Electron traps in long-chain alkanes

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Abstract. Positron lifetime spectra in long-chain alkanes were measured at various wavelengths of light illuminating the samples as a function of temperature, storage time. It was found that in *n*-alkanes with carbon chain longer than 30 atoms two kinds of electron traps exist; the depth of shallower of them is less than 0.52 eV. They are discharged already at a temperature of 120 K.

Key words: PALS • positron annihilation • electron traps • quenching by light

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Introduction

About 20 years ago it was observed for the first time that Ps formation intensity I_3 rises during the measurement (i.e. during irradiation of a sample by positrons). This effect was observed in many polymers, like PMMA [8, 14] or polystyrene [15] and also in simple molecular crystals, like cyclohexane [7] or *n*-alkanes [2]. The rise of Ps intensity was explained by Hirade *et al.* [4] as a result of additional Ps formation by quasi-free positron with an excess electron produced in previous ionization events, which is trapped in the medium structure. This mechanism of Ps formation was proved by these authors in several ways [3]:
– appearance of this effect at sample irradiation by a strong external gamma source,
– correlation of I_3 increase and the density of trapped electrons determined by EPR spectroscopy,
– elimination of the effect by sample illumination.
  Thus, the total amount of positronium observed in PALS spectra is formed in two ways: by combination of an electron-positron pair at the end of positron ionization track ("blob" component [11]), or by a positron diffusing through the medium and picking an excess electron trapped in a shallow trap in the medium. The first component is formed in a short time scale (time of blob existence), the other is delayed by the time of e$^+$ diffusion to the trapped electron, confirmed by AMOC measurements [12].
  The accumulation of excess electrons in the traps and their removal by light are well known and studied by classic methods [1, 10]. Among others, it was found that in polymers there is a certain set of various traps,

differing in depth. In the case of PALS technique, the *ortho*-Ps (*o*-Ps) component quenching by light was often applied, but so far, peculiar attention was not paid to the role of wavelength. It is known that the light of a xenon lamp, or even of an ordinary incandescent lamp is sufficient to eliminate the discussed surplus of Ps intensity.

In this paper we present our results concerning the influence of the light of various wavelengths on positronium annihilation process in selected long-chain alkanes at various temperatures.

Experimental

The samples of hydrocarbons were from Sigma-Aldrich and Fluka, with a nominal purity of over 99%. The radioactive source of ^{22}Na (0.3 MBq) in a Kapton envelope was fixed in the centre of a small copper chamber and surrounded by the molten sample of alkane. To avoid *ortho-para* conversion by dissolved oxygen [9] each sample in liquid form was degassed several times by a freeze-thaw method. The temperature of the sample was controlled with an accuracy of 0.1 K by a computer--coupled controller. Required value of temperature was obtained by a combination of a heating coil and a cold finger immersed in liquid nitrogen. At the top of the chamber, one could place two LEDs illuminating the sample on both sides of the source holder. Their optical power could be changed by regulating the diode current. The dependence of optical power on diode current was measured using an OP100P light-to-voltage converter; the result is shown in Fig. 1.

The positron lifetime spectra were registered by a fast--slow delayed coincidence spectrometer with a time resolution of 250 ps FWHM. The spectra were decomposed by LT program [5] into four exponential components (decays of *para*-Ps (*p*-Ps), *o*-Ps, unbound positron and positron annihilation in the Kapton source envelope).

