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Interaction of positronium with dissolved oxygen in liquids

P.S. Stepanov[1,a)], F.A. Selim[1,b)], S.V. Stepanov[2,3,c)], A.V. Bokov[2,d)], O.V. Ilyukhina[2,e)], G. Duplâtre[5,f)] and V.M. Byakov[2,4,g)]

[1]*Center for Photochemical Sciences, Department of Physics and Astronomy, Bowling Green State University, OH 43403 USA*
[2]*Institute for Theoretical and Experimental Physics named by A.I. Alikhanov of National Research Centre "Kurchatov Institute", Moscow, 117218 Russia*
[3]*National Research Nuclear University "MEPhI" (Moscow Engineering Physics Institute), 115409, Moscow, Russia*
[4]*D. Mendeleyev University of Chemical Technology of Russia, Miusskaya sq., 9, 125047, Moscow, Russia*
[5]*Institut Pluridisciplinaire Hubert Curien, CNRS/IN2P3, BP 28 67037 Strasbourg, Cedex 2, France*

a)Corresponding author: petrs@bgsu.edu
b)faselim@bgsu.edu
c)stepanov@itep.ru
d)av.bokov@yandex.ru
e)ilyukhina@itep.ru
f)gduplatre@estvideo.fr
g)byakov@itep.ru

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Abstract. The interaction of positronium (Ps) with molecular oxygen dissolved in liquids is experimentally investigated. A computer software has been developed for fitting the positron annihilation lifetime spectra in liquids using parameters with clear physical meaning: rate constants of the Ps chemical reactions, annihilation rate constants of the different positron states, probability of Ps formation in a quasifree state, typical formation time of a Ps nanobubble. Such processing of the spectra allowed to identify the dominant interaction of the Ps atom with dissolved oxygen. It comes out to be mainly ortho-para-conversion (Ps $\rightarrow$ 1/4 p-Ps + 3/4 o-Ps), but not oxidation (Ps + $O_2 \rightarrow e^+ + O_2^-$). Values of the reaction rate constants are obtained.

1. Introduction

Positron annihilation spectroscopy (PAS) has numerous applications in material science such as studies of structural defects, free volume, porosity of materials. At the same time PAS is also applied to study radiolytic processes in chemistry, radiobiology and medicine [1].

In experiments with radioisotope positron sources, positrons are born and injected into the studied material with continuous energy distribution, with the end point energies 1.47 MeV for ^{44}Ti-^{44}Sc-^{44}Ca-source and 0.54 MeV for ^{22}Na-^{22}Ne-source. During ionization the slowing down positrons form tracks (clusters of ion-electron pairs along their trajectory), and after getting thermalized e^+ start to explore the surrounding medium. Because typical lifetimes of the positron states (0.1-10 ns) are of the order of characteristic times of the intratrack processes in molecular media, the positron turns out to be a convenient probe for radiation phenomena.

In nonconducting (molecular) substances, a thermalized e^+ easily forms Ps, which is a bound state of e^+ and e^- (the lightest analog of a hydrogen atom). The formation of Ps occurs in the final part of the e^+ track (the positron blob) as a result of the combination of a thermalized positron with one of the track electrons. Depending on the relative orientation of e^+ and e^- spins, the Ps atom can exist either in the para-state (p-Ps) with a spin equal to zero, or in the ortho-state (o-Ps) with a spin equal to $1 \cdot \hbar$ [2].

In most molecular liquids, the o-Ps lifetime is much shorter than it is in vacuo (142 ns). It is decreased to a few ns, because of the so-called pick-off process, when the positron (in Ps) undergoes 2γ-annihilation with one of the nearest molecular electrons, whose spin is anti-parallel to the positron's spin. Nevertheless, the o-Ps atom can take part in chemical reactions not only with intratrack radiolytic products (in water, these are hydrated electrons, H_3O^+, OH-radicals), but also with dissolved substances, for example, with molecular oxygen, O_2 [3].

Recently, some interest in the phenomenon of shortening of the o-Ps lifetime (Ps quenching) in various liquids due to its interaction with dissolved oxygen has reemerged. This effect seems to be important when testing healthy and carcinogenic tissues by means of PAS because the oxygen content therein noticeably differs [4]. The reason is the so-called oxygen effect: there are relatively few blood tubes in cancerous tumors, so cancer cells develop under oxygen-lacking conditions. This explains enhanced radioresistance of the cancer cells, since just the products of interaction of dissolved oxygen with the chemically

active radicals (which appear because of irradiation) destroys the tumor. PAS studies in this direction are partially stimulated because of the development of a new type of positron annihilation tomographer at the Jagiellonian University in Krakow, Poland [5, 6].

The interaction of Ps with oxygen molecules (as well with some molecules possessing oxidizing properties, such as Cl_2, Br_2, I_2) is more important than with other neutral molecules (for example, N_2). The interaction with neutral molecules through elastic collisions leads to the pick-off annihilation of Ps: the time of such collision is very short. By contrast, Ps interaction with oxygen molecules results in the formation of an activated, unstable, complex (or compound, PsO_2 or $e^+O_2^-$): the time involved can thus be much longer. The O_2 molecule can either oxidize Ps atom ($Ps + O_2 \rightarrow e^+ + O_2^-$), or stimulate its ortho-para conversion ($Ps \rightarrow 1/4$ p-Ps $+ 3/4$ o-Ps), because O_2 molecule has a magnetic moment. All these processes lead to an observable decrease of the o-Ps lifetime (Ps quenching) [7, 8, 9, 10, 11]. Using conventional methods of processing of the positron annihilation lifetime (LT) spectra it is impossible to distinguish between oxidation and spin-conversion reactions.

Experiments with magnetic fields indicated the importance of the Ps ortho-para conversion and allowed to estimate a decrease of the Ps contact density parameter ($\eta_c = |\Psi_{liquid}^{Ps}(0)|^2|/|\Psi_{vacuum}^{Ps}(0)|^2$) only in few liquids: water (0.8; 0.65), benzene (0.84), methanol (0.68) and hexane (0.82) [12, 13]. So we adopt here that η_c is about 0.75-0.8 in all liquids studied here. It means that para-Ps being in a bubble state in a liquid lives about 160 ps (longer than in vacuum) before it undergoes the 2γ-annihilation.

