a hot (epithermal) Ps atom with a commensurate kinetic energy (10–25 eV). At very short times (just after e^+ birth) this Ps kinetic energy broadens the Doppler spectrum (i.e., reduces the value of the S -parameter at $t \approx 0$). In [8] the authors assumed that the p -Ps contact density is equal to unity (as in vacuum), and hence adopted a p -Ps lifetime equal to that in vacuum. Finally, from their interpretation of the AMOC data, typical hot-Ps thermalization times (10–30 ps) were derived.

Our viewpoint is different. Firstly, we take it that the thermalization of subionizing e^+ and e^- proceeds rather fast (fractions of ps), qf-Ps being formed from the thermalized particles [9]. The qf-Ps produced cannot have a kinetic energy much higher than its binding energy (E_b) in a dielectric continuum ($E_b \sim Ry/2\varepsilon^2 = 1.7$ eV), otherwise, it might just break up because of interaction of e^+ and e^- with the environment, while qf-Ps moves through a medium.

Secondly, the qf-Ps lifetime is determined by the time needed to find of a suitable structural trap, able to cap-

ture and bind it (some qf-Ps annihilate on surrounding molecular electrons via the pick-off process). By fitting the GiPS-AMOC spectrum of pure water [2] and LT spectra of NaNO₃ aqueous solutions (see below) we have estimated the qf-Ps lifetime to be some 50–100 ps. Lower values of the *S*-parameter at $t \approx 0$ (juvenile broadening) are ascribed to qf-Ps (both its *para*- and *ortho*-states) annihilation.

Analysis of the LT spectra of pure water and NaNO₃ aqueous solutions at concentrations 0.07, 0.17 and 0.38 M in various temperatures (measurements made by the Strasbourg group) was performed with the help of our program, which allows one to test various scenarios for Ps formation and kinetics of the subsequent intrablob reactions between radiolytic products and Ps until its annihilation. As the Ps precursors we have considered quasi-free (presolvated) and solvated electrons. We have also taken into account the oxidation reactions of the Ps localized in a bubble with OH radicals and H₃O⁺ ions, and Ps *ortho*-*para* conversion by the radical species (OH radicals, hydrated electrons). The possibility for the epithermal positron to escape outside the blob at the final stage of its thermalization was also taken into account.

To describe accumulation of the main radiolytic products in water and Ps reactions in the e⁺ blob we used non-homogeneous kinetic equations in the prescribed diffusion approximation [10]. Particularly, there are four equations related to populations of the e⁺ states (“free” e⁺, qf-Ps, o-Ps, p-Ps). These equations take into account Ps oxidation only (the contribution of the Ps *ortho*-*para* conversion is negligible):

$$\begin{aligned} \text{“free” e}^+ : dn_+/dt &= -\lambda_+ n_+ + R_{\text{oxi}}(t)(n_o + n_p), \\ n_+(t=0) &= 1 - P_{\text{qf-Ps}}, \\ \text{qf-Ps} : dn_{\text{qf-Ps}}/dt &= -(\lambda_{\text{loc}} + \lambda_{\text{qf-Ps}})n_{\text{qf-Ps}}, \\ \Rightarrow n_{\text{qf-Ps}}(t) &= P_{\text{qf-Ps}} \exp(-(\lambda_{\text{loc}} + \lambda_{\text{qf-Ps}})t), \\ \text{o-Ps} : dn_o/dt &= 3\lambda_{\text{loc}}n_{\text{qf-Ps}}/4 - (R_{\text{oxi}}(t) + \lambda_{\text{oPs}})n_o, \\ n_o(t=0) &= 0, \\ \text{p-Ps} : dn_p/dt &= \lambda_{\text{loc}}n_{\text{qf-Ps}}/4 - (R_{\text{oxi}}(t) + \lambda_{\text{pPs}})n_p, \\ n_p(t=0) &= 0. \end{aligned} \quad (1)$$

