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**Multicomponent Positron Lifetime Spectra
in Simple Molecular Media**

INTRODUCTION

The positron entering a molecular medium (crystal, polymer, liquid) is slowed down up to thermalization and, at the end of its path, annihilates in one of three possible ways: 1) as a free particle, in collisions, 2) from the short-lived singlet bound state — para-positronium, p-Ps, 3) from the triplet bound state — ortho-Ps. Thus, when processing the positron lifetime spectra one usually assumes the existence of three exponential components, each for one of above-listed ways of annihilation. While ascribing a single decay time for free annihilation seems obviously justified, the assumption of one component for the o-Ps decay is in many cases an oversimplification. It was observed very early that the lifetime spectrum in polymers contains four components and also in some crystalline media one can distinguish more than one component belonging to ortho-positronium. Classic examples were given by Eldrup *et al.* [1,2]: in the orientationally disordered crystals one observes ortho-Ps in the bulk, but also ortho-Ps trapped in vacancies, forming separate components. One can imagine the case, when there is more than one kind of o-Ps trapping centers; having a spectrum of defects we should observe a spectrum of exponentials (unless the dwelling time in a defect is shorter than mean o-Ps lifetime). Essentially all that could be said also about the p-Ps if it is of multielectronic nature [3] and effective electron density is different for various positronium locations before annihilation [4]. However, the p-Ps lifetimes can be determined with so poor accuracy that splitting the shortest component into several subcomponents is far outside the experimental possibilities. Thus, an average p-Ps lifetime has to be assumed.

In the paper below we give new examples of molecular media in which more than one o-Ps component in the lifetime spectrum is observed.

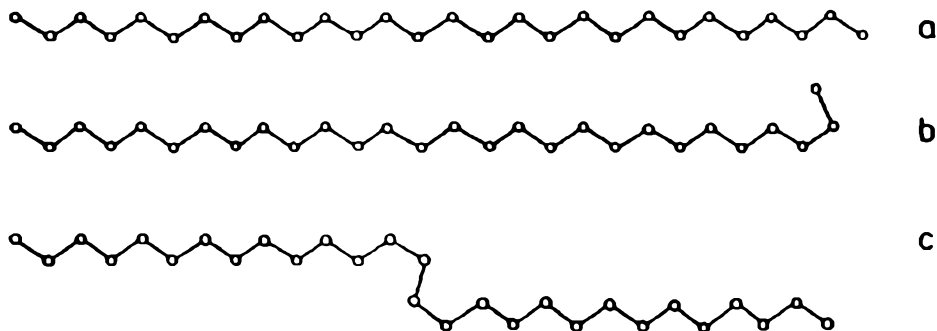


Fig. 1. Intramolecular defects in long chain paraffins: a) undistorted molecule, b) end-gauche defect, c) kink defect.

PARAFFINS

Two lifetime components belonging to the annihilation of o-Ps were found in solid phases of long chain hydrocarbons (paraffins) and their derivatives. With the increase of the temperature they undergo a series of solid-solid phase transitions; last such a transition occurs several K below the melting point and in that narrow range of temperatures so-called rotator phase (waxy phase) appears. The interest in rotator phase properties studied by positron annihilation was first shown in the papers by Lenc and by us [5-7]; the object of study were the long chain *n*-alkanols. First detailed positron investigation of long chain alkanes $C_{32}H_{66}$ and $C_{33}H_{68}$ was performed by Levay, Lalović and Ache [8], but these authors analysed their spectra in a simplified way, decomposing them into two exponentials, thus the spectrum structure discussed below could not be noticed.

Our measurements of lifetime spectra were performed using a standard fast-slow coincidence spectrometer with a digital peak stabilizer. One of two counters was BaF_2 , the other NE111. The sample with submerged positron source in a kapton envelope was placed in a copper container inside the vacuum chamber. Degassing the sample was necessary because the measurement covered the temperature range above the melting point too (the oxygen dissolved in the sample strongly reduces the o-Ps lifetime due to the conversion process and the lifetime in liquid paraffins becomes shorter than that in preceding solid phase). Vacuum chamber construction allowed the 180° geometry only, but it was assumed that the copper container and chamber walls reduce sufficiently the summing with backscattered quanta, moreover, the object of present study were the long-lived components only, with $\tau_i \geq 1.3$ ns, which should be practically insensitive to the summing effects. The lifetime spectra were analysed using the POSITRONFIT program.