In this paper, we present the results of our PAS experiments in organic liquids (cyclohexane, isooctane, isopropanol) and in water in order to identify the nature of the Ps-O_2 interaction (oxidation or conversion). Values of the reaction rate constants are obtained with the help of new software, which uses an advanced model of Ps formation for processing of LT annihilation spectra.

2. Experimental

All the reagents used were purchased from Russian Chemist (`www.rushim.ru`). Unlike previous studies [8, 9] we did not use the freeze-thaw method to remove dissolved O_2 to avoid the risk of damaging the positron source during freezing and evacuation. Therefore, oxygen was removed from the liquid phase by its bubbling with chemically pure argon. For determination of the rate constants of the Ps+O_2 reactions, the liquids were bubbled either with air or pure oxygen to increase the O_2 concentration.

The gases were previously cleaned by means of blowing them through dry alkali KOH and then through nanosieves Metrohm 0.3 nm previously kept for 24 h in forvacuum at 250 °C. Next, the purified gas was fed into a hermetically sealed vial containing the studied liquid. Input/output of the gas was performed by means of two long medical needles, tightly inserted into the lid of the vial.

The positron source was made from a 10 mm diameter, 0.2 mm thick titanium washer. Its central part (6 mm diameter) was welded on both sides with 10 μm titanium foils. In-between them a radioactive powder of $TiCl_4$, containing about 7.5 MBq of ^{44}Ti, was deposited. The positron source was fixed in the center of the vial using stainless steel clip. The clip itself was tightly fixed in the lid of the vial. The source correction was determined in a series of separate measurements of the reference (pure, well-annealed) samples (Al, Si, Fe and W). From these measurements we concluded that for the present experiments with liquids the source correction is 13%. It consists of the following components I1=32%, t1=0.15 ns; I2=50%, t2=0.38 ns; I3=18% and t3=1.8 ns.

The lifetime annihilation spectra were recorded using two γ-detectors with BaF_2 scintillators and fast timing nanosecond electronic units from ORTEC. The time resolution of the annihilation spectrometer was 280 ps. Spectra were recorded sequentially for each hour during one day. The total number of "start-stop" coincidence in each spectrum was about 1 million. All measurements were done at 20 °C.

The spectra were first analyzed through 3-exponential deconvolution. The lifetime of the shortest (parapositronium) component was fixed to the lifetime of p-Ps in a vacuum, 125 ps. Then, a more accurate model was used, taking into account formation of a quasi-free positronium and its subsequent transformation into a bubble state.

3. Ortho-para conversion and oxidation of Ps in the presence of dissolved O_2

Immediately after its birth, as a result of radioactive transformations of ^{44}Ti-^{44}Sc-^{44}Ca radioactive nuclei, the positron has a rather large kinetic energy (about 1 MeV). Within the next 10 ps, it loses its energy down to thermal energy because of ionization slowing down. At the end of its track in molecular media, the thermalized positron can combine with one of the electrons knocked out through ionization along the track. This process results in the formation of the quasi-free positronium, qf-Ps, a delocalized weakly bound state of e^+ and e^-, which also moves in a liquid at thermal velocity [14, 15]. Note that there is no need to specify the spin state of qf-Ps, because the contact density of its electron at the level of the positron is rather small. Therefore, the main channel of qf-Ps annihilation is annihilation of e^+ with one of the electrons of the surrounding molecules. Within 50-100 ps, qf-Ps transforms into a localized state (Ps bubble formation time) [16, 17]. Although the typical qf-Ps lifetime is rather short, this state is important for explaining of the extreme behavior of the S-parameter time dependence in AMOC experiments.

In the scheme to follow, we neglect initial picosecond-scale processes like electron and positron solvation, qf-Ps formation. The initial moment ($t = 0$) of the following system describing transformation of the positron states is the time moment of

formation of qf-Ps:

$$\dot{n}_+(t) = -\lambda_+ n_+ + \lambda_{ox} n_o, \qquad n_+(0) = 1 - P_{qf}, \tag{1}$$

$$\dot{n}_{qf}(t) = -\lambda_q n_{qf}, \qquad n_{qf}(0) = P_{qf}, \qquad \lambda_q = \lambda_{qf} + \lambda_b, \tag{2}$$

$$\dot{n}_o(t) = \frac{3\lambda_b}{4} n_{qf} - \lambda_o n_o, \qquad n_o(0) = 0, \qquad \lambda_o = \lambda_{po} + \frac{\lambda_{opc}}{4} + \lambda_{ox}, \tag{3}$$

$$\dot{n}_p(t) = \frac{\lambda_b}{4} n_{qf} + \frac{\lambda_{opc}}{4} n_o - \lambda_p n_p, \qquad n_p(0) = 0, \qquad \lambda_p = \lambda_{2\gamma} + \lambda_{po}. \tag{4}$$

Here, $n_+(t)$ and $n_{qf}(t)$ are probabilities of existence of the thermalized solvated positron and qf-Ps at a time t, respectively; $n_o(t)$ and $n_p(t)$ are the probabilities of observing the Ps atom localized in a bubble in ortho- and para-state, respectively; $\lambda_b = 1/(0.05...0.1 \text{ ns})$ is the rate constant of the qf-Ps transformation into positronium localized in a nanobubble, P_{qf} is the formation probability of qf-Ps, λ_{qf} and λ_+ are the annihilation rate constants of the qf-Ps and solvated positrons, λ_{po} is the pick-off annihilation rate constant of Ps and $\lambda_{ox} = k_{ox} c_{O2}^{(L)}$ and $\lambda_{opc} = k_{opc} c_{O2}^{(L)}$ are the oxidation and ortho-para conversion rate constants. $c_{O2}^{(L)}$ being the concentration of molecular oxygen. $\lambda_{2\gamma} \approx 8 \text{ ns}^{-1}$ is the 2γ annihilation of p-Ps and λ_{po} is the pick-off annihilation rate. In the above equations we neglected the para-to-ortho process, since, due to the rather low O_2 concentrations used, this reaction appears kinetically negligible as compared to the fast 2γ-decay of p-Ps. Solving Eqs. (1-4) gives the following equations for all 4 positron states:

$$n_{qf}(t) = P_{qf} e^{-\lambda_q t}, \qquad n_o(t) = \nu(e^{-\lambda_o t} - e^{-\lambda_q t}), \qquad \nu = \frac{3P_{qf}}{4} \frac{\lambda_b}{\lambda_q - \lambda_o}, \tag{5}$$

$$n_+(t) = (1 - P_{qf}) e^{-\lambda_+ t} + \nu \frac{\lambda_{ox}}{\lambda_+ - \lambda_o}(e^{-\lambda_o t} - e^{-\lambda_+ t}) - \nu \frac{\lambda_{ox}}{\lambda_q - \lambda_+}(e^{-\lambda_+ t} - e^{-\lambda_q t}), \tag{6}$$

$$n_p(t) = \frac{P_{qf}}{4} \frac{\lambda_b}{\lambda_q - \lambda_p}(e^{-\lambda_p t} - e^{-\lambda_q t}) + \nu \frac{\lambda_{opc}/4}{\lambda_p - \lambda_o}(e^{-\lambda_o t} - e^{-\lambda_p t}) - \nu \frac{\lambda_{opc}/4}{\lambda_q - \lambda_p}(e^{-\lambda_p t} - e^{-\lambda_q t}). \tag{7}$$

