Positronium Formation with Trapped Electrons in \( n \)-Alkanes

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(Received March 17, 2010; in final form December 5, 2010)

Positronium (Ps) formation during self-irradiation by positrons was observed in \( n \)-alkanes of various carbon chain length. The rise of Ps intensity with time of irradiation is the result of positronium formation with trapped excess electrons. In the range \( T < 190 \) K the saturation value of positronium intensity changes with temperature mainly due to the change of positron mobility. With the increase of the irradiation dose the process of charging traps is slowing down and this effect is ruled mainly by interaction of excess electrons with ionization products during electron’s migration to the traps.

PACS: 36.10.Dr, 36.20.Fz, 61.80.−x, 72.20.Jv, 78.70.Bj

1. Introduction

Positronium (Ps) formation in condensed matter consists in the capture of quasi-free electron by positron. In the case of high-energy positrons, e.g. from \( \beta^+ \) decay, this process can be described by the blob model [1, 2]. Positron combines with one of electrons from the cluster of ionization products (“blob”) at the end of its ionization track. However, positrons being slowed down produce free electrons along their whole ionization tracks. At low temperature, some of these electrons can be trapped in shallow traps in the solid, e.g. in intermolecular cavities. When the sample is continuously irradiated by positrons, the number of trapped electrons rises with time. If the Ps binding energy is higher than the trap depth, free positron has additionally a possibility to form positronium with one of trapped electrons. Depending on the carbon chain length, the electron trap depth in alkanes can be estimated as \( (1\pm3) \) eV [3], while Ps binding energy is 6.8 eV. Thus, excess electron trapping should lead to the rise of Ps intensity with irradiation time. This effect is well confirmed in the experiments with polymers [4, 5] and also with some crystalline media, like cyclohexane [6] or alkanes [7].

The total intensity of positronium consists of two components: one of blob origin, the other — related to electrons being picked up from the traps. This last one can be called “delayed component”, as diffusing positrons need time to migrate to randomly distributed occupied traps. Other processes, related to the presence of various ionization products in the sample irradiated by positrons also influence observed intensity of positronium. Trapped electrons can be thrown out from the traps by light, visible or near infrared, which restores the “zero dose level” of Ps formation probability. Although illumination is effective in emptying the electron traps, it has little effect on other post-ionization products.

The aim of this paper was to collect more data about the interaction of positrons with excess electrons, influence of temperature, irradiation time etc. Fragmentary data concerning this problem were published by us earlier [8].

2. Instrumental

As the media where positronium formation takes place we have chosen three \( n \)-alkanes: undecane \( C_{11}H_{24} \), heptadecane \( C_{17}H_{36} \) and tetraatriacontane \( C_{34}H_{70} \) (the longest carbon chain). At low temperature all these alkanes form rigid crystals, but in the range preceding the melting point by about 10 K they exhibit so-called rotator phase with orientational degree of freedom about long molecular axis. The samples of 90% purity were from Sigma-Aldrich, and we used them without any further refinement. The samples filled the container with positron source (0.3 MBq of \( ^{22} \)Na) fixed in the centre. Molten samples were degassed by freeze-thaw technique in order to avoid the ortho–para conversion in dissolved molecular oxygen. The sample was then attached to the cold finger with lower end submerged in liquid nitrogen. The chamber volume over the sample was evacuated to about 0.5 Pa. The sample temperature was regulated by heating coil placed just below the chamber. Two light emitting diodes placed inside the container could illuminate the sample when needed.

The positron annihilation lifetime spectra (PALS) were measured by a standard fast-slow delayed coincidence spectrometer with two scintillation heads; time resolution was about 250 ps FWHM. The collection time of one spectrum was 1 h (if not stated otherwise); such a spectrum contained typically \( 7 \times 10^5 \) to \( 10^6 \) coincident events. At that counting rate the dead time of spectrometer was negligible. The spectra were processed by the LT programme [9], assuming the appearance of three exponential components convoluted with the instrumental resolution curve. The shortest-lived component was ascribed to the decay of singlet para-Ps (p-Ps), the intermediate one — to the annihilation of unbound positrons and the longest-lived one to the decay of ortho-Ps (o-Ps). This last component, easily separable from the remainder of spectrum, was assumed to be a measure of positronium formation probability. If there is no participation of positronium in chemical reactions, the fraction

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(328)
of positrons forming Ps should be equal 4/3 of \( o \)-Ps intensity. For this reason at standard spectra processing described below the \( para \)-Ps to \( o \)-Ps ratio was fixed as 1:3 (the discussion how this constraint affects the results of fitting is given at the end of Sect. 3). A correction for positron absorption in the Kapton source envelope was also applied.

3. Results and discussion

Typical effects related to positron irradiation of the alkane sample are presented in Fig. 1 showing the time dependences of \( o \)-Ps intensity \( I_3 \) in heptadecane at 210 K. In darkness, the intensity rises with the time constant of several hours and then decreases slowly due to the interaction of excess electrons with radicals and other ionization products. Time constants of these processes depend on the source activity. Switching on the LEDs reduces the intensity to the level of Ps production in the blob. When the sample is illuminated from the beginning of measurements, a small decrease of \( o \)-Ps intensity \( I_3 \) with time is observed, which means that the reactions with post-ionization products have also an influence on the blob processes. It should be noted that lack of accumulation of trapped electrons is observed not only in liquids, but also in the rotator phase of \( n \)-alkanes.

Temperature dependence of \( I_3 \) saturation intensity was measured in \( n \)-heptadecane. The sample was cooled from the melt to 130 K and stored at that temperature for 15 h; then temperature was increased by steps. The time of spectra collection was set for 1 h and next the 0.95 µm LED diodes switched on, triangles — sample illuminated by LEDs from the beginning of irradiation. Temperature 210 K.