Results and discussion

The majority of measurements presented in this paper was performed with *n*-hexatriacontane $C_{36}H_{74}$ (for shortness we will write *Cn* instead of C_nH_{2n+2}).
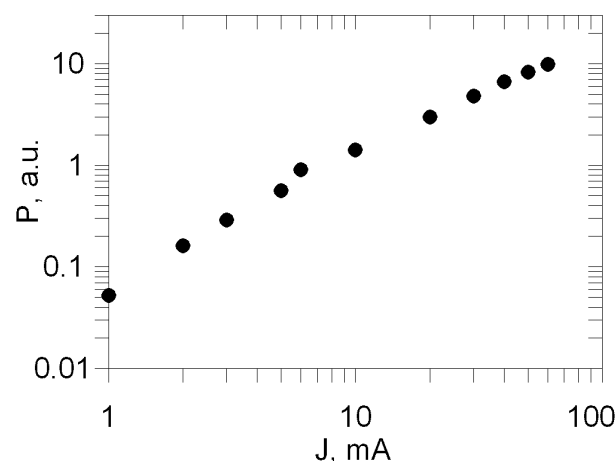

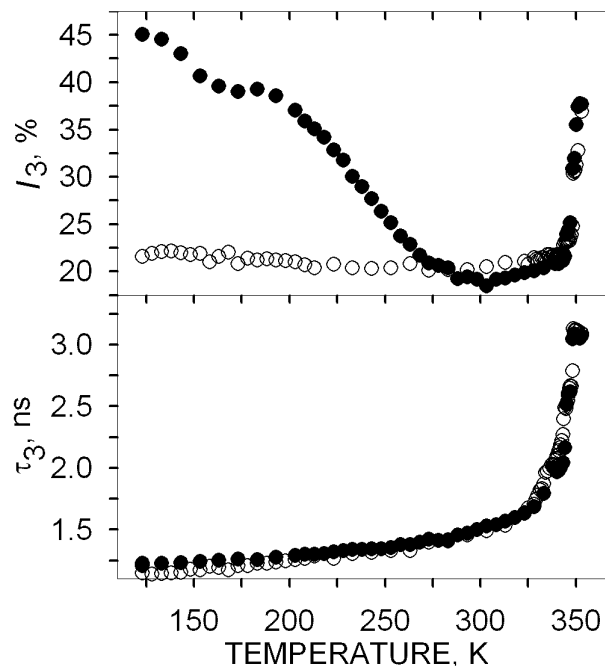**Fig. 1.** The dependence of optical power of 0.95 μm LED as a function of applied current.

Fig. 2. The intensity and lifetime of *o*-Ps vs. temperature in C36. Open circles – with sample illumination by LEDs with $\lambda_{max} = 0.95$ μm, full circles – without illumination.

The molten C36 sample was cooled at a rate of 6 K/min down to 123 K, and then the sample was stored for about 20 h until the positronium intensity approached the saturation value. Then, the temperature was increased by steps and the PALS spectra were recorded (1 h per spectrum). Such a cycle of measurements was repeated twice: with sample illumination by LEDs of $\lambda_{max} = 0.95$ μm and in the darkness (LEDs off). The *o*-Ps intensity I_3 and its lifetime τ_3 as a function of temperature is shown in Fig. 2. It is seen that I_3 in the illuminated samples is much smaller than in the darkness and equal to that observed immediately after sample cooling from the melt, i.e. before accumulation of trapped electrons. This means that near infrared radiation it is sufficient to remove the electrons from the traps (it could be expected, as the removal of trapped electrons by IR radiation > 1.0 μm was observed long time ago by ESR spectroscopy in hydrocarbon polymers [6]).

The trapped electrons are released by light, but at the same time the traps are loaded by next electrons, delivered due to continuous positron irradiation. The *o*-Ps intensity at low IR flux is determined by the balance of these two processes. Effectiveness of *o*-Ps quenching by light was checked by changing the diode optical power. The result for the wavelength $\lambda_{max} = 0.95$ μm is shown in Fig. 3. The higher is the optical power the lower is the final I_3 intensity. At sufficiently high illumination, re-loading the traps by newly delivered excess electrons can be neglected and I_3 corresponds practically to the blob component of positronium only. This condition is fulfilled already at LED current 50 mA or more. The data shown in Fig. 2 were collected at such high optical power. Generally, the intensity of "blob component" in various alkanes is weakly temperature dependent and amounts to about 20–23%.