2γ-annihilation of these four positron states gives the following contribution to the shape of the LT spectrum:

$$C_{2\gamma}(t) \propto \lambda_{qf} n_{qf} + \lambda_+ n_+ + \lambda_p n_p + \lambda_{po} n_o. \tag{8}$$

Thus, in this case the LT spectrum consists of 4 exponentials:

$$C_{2\gamma}(t) \propto \lambda_q I_0 e^{-\lambda_q t} + \lambda_p I_1 e^{-\lambda_p t} + \lambda_+ I_2 e^{-\lambda_+ t} + \lambda_o I_3 e^{-\lambda_o t}. \tag{9}$$

Of course, to compare this with the experiment, we must add contribution from e^+ annihilation within the positron source, convolute $C_{2\gamma}(t)$ with the resolution function of the spectrometer, and add a random coincidence background. Combining the terms corresponding to the same exponents, we find the intensities:

$$I_0 = P_{qf} \frac{\lambda_{qf}}{\lambda_q} - \frac{P_{qf}}{4} \frac{\lambda_p \lambda_b}{\lambda_q(\lambda_q - \lambda_p)} + \nu \frac{\lambda_p \lambda_{opc}/4}{\lambda_q(\lambda_q - \lambda_p)} + \nu \frac{\lambda_+ \lambda_{ox}}{\lambda_q(\lambda_q - \lambda_+)} - \nu \frac{\lambda_{po}}{\lambda_q}, \tag{10}$$

$$I_1 = \frac{P_{qf}}{4} \frac{\lambda_b}{\lambda_q - \lambda_p} - \nu \frac{\lambda_{opc}/4}{\lambda_p - \lambda_o} - \nu \frac{\lambda_{opc}/4}{\lambda_q - \lambda_p},$$

$$I_2 = 1 - P_{qf} - \nu \frac{\lambda_{ox}}{\lambda_+ - \lambda_o} - \nu \frac{\lambda_{ox}}{\lambda_q - \lambda_+},$$

$$I_3 = \nu \frac{\lambda_p \lambda_{opc}/4}{\lambda_o(\lambda_p - \lambda_o)} + \nu \frac{\lambda_+ \lambda_{ox}}{\lambda_o(\lambda_+ - \lambda_o)} + \nu \frac{\lambda_{po}}{\lambda_o}.$$

Particularly when there are no reactions between Ps and oxygen ($\lambda_{opc} = \lambda_{ox} = 0$), these expressions are reduced to:

$$I_0 = P_{qf} \frac{\lambda_{qf}}{\lambda_q} - \frac{P_{qf}}{4} \frac{\lambda_p \lambda_b}{\lambda_q(\lambda_q - \lambda_p)} - \frac{3P_{qf}}{4} \frac{\lambda_{po} \lambda_b}{\lambda_q(\lambda_q - \lambda_{po})}, \tag{11}$$

$$I_1 = \frac{P_{qf}}{4} \frac{\lambda_b}{\lambda_q - \lambda_p}, \qquad I_2 = 1 - P_{qf}, \qquad I_3 = \frac{3P_{qf}}{4} \frac{\lambda_b}{\lambda_q - \lambda_{po}}.$$

It is easy to verify that in this case the qf-Ps formation probability is $P_{qf} = I_0 + I_1 + I_3$ and $\sum_{i=0}^{3} I_i = 1$. In case of very fast formation of the Ps bubble ($\lambda_b \to \infty$, $\lambda_q \to \infty$) Eqs. 11 give $I_0 = 0$, $I_1 = P_{qf}/4$, $I_2 = 1 - P_{qf}$, $I_3 = 3P_{qf}/4$.

    Usually in positron lifetime experiments the short-lived components I_0 and I_1 cannot be resolved using the conventional exponential deconvolution, so these intensities are combined in one short-lived component, which is incorrectly identified with

the probability of p-Ps formation. As a result, a wrong conclusion is made about violation of the "one-to-three" ratio of p-Ps and o-Ps formation probabilities:

$$\frac{I_0 + I_1}{I_3} = \frac{1}{3} + \frac{4(\lambda_{qf} - \lambda_{po})}{3\lambda_b}. \tag{12}$$

Substituting here the probable values of the rates $\lambda_{qf} \simeq 2$, $\lambda_{po} \simeq 0.5$ and $\lambda_b \simeq 10\text{-}15$ ns^{-1}, this ratio increases from 1/3 to $\simeq 1/2$ in accordance with experimental observations in Fig. 1. Thus, an increase in this ratio is a consequence of the formation and presence of qf-Ps over several dozens of picoseconds, before its transformation into a bubble state.

In essence, the proposed model contains only 5 adjustable parameters: P_{Ps}, $\lambda_{qf} \approx \lambda_+$, λ_{po}, k_{opc}, k_{ox} since we fixed λ_b to 20 ns^{-1} based on AMOC experiments [16, 17].