The object of our study was *n*-octacosane, $C_{28}H_{58}$. Like in other paraffins, the positronium exists in all solid phases of that compound. The classic 3-component analysis shows in low temperature phases the o-Ps component of averaged lifetime ~ 1.4 ns, and it can be certainly debatable whether it belongs to the positronium in the bulk or to that trapped in small irregularities of the surface of intermolecular

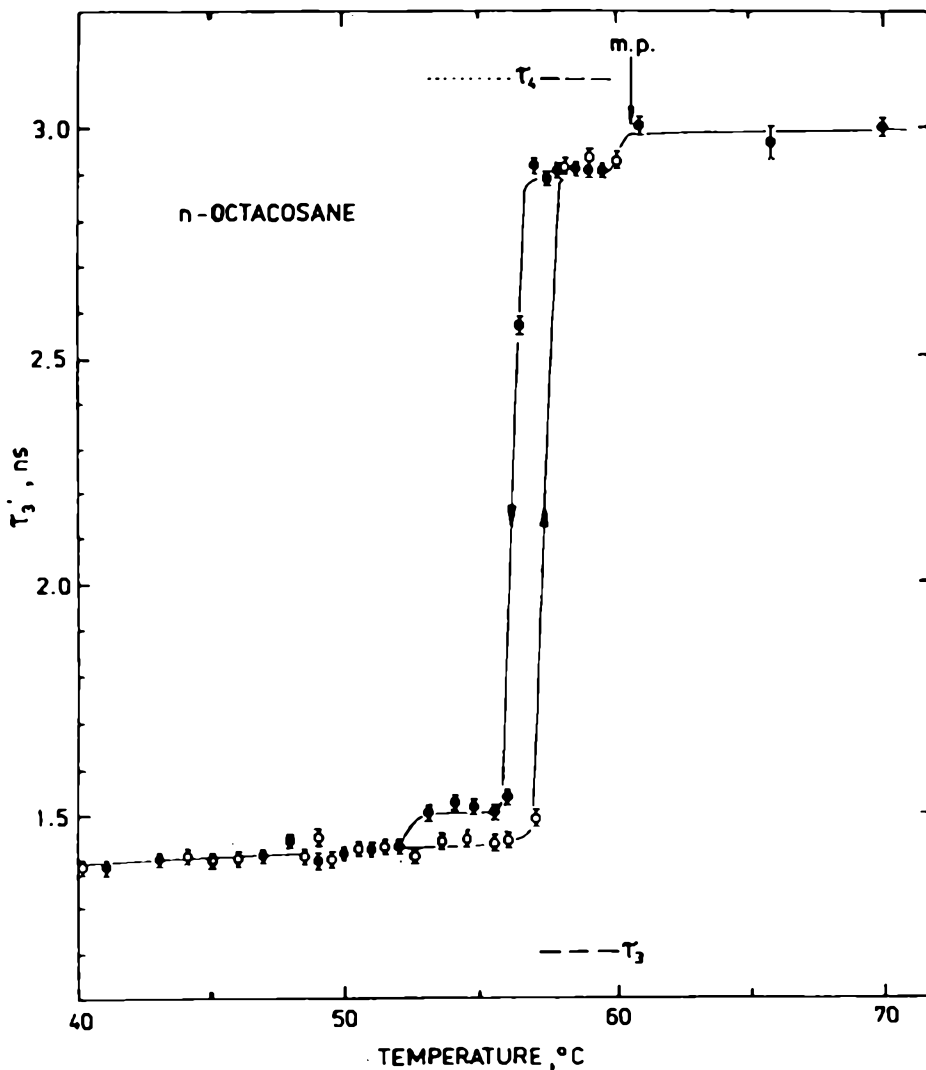


Fig. 2. Long-lived component lifetime τ_3' as a function of temperature (three component fit). The values of τ_3' and τ_3' from four component fit are also shown