As it is seen in Fig. 2, the I_3 (*T*) dependence taken without sample illumination shows two steps of de-
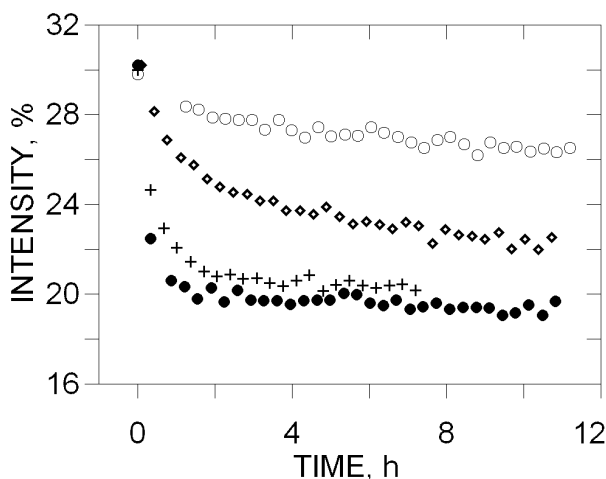
Fig. 3. Quenching the intensity of o-Ps in C36 at 173 K by the light 0.95 μm for several values of LED current. Open circles – 1 mA, diamonds – 4 mA, crosses – 20 mA, full circles – 100 mA. Zero of time scale corresponds to switching on LEDs after sample storage in the darkness.

crease; a small reduction of intensity occurs in the lowest temperature region (≈ 150 K), then after a short plateau the intensity I_3 begins to decrease considerably. Above 283 K there is no difference in intensity at light and in the darkness; the electron traps are empty. The step on I_3 (T) curve near 150 K is not visible in the spectra taken at sample illumination. In that temperature region we do not observe also any substantial τ_3 variation, thus there are no changes in the sample structure (e.g. change of free volume size) so I_3 decrease is related to detrapped electrons.

One can suppose that in the case of C36 there are two kinds of traps for electrons. One kind of traps is emptied by increasing the temperature to the value 150 K. We will call them "B-traps". From the value 200 K upwards, remaining traps, of the second type (referred here to as A-traps), are successively emptied by increasing the temperature.

One can try to estimate the depth of traps by changing the wavelength of the illuminating LEDs. The C36
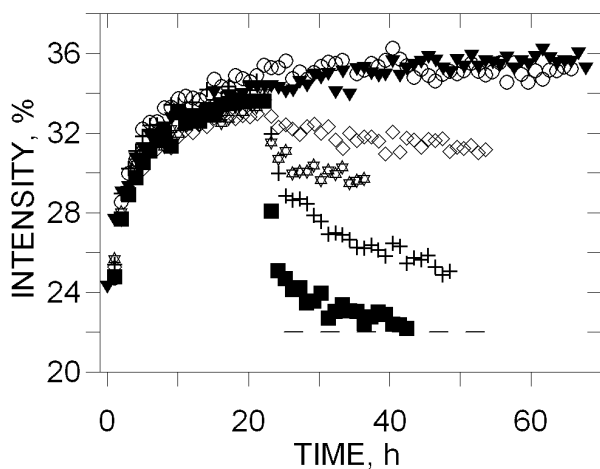
sample was cooled from the melt to 203 K, kept to reaching the saturation value of intensity I_3, and then the light was switched on and the measurements of PALS spectra were continued. This procedure was repeated for a set of diodes. The results are shown in Fig. 4. It is seen that the intensity is not sensitive to the illumination by 1.8 μm and 2.2 μm diodes (wavelength values given here relate to the maximum of their optical spectrum λ_{max}). Full elimination of trapped electrons (i.e. reaching the I_3 level $\approx 22\%$, typical for "blob" origin) occurs when the LEDs of $\lambda_{max} = 1.05$ μm, or shorter, are used, thus one can estimate roughly the depth of A-traps as ≈ 1.2 eV. The LEDs do not produce the monochromatic radiation; the emitted spectrum is continuous in a certain range of wavelengths, resembling the Gaussian distribution with a half-width of about 60 nm for 0.95 μm LED, or 250 nm for 1.8 μm one. A certain small decrease of I_3 intensity can be seen already at the illumination by $\lambda_{max} = 1.55$ μm. There are two possibilities of explanation of the observed small effect. The tail of wavelength distribution emitted by 1.55 μm LED is still non-zero at ≈ 1.1 μm and at very low optical power in this range of wavelength the reduction of intensity is small but measurable (see Fig. 3; reduction of I_3 at unchanged wavelength, but low power). However, the width of spectrum of 1.55 μm diode seems to be not so broad to induce trapped electron release from the traps 1.2 eV deep. The other possibility is that A-trap depths represent the spectrum continuous in a certain range (or a set of close lying states) reaching up to 0.8 eV.