The conventional approach for processing the LT spectra in liquids consists in their deconvolution into three exponentials decreasing with time. This can be derived from Eqs. 10, if we neglect the existence of qf-Ps, (assuming that the rate constant of the Ps bubble formation λ_b is very large). In this case Eqs. (1-4):

$$\dot{n}_p(t) = \frac{\lambda_{opc}}{4}n_o - \lambda_p n_p, \qquad \lambda_p = \lambda_{2\gamma} + \lambda_{po}, \qquad n_p(0) = \frac{P_{Ps}}{4}, \tag{13}$$

$$\dot{n}_+(t) = \lambda_{ox}n_o - \lambda_+ n_+, \qquad n_+(0) = 1 - P_{Ps}, \tag{14}$$

$$n_o(t) = \frac{3P_{Ps}}{4}e^{-\lambda_o t}, \qquad \lambda_o = \lambda_{po} + \frac{\lambda_{opc}}{4} + \lambda_{ox}. \tag{15}$$

Here P_{Ps} is already the probability of Ps formation just in a bubble state. The equations on n_+ and n_p can be easily solved

$$n_p(t) = \frac{P_{Ps}}{4}e^{-\lambda_p t} + \frac{3P_{Ps}}{4} \cdot \frac{\lambda_{opc}/4}{\lambda_p - \lambda_o}(e^{-\lambda_o t} - e^{-\lambda_p t}).$$

$$n_+(t) = (1 - P_{Ps})e^{-\lambda_+ t} + \frac{3P_{Ps}}{4} \cdot \frac{\lambda_{ox}}{\lambda_+ - \lambda_o}(e^{-\lambda_o t} - e^{-\lambda_+ t}),$$

after which it comes out that the LT spectrum consists of three exponents:

$$C_{2\gamma}(t) \propto \lambda_+ n_+ + \lambda_p n_p + \lambda_{po} n_o = \lambda_p I_1 e^{-\lambda_p t} + \lambda_+ I_2 e^{-\lambda_+ t} + \lambda_o I_3 e^{-\lambda_o t}, \tag{16}$$

$$I_1 = \frac{P_{Ps}}{4} - \frac{3P_{Ps}}{4} \cdot \frac{\lambda_{opc}/4}{\lambda_p - \lambda_o}, \qquad I_2 = 1 - P_{Ps} - \frac{3P_{Ps}}{4}\frac{\lambda_{ox}}{\lambda_+ - \lambda_o}, \tag{17}$$

$$I_3 = \frac{3P_{Ps}}{4}\left[\frac{\lambda_{po}}{\lambda_o} + \frac{\lambda_+}{\lambda_o}\frac{\lambda_{ox}}{\lambda_+ - \lambda_o} + \frac{\lambda_p}{\lambda_o}\frac{\lambda_{opc}/4}{\lambda_p - \lambda_o}\right], \qquad I_1 + I_2 + I_3 = 1, \quad \tau_1 = \frac{1}{\lambda_p}, \quad \tau_2 = \frac{1}{\lambda_+}, \quad \tau_3 = \frac{1}{\lambda_o}. \tag{18}$$

Such a simplified model (without qf-Ps) cannot explain the observed values of the ratio I_1/I_3 (larger then 1/3). It is seen from Eqs. 17-18 taking account of the Ps reactions with oxygen (conversion and oxidation; non-zero λ_{ox} and λ_{opc}) reduces even more the I_1/I_3 ratio and brings this model into conflict with experiment. Therefore, for a formal description of the LT spectra, these quantities I_1, I_2, I_3, τ_1, τ_2 and τ_3 are often considered as free adjustable parameters.

In Fig. 1 and Tab. 1 we have shown the results of such a formal treatment of the LT spectra measured in cyclohexane, isooctane, isopropanol and water before and after bubbling argon, oxygen and air through these liquids. The p-Ps lifetime τ_1 was assumed to be a "common free" parameter for each stage of gas bubbling. Comparison with the fit when τ_1 was fixed to 125 ps (p-Ps lifetime in vacuum) is given in the Supplementary information file. The obtained e$^+$ and o-Ps lifetimes are in agreement with the results of previous measurements [8, 9] done with deaerated liquids.

4. Concentrations of dissolved O$_2$ in the studied liquids

Gas solubility is often expressed by the Ostwald coefficient, L, which is the ratio of the gas concentration in the gas phase to its concentration in the liquid: $L = c_{O2}^{(L)}/c_{O2}^{(G)}$ (in some papers, the Ostwald coefficient is defined as $c_{O2}^{(G)}/c_{O2}^{(L)}$).[1]

When pure oxygen is bubbled through a liquid, its partial pressure is 1 atm and its gas phase concentration is $c_{O2}^{(G)} \approx 1/24.1$ mole/liter, since at 20 °C 1 mole of an ideal gas occupies 24.1 liters. The concentrations of O$_2$ in liquids can be easily obtained, knowing values of the Ostwald coefficients (Table 2): $L = c_{O2}^{(L)}/c_{O2}^{(G)}$. When air is blown through a liquid, the O$_2$ concentration in the gas phase is 0.21 times less: $c_{O2}^{(G)} = 0.0087$ mole/liter (since partial O$_2$ pressure in air is 0.21 atm). The O$_2$ concentration in the liquid phase decreases in the same proportion.

In our experiments dissolved oxygen is completely removed from a liquid phase after 2 hours bubbling of argon through the liquid.