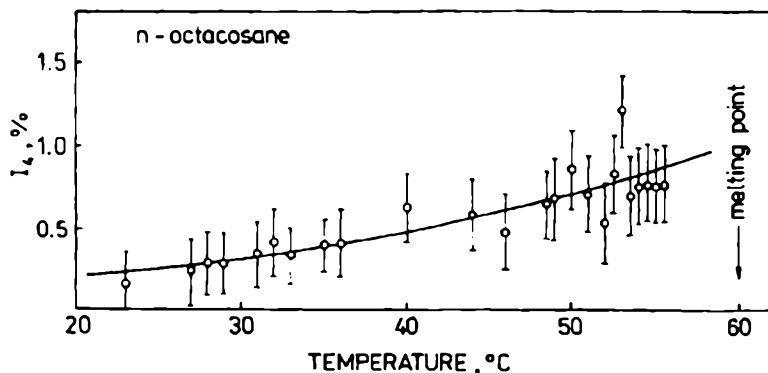


Fig. 3. Intensity of fourth component in the rigid phase. The curve represents $\exp(-H/kT)$ fitted to experimental data

layers (the molecules can have a certain degree of longitudinal motion). On the rotator phase the lifetime drastically increases up to ~ 3 ns. Using the Eldrup model [2] one can estimate that the transition from rigid to the rotator phase increases the volume of trapping center by $\sim 160 \text{ \AA}^3$ (i.e. to 210 \AA^3). That should be assumed as the lower limit only, because for the elongated cylinder-shaped voids (as we expect in this case) the lifetime rises slower with the void volume than in spherical case discussed in Eldrup's paper [7]. Molecular volume per unit of carbon chain is $(25\text{--}28) \text{ \AA}^3$ [8], thus the defects dominating in the rotator phase should be larger than 7–8 segments of the chain. Such large defects can be vacancies or free volumes near the intramolecular defects in the form of kinks in the molecular chain (Fig. 1). The typical concentration of vacancies near the melting point is of the order of 1%, while in the rotator phase of C_{28} alkane about 70% of molecules are kinked conformers [9], thus the vicinities of distorted molecules represent preferably these large free volumes responsible for the longest observed o-Ps lifetime. The lifetime of o-Ps in low temperature phases corresponds to the free volume equivalent to about two carbon chain segments.

It was found that in the rotator phase as well as in certain range of temperatures in the rigid phases two long-lived components appear simultaneously. In the rotator phase the dominant component is the longest lived one, 3.2 ns, but there is also an admixture of 1.2 ns component, slightly shorter than that typical for low temperatures. In the range $53\text{--}56^\circ\text{C}$, just below the rotator phase, the four component fit has shown that the longest lived component still exists, with the intensity up to 1.5%. Its lifetime, determined for very high statistics spectrum obtained by summing all the spectra in that range, was found exactly the same as in rotator phase, indicating the same nature of large o-Ps trapping centers. Thus the lifetime of fourth component was fixed during processing the data on the temperature dependence of positron spectrum.

In the classic three component analysis one observes a stepwise decrease of τ_3 ("average lifetime" of o-Ps) at 53°C when the temperature is lowered, but

such a step is not observed when the sample temperature increases (Fig. 2). Four component analysis indicates that there is no new lifetime (no new kind of defects), but comparing with the temperatures below 53°C the intensity of longest lived component is increased and amounts $\sim 1.5\%$. The lifetimes of two o-Ps components in the range 53–56°C are exactly the same as in neighbouring phases: τ_3 is like that below 53°C, τ_4 — like in rotator phase. It is known [10] that the region 53–56°C corresponds to the rotator phase R_3 . Octacosane is the only even long chain alkane in which two rotator phases can exist, the phase R_3 is in this case not stable and can be obtained as a supercooled only. The intensity of fourth component is low, it means that the large defects are present in that phase too, but in considerably lower concentration than in the normal R_4 phase, or the supercooled phase exists in a small part of sample only.

The lifetime τ_4 is the longest lived one in the whole spectrum, thus that component, visible at the end of the spectrum, is relatively easy recognizable even in the case of very low intensity. It was found that below 53°C the intensity I_4 is not zero; its value decreases gradually from about 0.7% at high temperature end to the value comparable to the experimental error below the room temperature. Thus it was possible to make the Arrhenius plot through the experimental points in that range and to estimate the formation enthalpy of big defects in the rigid phase (Fig. 3). This enthalpy was found (0.34 ± 0.05) eV, while the sublimation heat L , for *n*-octacosane exceeds 1.5 eV. This is a direct indication that our Ps trapping defects cannot be vacancies, and the enthalpy 0.34 eV relates to the activation of intramolecular defects of "kink" type in the rigid phase.