The initial conditions for these equations refer to some 10 ps after the birth of e⁺. By this time the formation of the e⁺ blob and hydration of e⁻ and e⁺ are completed, and qf-Ps is formed (with probability $P_{\text{qf-Ps}}$). Accordingly, the probability of formation of the hydrated (“free”) positrons is $1 - P_{\text{qf-Ps}}$. Each positron state (free e⁺, qf-Ps, o-Ps, p-Ps) annihilates with its own rate constant: λ_+ , $\lambda_{\text{qf-Ps}}$, λ_{oPs} , λ_{pPs} . To reduce the number of parameters we have assumed that $\lambda_+ = \lambda_{\text{qf-Ps}}$, and $\lambda_{\text{loc}} = 1/t_{\text{loc}}$ — transformation rate constant of qf-Ps in a bubble state. In the fitting procedure of the LT spectra t_{loc} (average time of searching the trap and its growing to the equilibrium size) was set to to 50–100 ps, as induced from the analysis of the GiPS-AMOC spectrum [2]. At $t > t_{\text{loc}}$ qf-Ps is practically absent: partly annihilated, partly transformed into a bubble state (both *ortho*- and *para*-states, as expected, in a ratio of 3/1). $R_{\text{oxi}}(t)$ de-

scribes oxidation of Ps (in a bubble state), i.e. its reversion to a hydrated e⁺, although complex formation may occur, too (positron + negative ion of the oxidizer: the e⁺ annihilation rate in this complex should be close to that of a free e⁺). According to the model of e⁺ blob, the value $R_{\text{oxi}}(t)$ has the form (see [9, 10]):

$$\begin{aligned} R_{\text{oxi}}(t) &= \sum_{k_i, \text{Ps}} c_i / V_{i, \text{Ps}}(t), \\ V_{i, \text{Ps}}(t) &= V_{\text{bl}} [1 + 4(D_i + D_{\text{Ps}})t/a_{\text{bl}}^2]^{3/2}, \\ k_{i, \text{Ps}}(t) &= k_{\text{oxi}} \left[1 + (R_i + R_{\text{Ps}})/\sqrt{\pi(D_i + D_{\text{Ps}})t} \right]. \end{aligned} \quad (2)$$

Here $k_{i, \text{Ps}}$ is the Ps oxidation rate constant by radiolytic oxidizers (OH, H₃O⁺), $D_i + D_{\text{Ps}}$ is the sum of the diffusion coefficients of reactants, a_{bl} is the initial size of the blob and $V_0 = (2\pi)^{3/2}a_{\text{bl}}^3$ is its characteristic volume. Substituting typical numbers ($a_{\text{bl}} \approx 40 \text{ \AA}$, $D_i + D_{\text{Ps}} \approx 5 \times 10^{-5} \text{ cm}^2/\text{s}$), we find that the characteristic time of the blob expansion is 0.5–1 ns: clearly, the intrablob oxidation of Ps implies inapplicability of the 3-E analysis of LT spectra. According to the latter approach, it is assumed that I_1 describes the decay of *p*-Ps, and I_3 — *o*-Ps. As follows from the above consideration I_1 includes also decays of qf-Ps, because they occur on a very short time scale

$$I_{\text{qf-Ps}} = \lambda_{\text{qf-Ps}} \int_0^\infty n_{\text{qf-Ps}} dt = P_{\text{qf-Ps}} \lambda_{\text{qf-Ps}} / (\lambda_{\text{qf-Ps}} + \lambda_{\text{loc}}). \quad (3)$$

This contribution increases I_1 and, therefore, the I_3/I_1 ratio approaches to 2/1 which is in reasonable agreement with the experiment, Fig. 1.

3. Ps formation in NaNO₃ aqueous solutions at different temperatures

Radiation-chemical data suggest that the nitrate ion is an efficient scavenger of a “hot” electron (precursor of a thermalized electron). This is deduced from the exponential inhibition (suppression) of the yield of the hydrated electron vs. scavenger concentration (Fig. 3):

$$G_e(c_S) \sim \exp(-c_S/c_{37}), \quad \text{for } \text{NO}_3^- \quad c_{37} = 0.53 \text{ M}. \quad (4)$$

Here c_{37} is the concentration of the scavenger at which the yield decreases 1/e (= 0.37) times.

This dependence can be obtained on theoretical grounds, provided the electron capture (by a scavenger) occurs earlier than electron hydration, i.e. capture and hydration do not compete but are subsequent.