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[1]Gas solubility may also be expressed in terms of the mole fraction, x, which is the ratio of the number of moles of the solute (gas molecules) to the total number of moles of all substances per unit volume of the solution.
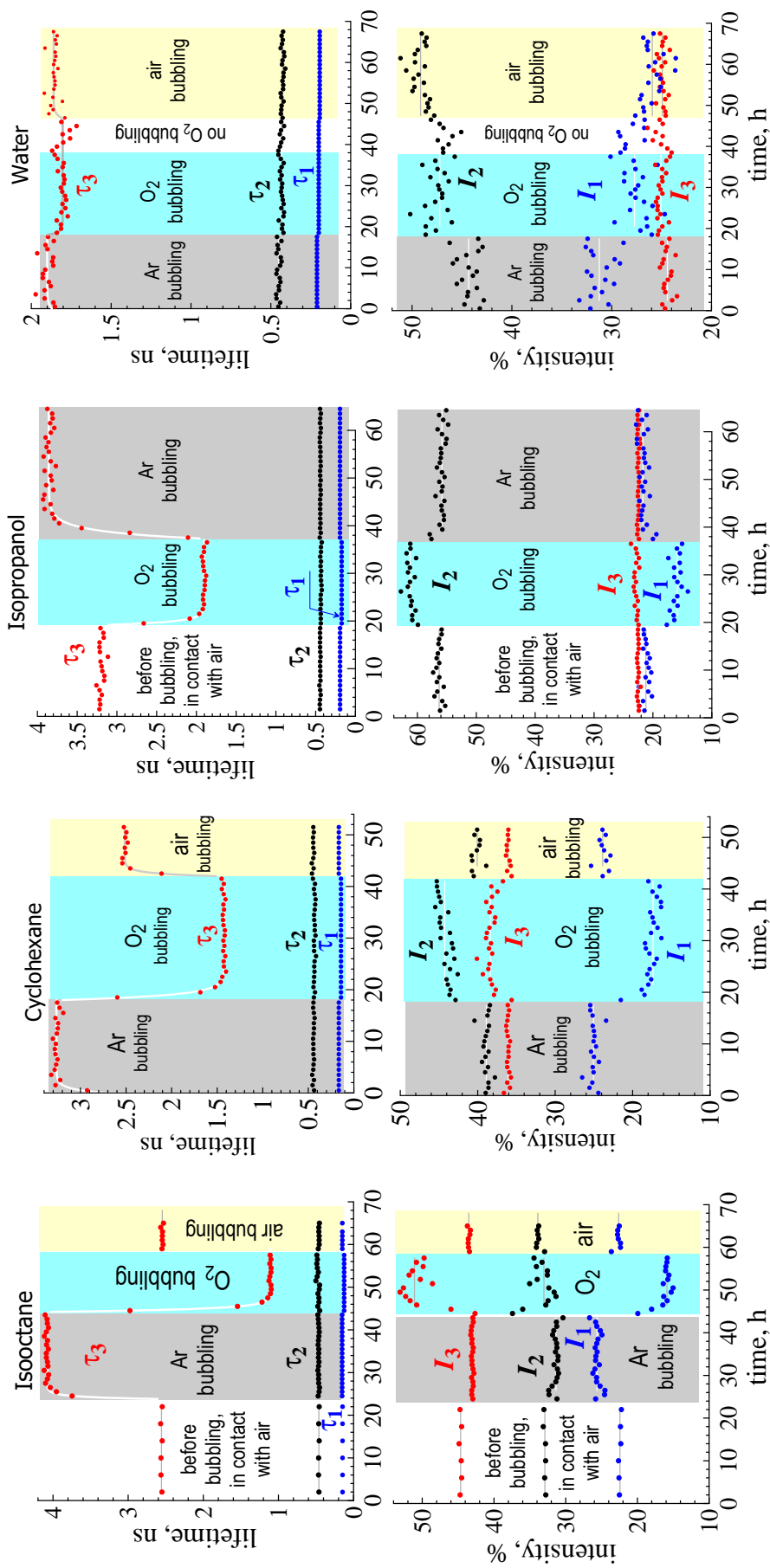
Figure 1. The parameters of 3-exponential deconvolution of the LT spectra in cyclohexane, isooctane, isopropanol and water before and during their bubbling with argon, oxygen and air at room temperature. The lifetime of the shortest (τ_1) component was a "common free" parameter for each stage of the gas bubbling.

Table 1. Parameters of the 3-exponential decomposition of the LT spectra of the initially aerated isooctane, cyclo-hexane, isopropanol and water, and also after their bubbling with argon, oxygen and air at room temperature. τ_1 is considered as a "common free" parameter for each gas bubbling. Statistical uncertainties of the fitting parameters are indicated in parenthesis.

Liquid	I_1, %	τ_1, ps	I_2, %	τ_2, ns	I_3, %	τ_3, ns	$\lambda_o = 1/\tau_3$, ns^{-1}
Isooctane							
– Ar bubbling	24.6	148(1)	32.3(1)	0.45(1)	43.1(1)	4.01(1)	0.249(3)
– air bubbling	21.8	145(1)	34.4(2)	0.45(1)	43.8(1)	2.51(1)	0.398(5)
– before bubbling	22.6	149(1)	32.7(1)	0.46(1)	44.7(1)	2.546(3)	0.393(2)
– O$_2$ bubbling	14	116(3)	31(1)	0.43(1)	55(2)	1.077(6)	0.929(6)
Cyclohexane							
– Ar bubbling	25	165(2)	38.9(4)	0.44(1)	36.1(4)	3.26(4)	0.307(12)
– air bubbling	23.9	165(2)	40.1(4)	0.45(1)	36.1(4)	2.515(40)	0.398(16)
– O$_2$ bubbling	17.4	141(2)	44.3(4)	0.43(1)	38.4(4)	1.42(4)	0.703(29)
Isopropanol							
– Ar bubbling	21.7	194(3)	56(1)	0.44(2)	22.5(1)	3.75(10)	0.267(26)
– before bubbling	21	193(3)	56(1)	0.44(2)	22.5(10)	3.2(1)	0.313(30)
– O$_2$ bubbling	16	173(4)	61(1)	0.43(2)	22.9(8)	1.905(10)	0.525(6)
Water							
– Ar bubbling	31	213(4)	44(4)	0.44(2)	25(4)	1.833(16)	0.546(9)
– air bubbling	25	194(3)	49(1)	0.42(2)	25.5(1)	1.802(15)	0.555(9)
– O$_2$ bubbling	27	200(3)	47(4)	0.42(1)	26(3)	1.746(14)	0.573(8)

Table 2. Values of the Ostwald coefficients $c_{O2}^{(L)}/c_{O2}^{(G)}$, concentrations of O$_2$ in liquids after their bubbling with oxygen and air at room temperature (20 °C) and pressure 1 atm. Values of k_{Ps+O2} and λ_{po} were obtained by fitting the data shown in Fig. 2, using Eq. (19).

Liquid	$c_{O2}^{(L)}/c_{O2}^{(G)}$	$c_{O2}^{(L)}$, M O$_2$ bubbling $c_{O2}^{(G)}$ = 0.0415 M	$c_{O2}^{(L)}$, M air bubbling $c_{O2}^{(G)}$ = 0.0087 M	k_{Ps+O2}, M^{-1}s^{-1}	λ_{po}, 1/ns
Isooctane	0.362 [18]	0.0148	3.2 · 10^{-3}	4.50(6) · 10^{10}	0.25(1)
	0.3725 [19]	0.0154			
Cyclohexane	0.27 [18, 20]	0.0112	2.35 · 10^{-3}	3.51(7) · 10^{10}	0.31(1)
Isopropanol	0.2463 [19]	0.010	2.1 · 10^{-3}	2.61(6) · 10^{10}	0.26(1)
Water	0.0334 [18]	0.00139	2.9 · 10^{-4}	1.86(10) · 10^{10}	0.55(2)