Analogous experiment was repeated at a temperature of 123 K, where the existence of two kinds of traps is expected. The C36 samples were kept in the darkness for 22 h and then the LEDs with $\lambda_{max} = 1.8$ μm or 2.2 μm were switched on. The result is shown in Fig. 5. In this case the intensity I_3 was reduced by light very rapidly to a certain level only, much higher than expected at total emptying the electron traps ($I_3 \approx 20\%$). Final intensity using both types of LED was the same, but much higher than the level of "blob" component. This partial I_3 reduction is not due to insufficient LED optical power, as increasing the diode current by a factor of two does not introduce any further reduction of intensity. This means
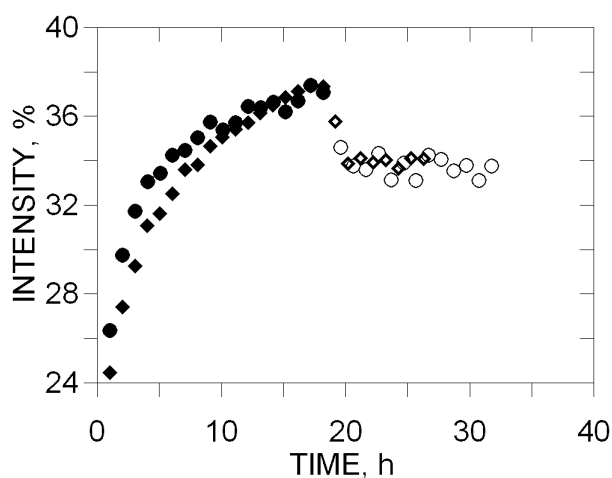

Fig. 4. Quenching the o-Ps intensity in C36 at 203 K at different wavelengths: open circles – 2.2 μm, triangles – 1.8 μm, diamonds – 1.55 μm, stars – 1.3 μm, crosses – 1.2 μm, squares – 1.05 μm. Diodes switched on after 22 h. Dashed line indicates the intensity level expected when the "blob component" only is present.

Fig. 5. Quenching the o-Ps intensity in C36 at 123 K. Open symbols denote the measurements with LEDs switched on: circles – $\lambda_{max} = 1.8$ μm, diamonds – $\lambda_{max} = 2.2$ μm, full symbols – storage in the darkness.
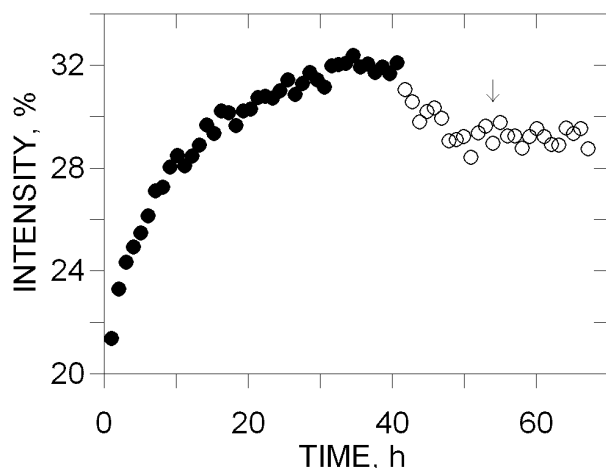
Fig. 6. Quenching the *o*-Ps intensity in C34 at 123 K by λ_{max} = 2.2 μm radiation. Open symbols mean the measurements with light on. The arrow denotes the beginning of measurements with the LED current increased twice.

that $\lambda > 1.8$ μm eliminates electrons from B-traps only. The depth of B-traps has to be less than 0.52 eV. At a temperature of 200 K, these traps are empty (or even destroyed).