![Fig. 1. Variation of ortho-positronium formation intensity \( I_3 \) with irradiation time in \( n \)-heptadecane \( C_{17}H_{36} \). Open circles — in darkness, full circles — 68 h in darkness and next the 0.95 µm LED diodes switched on, triangles — sample illuminated by LEDs from the beginning of irradiation. Temperature 210 K.](image)

The rise of \( I_3 \) saturation value between 130 and 290 K can result from either an increase of trapped electron density or greater positron mobility facilitating its migration toward the occupied traps. In order to check the mechanism of \( I_3 \) rise, the sample of heptadecane was kept for 44 h at the temperature of 130 K and then the temperature was increased to 185 K; the sample was stored at that temperature for 11 h and returned stepwise to 130 K for 11 h and once more to 185 K. The result is shown in Fig. 3. It can be seen that sudden change of temperature is immediately followed by the change of intensity up to the value corresponding to new temperature; \( I_3 \) increase is the same as seen in Fig. 2 (in that figure the temperature increase lasted 8 h, while at the skips in Fig. 3 — less than 15 min). Charging the traps occurs in the time scale of several hours (here the time constant is about 7.5 h), while the intensities \( I_3 \) observed in the first spectrum after the skip were already the final ones, even after reduction of the spectrum registration time to 15 min. It means that the transition to new \( I_3 \) values was practically immediate and during 10 h after the increase of temperature the intensity \( I_3 \) remained constant. The heating time was too short to allow the trapped electron density to change, thus the results indicate that the change of \( I_3 \) is due to increased mobility of positrons with temperature.

Analogous measurements were done with \( n \)-tetraatriacontane (Fig. 4). The sample was cooled from the melt to 123 K, stored 28 h at that temperature up to reaching \( I_3 \) saturation (time constant \( \approx 8 \) h) and then the cycle of steps 123–173–123 K, like in previous case, was performed. Also in this case the intensity \( I_3 \) followed rapidly the changes of temperature. When the cycle of temperatures is repeated at slightly higher temperatures, 153–203–153 K one can notice a different behaviour of \( I_3 \).
with time: directly after the increase of temperature up to 203 K the intensity $I_3$ is high, but decreases with time (at 173 K it was stable in time). It means that trapped electron density, characteristic for 153 K, is too high for the temperature 203 K; partial emptying of traps already begins, $I_3$ decreases with time constant $\approx 3$ h to the equilibrium value. The change $\Delta I_3$ at the step 153–203 K is the same as $-\Delta I_3$ at reverse step. Now the trapped electron density is too low for equilibrium state and it should rise with time. It is seen in Fig. 4 that the rise is very slow. This is a common property of all alkanes we investigate here: time constant of trap loading rises with the time of irradiation. The effect is well visible in Fig. 5, where the measurements performed on a heptadecane sample at 130 K are shown. First 40 h of sample storage was the same as in Fig. 3, then after next 60 h the trapped electrons were removed by keeping the sample in the rotator phase, close to the melting point. The temperature was lowered again to 130 K and the lifetime spectra were collected during over 60 h. In the first run the time constant of $I_3$ rise was about 7.5 h, in the second one — 45 h. Moreover, the saturation intensity $I_{3\text{max}}$ which in the first run was 45%, in the second one the extrapolation of exponential curve fitted to the data, gives the intensity of about 37%.

Trapping of excess electrons does not affect the para-Ps lifetime, but changes the lifetime of free positrons $\tau_2$. The decay rate $\lambda_2$ is now

$$\lambda_2 = \frac{1}{\tau_2^0} + Kn,$$

where $\tau_2^0$ is the lifetime in absence of trapping, $n$ — the density of electrons in the traps, $K$ — the rate of positron capture by trapped electrons. Trapping leads to the shortening of free positron lifetime. One can see in Fig. 5 that the term $Kn$ was smaller for the sample irradiated during over 100 h than in the fresh one ($\tau_2$ is longer).

There is to note that annealing the sample in the rotator phase eliminates electrons from the traps, but not the post-ionization products (radicals, ions, etc.); full restoration of $I_3$ dependence on time occurs after the melting (diamonds in Fig. 4).

In all data processing procedures described above we assumed the para to ortho-Ps ratio as 1:3. In order to check whether such assumption affects the results, all spectra were processed once more without any constraint. The distribution width ($2\sigma$) of fitted $\tau_1$ values (para-Ps life-
The positronium behaviour in n-alkanes with various length of carbon chain (from 11 to 34 atoms) is very similar. The effect of electron trapping is best visible in the changes of o-Ps intensity, but also can be seen in time variations of free positron lifetime.

If the accumulation of ionization products disturbs the migration of positrons in the medium, one could expect the change of $\tau_2$ with time in irradiated and IR illuminated sample. Lack of such an effect can be an indication that positron capture is irradiation independent (in the limits of uncertainty). Localization of positrons, postulated by some authors [11] does not measurably modify the $\tau_2$ lifetime. Excess electrons produced along the ionization track are much more sensitive to the presence of irradiation products; they recombine with ions, react with radicals etc. Modification of PALS spectra with time is related mainly to the density of trapped electrons. The rise of $I_3$ saturation value with temperature in the range 130–190 K is due to increasing positron mobility; the decrease observed above 200 K is the result of thermal emptying the traps. In the correcting term in the expression for $\tau_2$ lifetime (Eq. (1)) the constant $K$ is ruled mainly by positrons, while $n$ — by trapped excess electrons.

Acknowledgments

Authors wish to thank Dr. Mark Pietrow for his participation in undecane measurements and Dr. Jan Wawryszczuk for his technical assistance.

References