5. Determination of the Ps-O$_2$ reaction rate constants

If we neglect any influence of the intratrack radiolytic products on Ps (which can also promote Ps oxidation and conversion, although mostly on a short time-scale) and in the absence of dissolved oxygen, the o-Ps lifetime is determined only by the pick-off annihilation of e$^+$ with one of the electrons of nearby molecules. In the presence of O$_2$, the o-Ps lifetime can also be shorten because of conversion to the para-state and Ps oxidation:

$$\lambda_o(c_{O2}^{(L)}) = \lambda_{po} + \frac{\lambda_{opc}}{4} + \lambda_{ox} = \lambda_{po} + k_{Ps+O2} \cdot c_{O2}^{(L)}, \qquad k_{Ps+O2} = \frac{k_{opc}}{4} + k_{ox}. \tag{19}$$

Our experimental data for $\lambda_o(c_{O2}^{(L)})$ at different O$_2$ concentrations in liquids are summarized in Tables 1 and 2. Approximating these dependencies using Eq.(19), one can determine the values of the "total" rate constant k_{Ps+O2} reaction with oxygen and the pick-off annihilation rate λ_{po} (see Table 2 and Fig. 2).

In Fig. 3 our data for k_{Ps+O2} are plotted vs. the inverse dynamic viscosity $1/\eta$ of the liquids together with the previous data for other liquids [7]. Linear dependence of k_{Ps+O2} over T/η indicates that the Ps+O$_2$ reaction is diffusion-controlled:

$$k_{Ps+O2} = 4\pi(D_{Ps} + D_{O2})(R_{Ps} + R_{O2}), \qquad D_{Ps} + D_{O2} = \frac{k_B T}{4\pi\eta R_{Ps}} + \frac{k_B T}{6\pi\eta R_{O_2}} \propto \frac{T}{\eta}. \tag{20}$$

Here k_B is the Boltzmann constant, T is the absolute temperature, D_{Ps} and D_{O2} are the diffusion coefficients of the reactants, $R_{Ps} \approx$ 3-4 Å and $R_{O2} \approx$ 2 Å are bubble radii of Ps and O$_2$.

Eq. 20 brings us two problems. The first one is that the rate constant should tend to zero with increasing viscosity of the solvent, whereas Fig. 3 shows that it is not (k_{Ps+O2} remains finite at high viscosity). This means that the interaction of Ps and O$_2$ occurs not only at a distance of a direct contact of the reactants, but also at greater distances (for example, electron
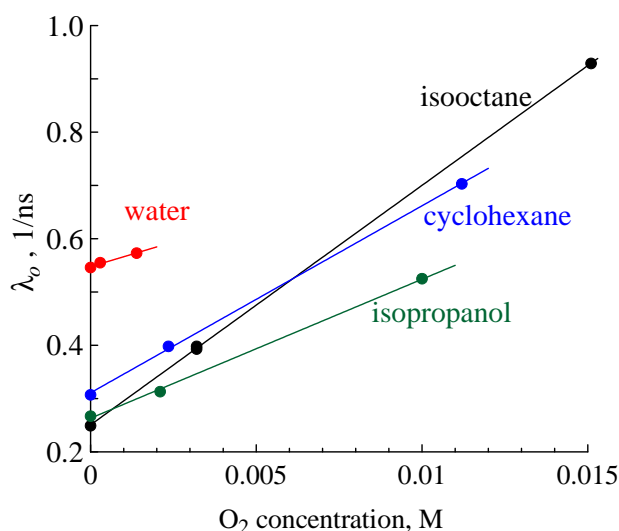
Figure 2. Dependencies of λ_o (data taken from Tab. 1) vs. concentration of dissolved oxygen in different liquids. Solid lines – Eq. (19).
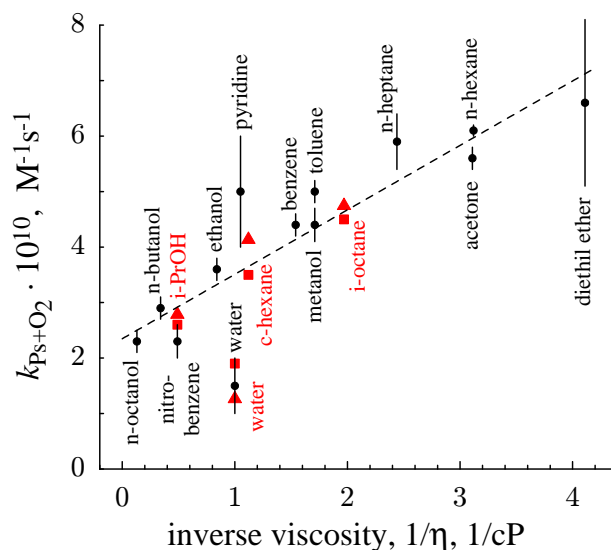

Figure 3. The linear dependence of the rate constants k_{Ps+O2} of the Ps reaction with dissolved oxygen in different liquids vs. the inverse viscosity, $1/\eta$ Eq. (20). Black circles ● are taken from [7]; red symbols ▲, ■ – from Tab. 2 and 3. All the data correspond to room temperature.

or Ps as a whole may tunnel to the oxygen molecule) [21]. The second problem is that the predicted value of the slope of the dependence k_{Ps+O2} versus $1/\eta$ according to Eq. (20) is several times smaller than it really is in Fig. 3. It may indicate that we must distinguish between reaction radii of the reagents and their "hydrodynamic" radii entering the diffusion coefficients. Seemingly, the reaction radii are larger then the hydrodynamic ones.

6. Processing of the spectra through a model taking into account the formation of qf-Ps

In the present study, we take into account that Ps atoms are not formed in nanobubbles instantly. It takes a certain time to find a pre-existing place suitable for localization (Section 3). More subtle effects such as the time-dependence of the rate constant k_{Ps+O2} according to the Smoluchowski theory are not considered in this paper [23].

In section 5 we discussed only values of the "total" rate constants k_{Ps+O2} (but not k_{opc} and k_{ox} separately) because it is hardly possible to distinguish the interaction mechanisms of the Ps with O_2 (conversion or oxidation) on the sole basis of the quenching rate constant $\lambda_o(c_{O2}^{(L)})$. However, the equations developed in Section 3 show that the processes of Ps ortho-para conversion and Ps oxidation result in different redistribution of the lifetime components (I_i) of the LT spectra. This makes it possible to determine the dominant mechanism of the Ps+O_2 interaction.

