Khulna University Studies Volume 10 (1&2) : 255-262 : June-December 2010

SCIENCE AND ENGINEERING

Copyright©Khulna University

THE ROLE OF THERMAL HISTORY ON POSITRONIUM FORMATION AT LOW TEMPERATURE STUDIED BY POSITRON ANNIHILATION LIFETIME SPECTROSCOPY

Farzana Nahid

Physics Discipline, Khulna University, Khulna 9208, Bangladesh

KUS: 10/08-230510

Manuscript received: May 23, 2010; Accepted: March 10, 2011

Abstract: Thermal history dependence of positronium formation at low temperature has been studied on high density polyethylene (HDPE) by positron annihilation lifetime spectroscopy (PALS). The study shows that the ortho-positronium formation at low temperature depends on both the temperature and thermal history. Two temperature studies of positron formation have been performed. The first study ortho-positronium (o-Ps) formation were measured at 20, 40, 60, 80, 120, 150 and 200 K. In the second one the same measurement was performed during heating through the same temperature after passing through a low temperature of 20 K. It has been found that the time saturated values of intensity (I_3) of o-Ps at each temperature after passing through 20 K were generally higher than that of obtained by direct cooling at the same temperature. This result has been explained on the basis of o-Ps formation mechanism and structural change of polymer with temperature.

Keywords: Positronium, Positron annihilation lifetime spectroscopy, Positronium formation, Ortho-positronium, High density polyethylene

Introduction

PALS enables one to measure the lifetimes and relative abundances or intensities of various positron state. The positronium (Ps) is formed in two states: 25% of Ps is formed as para-positronium (p-Ps) in which the spins of the two particles have opposite directions and 75% is formed as ortho- positronium (o-Ps) in which the spins are parallel. The lifetime of p-Ps is about 0.125 ns. In vacuum o-Ps annihilates into three γ-rays with a mean lifetime of 142 ns. However, in condensed matter the typical o-Ps lifetime varies from (1-5) ns. The o-Ps formed in a typical molecular material is localized in free volume spaces.

When positrons are injected into condensed matter from a radioactive source, after a fast slowing down it becomes thermalised. In terms of the blob model of o-Ps formation, the positron loses the last part of its kinetic energy in creating a blob, which is a small region (radius ~ 5 nm) of typically ~30 electron-ion pairs (Stepanov *et al*., 2002). Kansy and Suzuki, (2007) found two modes of o-Ps formation. An o-Ps can be formed when the epithermal positron escapes from the blob and comes within the Coulomb field of another epithermal electron that has also been ejected from the blob. This is referred to as the Slow Localization of Ps (SLP) mode. The second channel of o-Ps formation that is the Delayed Formation of Ps (DFP) mode. In this mode, o-Ps formation occurs not from an electron from the blob, but from a trapped (localized) electron that was introduced into the material from ionization events. Over the exposed region of the sample in the vicinity of the positron source a large number of electrons are released by ionization and acc

Corresponding author: <farzana97@hotmail.com>

DOI: https://doi.org/10.53808/KUS.2010.10.1and2.1008-E

umulate due to irradiation. At low temperature, when the segmental motions of the polymer freeze out, electrons with very low kinetic energy localize at shallow potential wells that form in intermolecular regions. A thermalized positron that has diffused out of the blob, can therefore pick up one of these electrons and form an o-Ps atom. With increasing measurement time, the concentration of the weakly bound electrons increases leading to an increased formation of o-Ps through this second channel.

The increase in o-Ps intensity (I_3) as a function of measuring time in the course of PALS measurements at low temperature has been reported by many authors (Kindle and Reiter, 1987; Levay *et al*., 1989; Uedono *et al*., 1997, and the references therein). The enhancement of o-Ps formation at low-temperature polymers was suggested to be due to the storage of weakly bound (trapped) electrons (Wang *et al*., 1998). This conclusion was confirmed by Hirade *et al*. (2000), who observed the effect of light bleaching of the enhanced o-Ps formation.

This behaviour of the enhanced o-Ps formation with the temperature was studied to investigate the transition and relaxation properties (Uedono *et al*., 1997 Suzuki *et al*., 2003), free volume distribution (Wang *et al*.,1998), mechanism of Ps formation process (Kansy and Suzuki, 2007) in many works. It has been shown that the activation energy of electron detrapping can be derived from the temperature dependence of the additional o-Ps formation (He *et al*., 2003; Hirade, 2003).

Based on the Hirade's theoretical study and his mathematical formulation we focus on the measurement of o-Ps yields at low temperature in the HDPE using PALS. The aim of this study is to investigate the thermal history dependence of the number of trapped electrons available for o-Ps formation.

Materials and methods

Background : The explanation for the rise in I_3 is due to the accumulation of weakly bound electrons those produced from the positron source irradiation (Hirade *et al*., 2000; Suzuki *et al*., 2000). He *et al*. (2003) gave a reason why the value of I_3 starts to increase at a fast rate and becomes asymptotically slower in terms of the detrapping of the weakly bound electrons at higher temperatures as shown in Fig. 1.