It is also known that NO₃⁻ ions react with hydrated electrons (rate constant at about $k(\text{NO}_3^-) \approx 10^{10} \text{ M}^{-1} \text{ s}^{-1}$). Therefore, being in a solution at concentration $[\text{NO}_3^-] \approx 0.1 \text{ M}$, NO₃⁻ ions during 1 ns may capture most of the hydrated electrons in the e⁺ blob: $\exp(-k(\text{NO}_3^-)[\text{NO}_3^-](1 \text{ ns})) \approx 1/3$ (typical concentration of the hydrated electrons therein is $\approx 0.01 \text{ M}$). However, processing of the LT spectra of nitrate aqueous solutions showed that Ps inhibition (more precisely, qf-Ps inhibition) takes place in agreement with the exponential

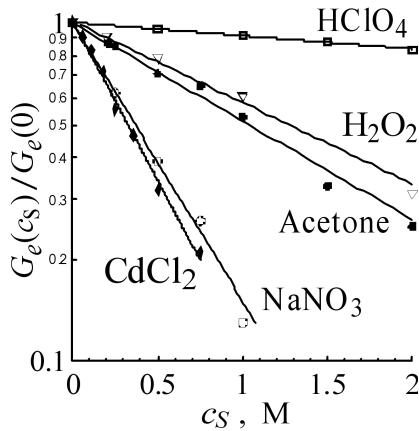


Fig. 3. Inhibition of the hydrated electron yield in aqueous solutions of various electron scavengers [11].

law (Eq. (4)):

$$P_{\text{qf-Ps}}(c_S) = P_{\text{qf-Ps}}(c_S = 0) \exp(-c_S/c_{37}), \quad (5)$$

where c_{37} has the same numerical value (0.53 M) as in Eq. (4), describing inhibition of the hydrated electrons in picosecond pulse radiolysis experiments. Thus, capture of hydrated e^- by NO_3^- ions does not affect Ps formation probability. It ensues that the hydrated e^- is not a Ps precursor; the (hydrated) positron does not react with it. So, in the case of nitrate solutions, in the system (1) just $P_{\text{qf-Ps}}(c_S/c_{37})$ must be used as the initial condition should as the initial probability of qf-Ps formation.

Some parameters obtained in fitting the LT spectra of NaNO_3 aqueous solutions are shown in Fig. 4. Therein f_{oPs} , $f_{\text{qf-Ps}}$ and f_{pPs} are the proportions of e^+ annihilation in its different states o-Ps , qf-Ps , p-Ps , respectively (we shall call f as decay fractions). To draw a rough analogy with 3-E analysis, we must adopt $I_3 \Leftrightarrow f_{\text{oPs}}$, $I_1 \Leftrightarrow f_{\text{qf-Ps}} + f_{\text{pPs}}$ and $P_{\text{qf-Ps}} \Leftrightarrow I_3 + I_1$ — total probability for Ps. So qf-Ps decays mostly contribute to I_1 .

4. Conclusions

1) Inclusion of quasi-free Ps, as a precursor of the Ps bubble state, into the Ps formation scheme allows to understand the cause of the underestimated ratio I_3/I_1 ($\approx 2/1$ instead of 3/1). It also naturally explains the presence of a “hump” of the S -parameter at about 100 ps after the e^+ birth (“juvenile broadening”), attributable to the fact that annihilation of qf-Ps results in a wider Doppler spectrum than *para*-Ps, localized in a bubble.

A better understanding of the physical nature of qf-Ps comes from ACAR experiments in crystalline ice, where qf-Ps is observed in the Bloch state (formation of the bubble state is not possible there). For simplicity, on interpreting the LT and AMOC spectra we have assumed that the qf-Ps annihilation rate is equal to that of the free e^+ (more correctly, hydrated e^+). However, this is not fully true. In the *para*-state qf-Ps can annihilate into