In the mid 60's of the last century the Ps+O_2 interaction was generally accepted to be just conversion [7]. However after the ACAR experiments in deairated and oxygenated n-hexane [24], this viewpoint was rejected. No increase of the "narrow" parapositronium component in O_2 saturated n-hexane was observed. This result points to Ps oxidation by O_2 as the dominant

process. However, the questions remain about this experiment [24], as the o-Ps lifetime found in oxygen-saturated n-hexane (1 ns) was almost two times less than that obtained by other authors [7, 8, 9].

Unfortunately existing software products like LT-10 [25] or PALSfit3 [26](`http://palsfit.dk/`) do not include fitting models that account for the physical behavior outlined in Section 3. Therefore in order to shed some light onto the interaction mechanisms of Ps and O_2, we developed a special computer software "RooPositron" for processing lifetime annihilation spectra (`https://github.com/petrstepanov/roopositron`).
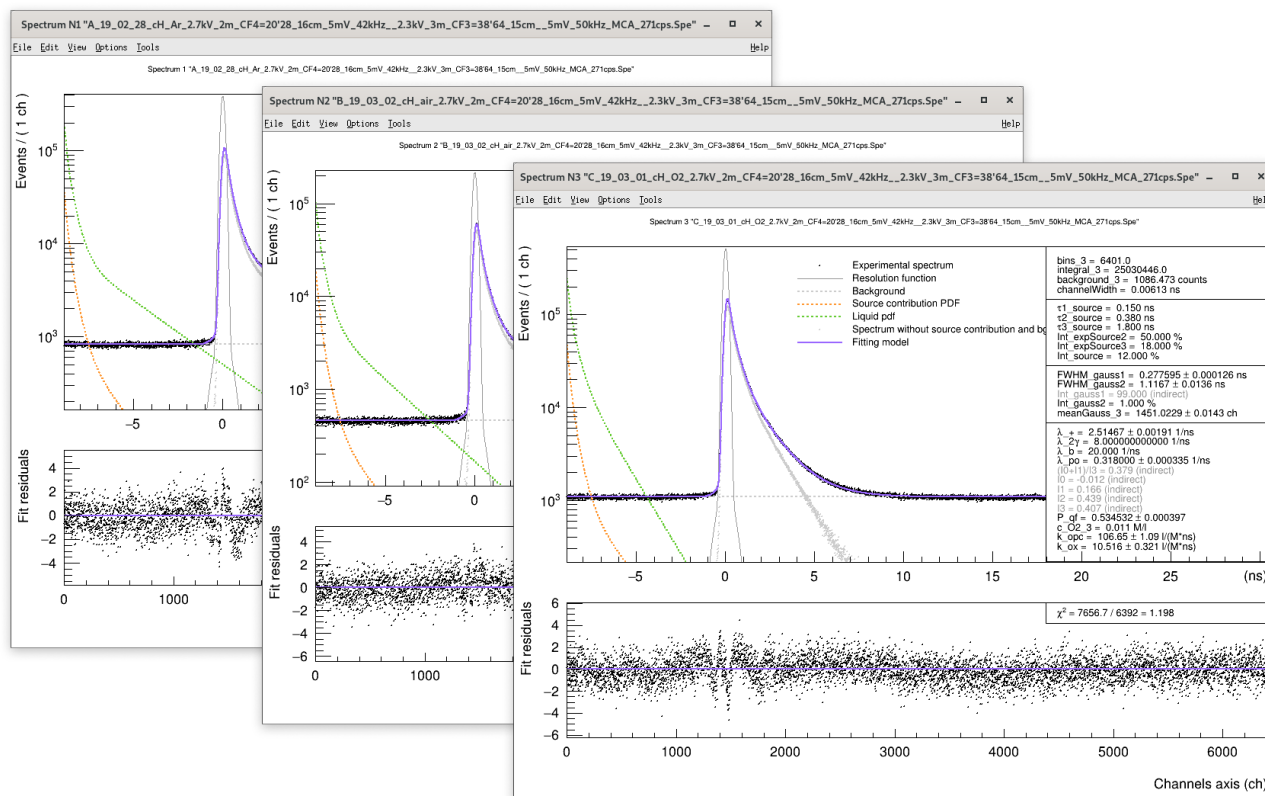

Figure 4. Screenshots of the RooPositron software [29] depicting series of spectra fitted with a model derived from equations (1)-(4).

The program is written in C++ language and utilizes the ROOT framework [27] developed by CERN. ROOT is a set of object-oriented classes that provide a vast functionality for analyzing scientific data. The RooFit [28] package allows the user to built up custom fitting models based on corresponding parameters and performs simultaneous fits of multiple spectra by minimizing the chi-square.

In RooPositron we implemented functionality that is similar to the existing products on the market, such as: simultaneous spectra fitting, ability to fit spectra with various channel width, introduced common and fixed fitting parameters, graphical visualization of the fit and residuals (Fig. 4), and plots export to ASCII files.

Some competitive features of RooPositron program that make it outstanding with respect to the existing solutions include:

- RooPositron's code is open-source and program is distributed free of charge. Any researcher in the field can contribute and improve the functionality.
- Program supports integration of custom fitting models that correspond to meaningful physical parameters of the environment.
- Fitting models support calculation of indirect parameters as functions of the regular parameters of the model.
- Various types of minimizer functions can be used in order to fit the spectra (MINUIT, FUMILI and some others).
- User has a control on the the convolution operation parameters. By adjusting the convolution binning user can either select a quicker fitting speed or obtain higher fit precision.

Program comes with a detailed instructions that covers installation, usage and explain how to add custom models. RooPositron is hosted on GitHub (https://github.com/petrstepanov/roopositron).

Currently RooPositron can perform conventional multiexponential fits, trapping model, and diffusion-trapping model. In this work the program was extended with a fitting model of formation of Ps atom in liquid media that accounts for the qf-Ps state as formulated in Section 3. The integrity of the fitting equations added into the program was additionally verified by means of Wolfram Mathematica computing system. Parameters P_{Ps}, $\lambda_{qf} = \lambda_+$, λ_{po}, k_{opc}, k_{ox} are set as free during the fit. The rate constant of Ps bubble formation λ_b is fixed to 20 ns^{-1} to be in agreement with the AMOC data [16, 17].