BIPHENYL

More than one long-lived component was also found in the positron lifetime spectrum of biphenyl. The measurements were performed for room temperature only. In that case the three component fit shows the longest lived component of ~ 1.1 ns, thus if four components are needed to describe the spectrum, all exponentials are tightly packed in a narrow range of time. To perform more careful analysis we needed high statistics, good resolution of the spectrometer and perfectly linear time to amplitude conversion. To avoid the backscattering and summing effects the measurements were performed in "triangular" geometry, i.e. with two BaF_2 scintillators placed face-to-face, but with the source-sample sandwich moved out from the slit between the counters. The resolution was about 220 ps (FWHM), a correction for nonlinearity was also applied. The spectrum containing 6.6×10^5 coincidences (Fig. 4) was collected in the range of 990 channels of the width 16.2 ps. Within our computing possibilities it was possible to determine the instrumental ("prompt") curve approximated by 3 gaussians for the spectrum containing 4 components (3 for the sample, one for the source, this last fixed) if the number of channels processed by the RESOLUTION program [11] was limited to 690 only. The prompt curve determined this way was then used for more detailed analysis of the spectrum using the POSITRONFIT EXTENDED program [11].

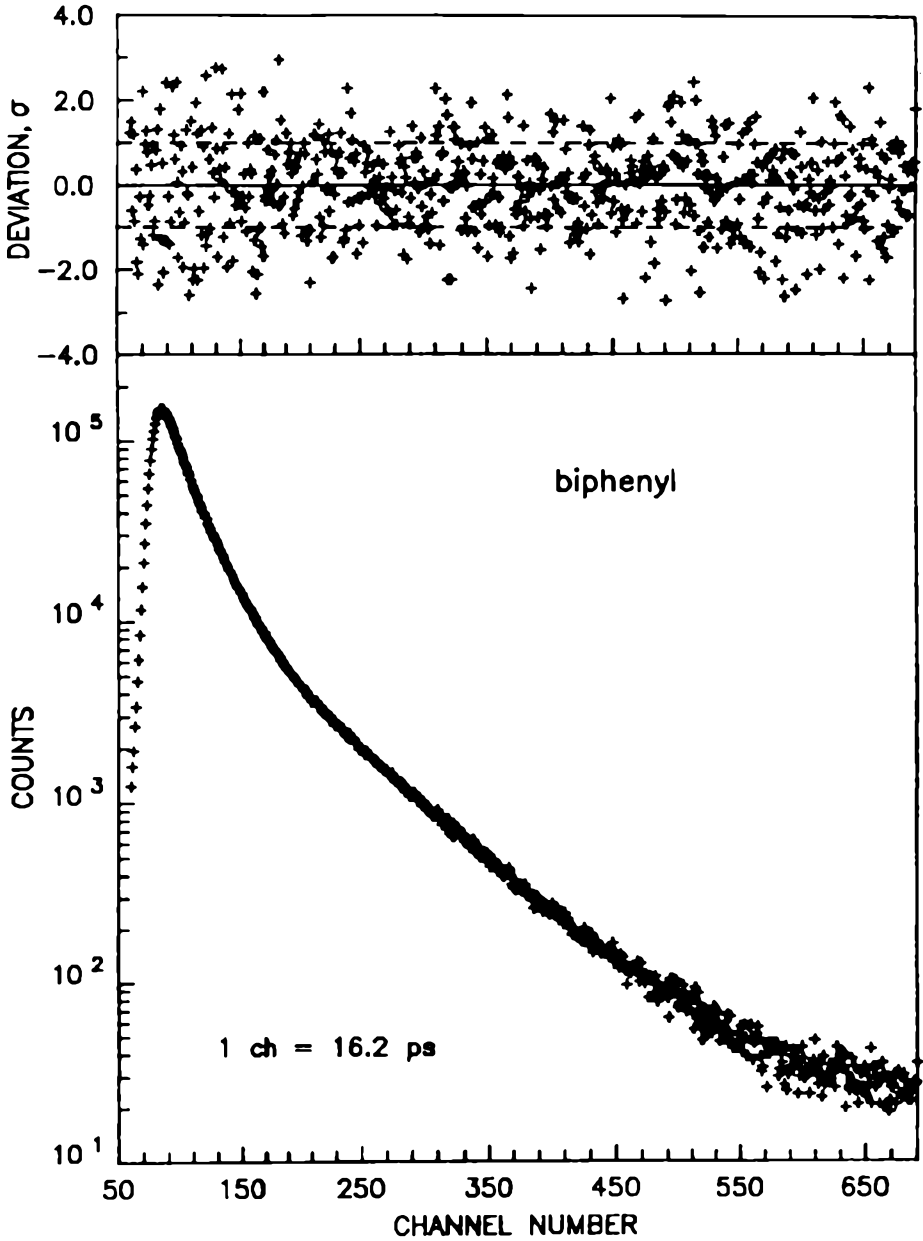


Fig. 4. Positron lifetime spectrum in biphenyl at room temperature. The normalized residuals are shown at the top of figure