Similar measurements with long-wave LEDs were performed using as a sample the neighbouring even *n*-alkane, C34. In this case the dependence of I_3 on temperature near 150 K in the darkness does not show any step similar to that in C36 (Fig. 2). Nevertheless, as it is seen in Fig. 6, at 123 K the 2.2 μm light acts on the trapped electrons in a similar way as in the case of C36. When temperature is set at 233 K, one cannot observe the influence of those quanta of light on the *o*-Ps intensity (Fig. 7); in full analogy to the case of C36 (the temperature 233 K in C34 and 203 K in C36 lie in the same region of I_3 (*T*) dependence, where we expect the existence of A-traps only). It means that the B-traps in this alkane exist too, although their presence is not so well pronounced in I_3 (*T*) dependence.

Next series of measurements was performed with C24 sample. At a temperature of 123 K, the sample was stored for 20 h and then illuminated by the LED λ_{max} = 1.8 μm. No change of I_3 intensity is observed, thus there are no B-traps in C24.

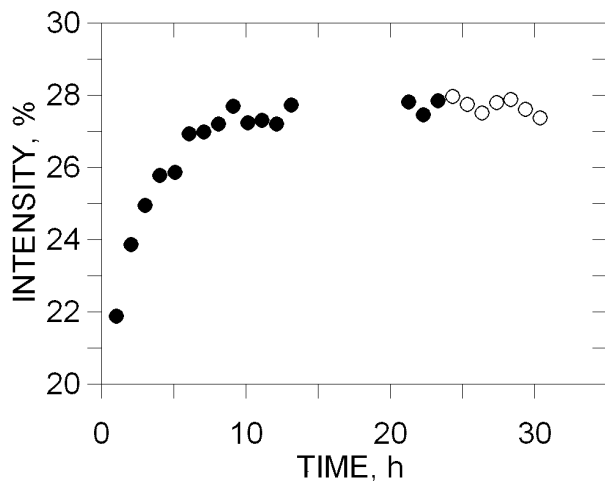**Fig. 7.** Quenching the *o*-Ps intensity in C34 at 233 K by 2.2 μm radiation. Open symbols mean the measurements with light on, full circles – in the darkness.

Conclusions

We have shown that in even *n*-alkanes with the carbon chain longer than $n = 32$ there are two kinds of electron traps. The depth of shallower traps is less than 0.52 eV. Determination of the depth (i.e. of the threshold of wavelength sufficient for electron release) was not possible due to the lack of LEDs of adequate optical power in the region of $\lambda > 2.5$ μm.

The nature of B-traps is unknown to us. Positronium locates in the interlamellar gaps [2, 16], which are identical for all alkanes and it should not feel the molecular lamella interior.

Molecular motions releasing electrons from the traps are reflected in the IR spectra of alkane molecules, which are rather similar to each other. Appearance of new traps should be related to a new kind of molecular motion distinctly different from that emptying the A-traps. May be it is due to the presence of various conformers, whose number and geometric form rise rapidly with *n* even at low temperature, or due to the change of crystalline structure which occurs in the homologous series at $n = 26$ (monoclinic-triclinic) [13]. It cannot be excluded that B-traps depth vary with *n* and can avoid detection if, say, approaches the depth of A with decreasing the chain length.

Thus, to gain more information about shallowest traps, it is advisable to perform similar experiments for broader set of homologues and to compare the results with analogous ones for odd-numbered alkanes (not studied from this point of view yet). More data can be obtained applying the monochromatic light, in particular with $\lambda > 2.5$ μm, instead of LEDs.

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