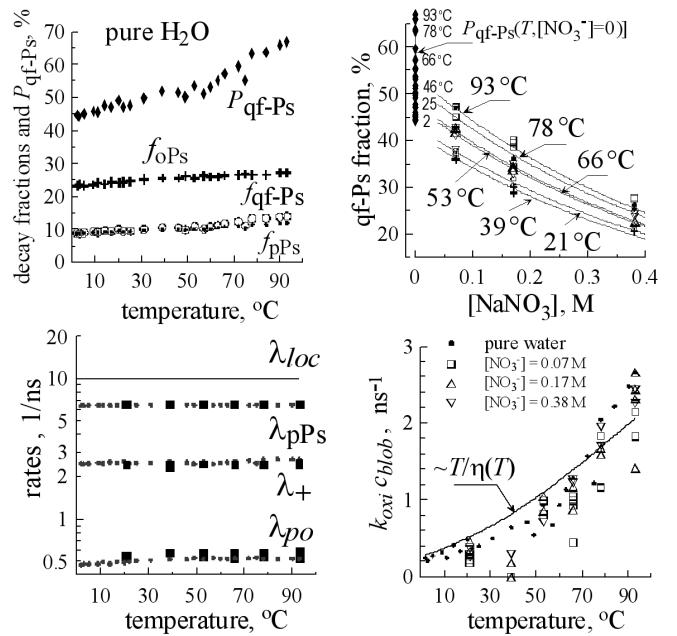


Fig. 4. Temperature and concentration dependences of the decay fractions (\bullet f_{pPs} ; \circ $f_{\text{qf-Ps}}$; $+$ f_{oPs}) of different e^+ states (free e^+ , qf-Ps, p-Ps, o-Ps), qf-Ps formation probability, $P_{\text{qf-Ps}}(T, c_S = [\text{NO}_3^-])$, the annihilation rates (localization rate constant is fixed at 10 ns^{-1} ; bold symbols show data obtained in nitrate solutions, small symbols — in pure water) and the oxidation rate constant k_{oxi} (solid line shows the Stokes–Einstein temperature behaviour of the diffusion controlled reaction rate constant $\eta(T)$ is the viscosity of water).

two gammas with its own electron. Although the probability of this process is low (the qf-Ps contact density is small), it is this annihilation channel that leads to the appearance of the Bloch peaks in the ACAR spectrum. Let us note that a large fraction of the Bloch *para*-qf-Ps can be produced from the *ortho*-qf-Ps due to its spin conversion into *para*-state at longer times. In the nowadays classical ACAR experiment [12] this was possible due to the presence of paramagnetic impurities in the ice (dissolved atmospheric O_2) stimulating *ortho*-*para* conversion of the qf-Ps.

2) Analysis of the LT spectra of aqueous solutions of NaNO_3 confirms that hydrated electrons do not take part in Ps formation. Most likely, this is due to the minute energy gain in this reaction between hydrated species: the energy of the Ps bubble state is only slightly below the sum of the energies of the hydrated e^+ and e^- , whereas significant rearrangement of the surrounding molecules is needed in the reaction. It would be interesting to study Ps formation in solution of other electron scavengers (acidic aqueous solutions) and in other solvents.

3) The temperature dependence of the Ps oxidation reaction rate constant by intrablob radiolytic species (OH radicals, H_3O^+ ions) is well described by the Stokes–Einstein law ($\sim T/\eta(T)$, η is the viscosity of water), indicating that this reaction is diffusion-controlled. The

value of the constant (for example, at room T) is in a good agreement with its theoretical estimate $k_{\text{oxi}}c_{\text{blob}} = 4\pi(D_i + D_{\text{Ps}})(R_i + R_{\text{Ps}})([\text{OH}] + [\text{H}_3\text{O}^+]) \approx 0.4 \text{ ns}^{-1}$, Fig. 4 [13];

4) Ps *ortho-para* conversion on intrablob radical species is not witnessed, due to the fact that in water a spin-converter (paramagnetic particle) as OH radicals is primarily also a strong oxidizer.

5) In water, the mobility of positively charged H_3O^+ ions is twice as large as that of the hydrated electrons. As a result, an excess negative charge appears in the center of the blob which retains thermalized e^+ inside the blob. The Debye screening of the e^+ charge by other charged blob species also leads to e^+ confinement inside the blob. In other molecular substances where electron mobility is greater than the mobility of positive ions, there is an opposite effect: e^+ may escape during thermalization outside the blob [14].

6) The Smoluchowski time correction (the factor $1 + (R_i + R_{\text{Ps}})/\sqrt{\pi(D_i + D_{\text{Ps}})t}$ in Eq. (2)) for the diffusion-controlled reaction rate constant is really negligible, since the diffusion displacement ($\sqrt{\pi(D_i + D_{\text{Ps}})t}$) of the reagents for typical times 0.1–1 ns is much larger than the reaction radius $R_i + R_{\text{Ps}}$ (a few Å). Only for $t \approx 1 \text{ ps}$, $(R_i + R_{\text{Ps}})/\sqrt{\pi(D_i + D_{\text{Ps}})t} \approx 1$.

7) The temperature increase of the positronium formation probability $P_{\text{qf-Ps}}$ is related to a decrease in the energy needed for the production of one ion-electron pair (i.e. a decrease in the ionization potential of water). Hence it is a consequence of the increase of the total number of ion-electron pairs in the e^+ blob. The second plot in Fig. 4 shows some difference between the values of $P_{\text{qf-Ps}}(T)$ in pure water and that extrapolated to zero concentration in NaNO_3 solutions. It is possible that nitrate anions capture “hot” e^+ to a small extent. This effect has often a resonant character, the acceptor capturing a positron of a certain energy, corresponding to the maximum of the capture cross-sections.

Acknowledgments

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