Table 3. Parameters of the model Eqs. (5-10) obtained as a result of fitting of the LT spectra of liquids with different O_2 contents, $\lambda_{qf} = \lambda_+$, $\lambda_b = 20$ ns^{-1}, $\lambda_{2\gamma} = 1/0.16$ ns^{-1} (in accordance with the magnetic quenching experiments [12, 13]). Statistical uncertainties of the fitting parameters are indicated in parenthesis.

Liquid	$\lambda_+ = \lambda_{qf}$; $\tau_+ = 1/\lambda_+$ ns^{-1} ; ns		λ_{po} ; $\tau_{po} = 1/\lambda_{po}$ ns^{-1} ; ns		P_{qf}	k_{opc}, M^{-1}s^{-1}	k_{ox}, M^{-1}s^{-1}	$k_{opc}/4 + k_{ox}$, M^{-1}s^{-1}
Isooctane	2.430(1)	0.412(1)	0.252(1)	3.968(4)	0.639(2)	$9.62(9) \cdot 10^{10}$	$2.37(3) \cdot 10^{10}$	$4.78(5) \cdot 10^{10}$
Cyclohexane	2.568(2)	0.389(1)	0.320(3)	3.125(10)	0.542(1)	$12.6(2) \cdot 10^{10}$	$1.02(4) \cdot 10^{10}$	$4.17(5) \cdot 10^{10}$
Isopropanol	2.509(1)	0.399(1)	0.276(2)	3.622(10)	0.340(2)	$9.8(1) \cdot 10^{10}$	$0.35(5) \cdot 10^{10}$	$2.82(5) \cdot 10^{10}$
Water	2.516(8)	0.397(4)	0.556(1)	1.799(2)	0.451(3)	$1(1) \cdot 10^{10}$	$1.1(4) \cdot 10^{10}$	$1.3(8) \cdot 10^{10}$

All experimental spectra were analyzed and fitted by the proposed model. The obtained parameters including values of the Ps spin-conversion rate constant (ortho-Ps ⇔ para-Ps) and Ps oxidation rate constant (Ps + O_2 ⇒ e$^+$ + O_2^-) are given in Table 3. Oxidation of the Ps atom turned out to be about 5-10 times less favorable process. In conventional three-exponential deconvolution of the spectra, the Ps-O_2 interaction manifests only in a variation of only one parameter – the o-Ps annihilation rate λ_o vs. O_2 concentration. It does not allow to distinguish between conversion and oxidation.
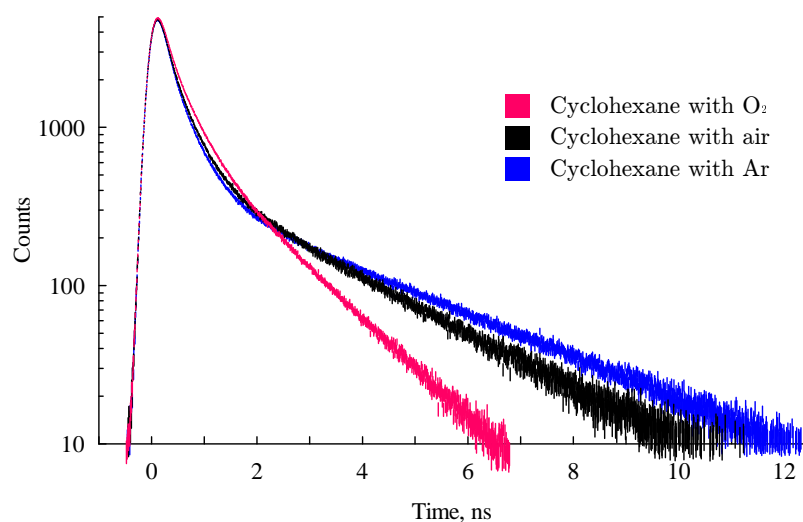

Figure 5. The effect of the presence of O_2 on the shape of lifetime annihilation spectra in cyclohexane. Blue – blowing argon, black – blowing with air, red – blowing oxygen. Source contribution and background are subtracted from the spectra. The spectra are normalized to 10^6 counts.

7. Conclusion

The interaction of the Ps atom with oxygen dissolved in liquid media is a rather complex problem. In fact it is a special case of a general problem of random walks of a particle and its acceptors when they can interact on a random distance [22]. The problem is even more complex because formation of Ps atoms in nano-bubbles does not happen at the same moment of time (say, $t = 0$). Instead every formation event happens to have a certain random time delay. These delays occur due to existence of a delocalized intermediate transient state of an e$^+$-e$^-$ pair named quasi-free positronium (qf-Ps). The localization event of qf-Ps is preceded by a process of seeking for a suitable preexisting trap in the solvent. This aspect is studied in current paper.

Following the spin statistics, it has long been thought that the formation of the ortho- and para-states of Ps should strictly result in the ratio $I_1/I_3 = 1/3$. However, by taking into account the existence of the qf-Ps, as a precursor of the ensuing bubble state of Ps, we were able to explain the anomalously high ratio for I_1/I_3 (at 1/2 or more) as it is usually found through conventional analysis of the LT spectra into 3 decaying exponential components. Moreover, the proposed model, which takes into account formation of qf-Ps naturally explains the extremal behavior of the $S(t)$ parameter (juvenile broadening) observed in AMOC experiments.

The presence of oxygen does not affect the lifetime of "free" positrons, $\tau_+ = 1/\lambda_+$. It is mostly determined by the structure of the solvated state e$^+$ and the average electron density of the solvent.

A new open-source program RooPositron that fits lifetime annihilation spectra is developed [29]. The software supports integration of custom fitting models. A model derived from Eqs. (5-10) is integrated into the new program as a fitting function. By contrast with the conventional multiexponential deconvolution, the new fitting model parameters represent values with real physical meaning (such as Ps reaction rate constants, annihilation rate constants of the various positron states, probability of qf-Ps formation, localization rate of qf-Ps in a nanobubble). Application of the RooPositron program revealed the ortho-para-conversion of Ps atom to be a dominant process of the interaction between Ps atom and dissolved oxygen. Oxidation of the Ps

atom turned out to be about 5-10 times less favorable. In conventional three-exponential analysis it is not possible to distinguish between conversion and oxidation.

Spectra of water with dissolved oxygen show almost no difference in shape and fitting parameters with respect to pure water spectra. This is explained by a very low solubility of O_2 molecules. Therefore pure water is often used as a "reference" medium for testing the operation of the lifetime positron spectrometers.

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