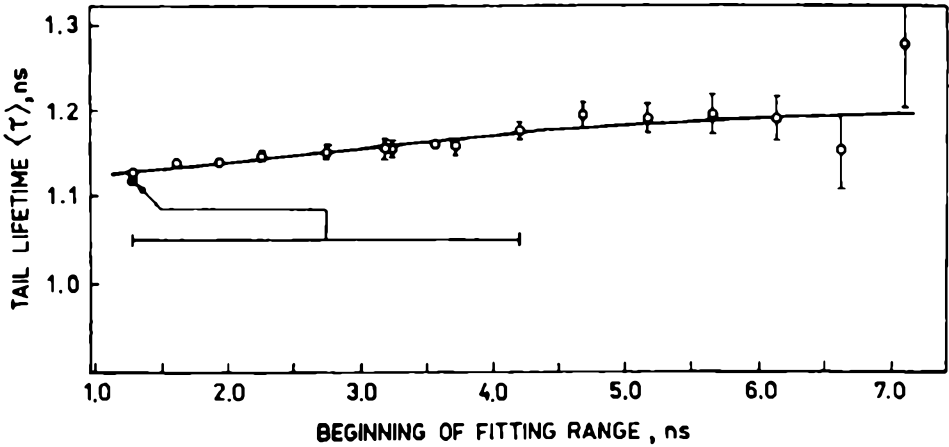


Fig. 5. Average lifetime fitted to the tail of spectrum as a function of initial point of fitting range (open symbols). Full dot represents the lifetime fitted in limited range of time shown by the horizontal bar

Table 1. Four component fit to the positron lifetime spectrum in biphenyl

Rel. intensity constrain	τ_1 [ps]	I_1 [%]	τ_2 [ps]	I_2 [%]
no	159 ± 15	11.4 ± 2.9	327 ± 10	60.3 ± 1.9
yes	152 ± 6	9.9 ± 0.6	320 ± 3	60.5 ± 2.3
Rel. intensity constrain	τ_3 [ps]	I_3 [%]	τ_4 [ps]	I_4 [%]
no	854 ± 94	8.7 ± 0.6	1205 FIX	19.7 ± 1.2
yes	714 ± 213	7.0 ± 2.7	1181 ± 42	22.6 ± 4.1
Rel. intensity constrain	$(I_3 + I_4)/I_1$			
no	2.50 ± 0.65			
yes	3 FIX			

The longest lived component, ~ 1.1 ns, is practically insensitive to the details of prompt curve shape, thus, first we analysed the tail of distribution only, from 1.3 ns above the zero time. It was found that average lifetime $\langle \tau \rangle$ fitted to that tail changes systematically from 1.127 ns to 1.195 ns with moving the beginning of fitting range from 1.3 to 4.7 ns (Fig. 5). It means that we have in fact more than one long-lived component. Positronium in biphenyl is formed in thermally produced defects [12], in free volumes smaller than these of vacancies; it cannot be excluded that there is a distribution of the sizes of these free volumes leading in consequence to the distribution of lifetimes.

The analysis of the tail of time spectrum from 160th channel (1.3 ns past time zero) to 990th channel shows that it is possible to distinguish two long-lived components. The longest lived one, $\tau_4 = (1205 \pm 38)$ ps, was then fixed and the spectrum from the beginning up to 690th channel was analysed by POSITRONFIT EXTENDED, assuming four components. The source correction was 10%, 374 ps. The results are shown in Table 1. The ratio of intensities $(I_3 + I_4)/I_1$ was found

2.50 ± 0.65 , thus it contains in the limits of error the value 3, expected on the basis of statistical character of Ps substates formation. One can expect, that introducing the constraint on the mentioned ration, $(I_3 + I_4) = 3I_1$, and making τ_4 free we should get the parameters not strongly deviating from previously obtained ones. The result is shown in the second row of Table 1. Note good reproduction of intensities I_3 , I_4 and also of respective lifetimes. It cannot be eluded that we have a continuous spectrum of ortho-positronic components in biphenyl and the two component split is a first approximation only. Remeasuring the lifetime spectra for other organic crystals with the aim of search of multicomponent structure is then advisable.

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