He *et al*. (2003) considered a constant rate of radiation induced electron production and trapping J by the ^{22}Na source. This allowed them to write the dynamic equation for the concentration of trapped electrons N_e as

$$\frac{dN_e}{dt} = J - \lambda_d N_e, \qquad N_e(0) = 0 \tag{1}$$

where the temperature dependent detrapping rate λ_d is determined by the molecular motions that exists in the vicinity of the trapping site and is written as

$$\lambda_d = \nu_0 e^{-E/k_B T} \tag{2}$$

where ν_0 is the typical molecular component oscillation frequency, E is the activation energy of detrapping (i.e. the trap electron binding energy). The solution of Eq. (1) is

$$N_e(t) = \frac{J}{\lambda_d}\left[1 - e^{-\lambda_d t}\right]. \tag{3}$$

He *et al*. (2003) then define the enhancement of I_3 due to trapped electron accumulation as ΔI_3. From an experimental point of view ΔI_3 is the difference between the value of I_3 at low temperature after measurement time t and the high temperature value.

To explain the saturation of increase in I_3 , Hirade (2003) suggests that trapped electrons do not just get released through thermal activation, but in addition have other natural ways of decaying. Hirade (2003) is not specific to the mechanism of the loss of trapped electrons, although it is clear that the mechanism is not thermal. But according to Hirade (2003) Eq. (1) is written as

$$\frac{dN_e}{dt} = J - \lambda_d N_e - \lambda_0 N_e = J - \lambda_{eff} N_e \tag{4}$$

here $\lambda_0 N_e$ is the temperature independent decay rate . Where

$$\lambda_{eff} = \lambda_0 + \lambda_d \tag{5}$$

is the effective decay rate of the trapped electron. It is argued that since ΔI_3 results from epithermal positrons that have escaped the blob, interacting with trapped electrons to form o-Ps, there should be a direct proportionality between ΔI_3 and N_e

$$\Delta I_3 = CN_e = \frac{CJ}{\lambda_{eff}}\left[1 - e^{-\lambda_{eff} t}\right] = \frac{\alpha}{\lambda_{eff}}\left[1 - e^{-\lambda_{eff} t}\right] \tag{6}$$

From Eq. (2) and Eq.(5) it follows that:

$$\lambda_d = \lambda_{eff} - \lambda_0 = \nu e^{-E/k_B T} \tag{7}$$

from which it can be writen as:

$$\ln\left[\lambda_{eff} - \lambda_0\right] = \ln(\nu_0) - \frac{E}{k_B T} \tag{8}$$

Thus one can make an Arrhenius plot of Eq. (8). The activation energy can be obtained from the gradient of the straight line.

Experimental: The PALS measurements were carried out using a fast-fast coincidence system with Barium Floride (BaF_2) scintillators having a time resolution of 230 ps. Each spectrum contained two million counts per hour. A 30 µCi source of spot size 2 mm deposited on a 1.5 µm thick Al foil was sandwiched between the samples. PALS spectra were analysed using POSITRONFIT.

The HDPE samples used for this experiment were obtained from Goodfellow Metals Ltd (UK). The 1 mm thick HDPE sheet was cut into 10×10 mm^2 pieces. The HDPE had a quoted crystallinity of 70-80%.

The HDPE samples were taken to low temperature using a '10K EBERA' closed cycle He fridge. Two hours are required to attain the lowest temperature of about 20 K. A temperature controller (Lakeshore 330) was used to maintain the sample temperature at the correct value.

The following two measurement series were performed on HDPE samples.

(i) In the first series of measurements the positronium formation in HDPE has been measured at the temperatures 20, 40, 60, 80, 120, 150 and 200 K for about 4 days while PALS data were taken every hour. At each temperature two new pieces of sample were used to avoid any problems associated with radiation damage through radical build up. The same positron source was used in each case to assure the same dose rate remained the same.

(ii) In the second measurement a sample was cooled quickly to 20 K and kept at this temperature for 100 hours while the trapped electron density and o-Ps

enhancement increased to maximum. This rise can be seen from Fig.3. Heating was then performed keeping the sample at successively higher temperatures (60, 80, 120, 150 and 200 K) for about 35 hours or more in order to obtain the saturation value of I_3.

Results

The enhancement effect of o-Ps at low temperatures has been found in the first measurement. The variation of I_3 and o-Ps lifetime (τ_3) at different temperature with time has been measured. In the second measurement I_3 has also been measured by heating from 20 K to the same different higher temperatures as first measurement. A three component analysis has been performed. The short-lived component with a lifetime τ_1 = 0.13-0.16 ns and the intermediate-lived component with a life time τ_2 = 0.35 ns are attributed to the p-Ps and free positron annihilation. The longest lived component τ_3 = 1.19-1.67 ns which is very sensitive to the structural changes in polymer and is attributed to the o-Ps pickoff annihilation in free volume holes.

Fig. 1 shows that I_3 has been plotted against the elapsed time during directly cooling at the temperatures 20, 40, 60, 80, 120, 150 and 200 K. The general trend for the lower temperatures (20, 40, 60, 80 and 120 K) is that initially I_3 increases quickly with time followed by an asymptotic approach to some constant saturation value. At 150 K the behaviour shows a slow rise in I_3 for the whole range, while at 200 K no rise is seen. It is also noted that the 20, 40, 60 K data are close to each other, while for 80 and 120 K the saturation values of I_3 are more quickly diverging.

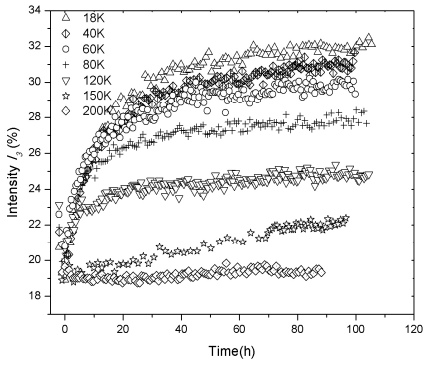

Fig. 1. o-Ps intensity I_3 with elapsed time during directly cooling at different temperature

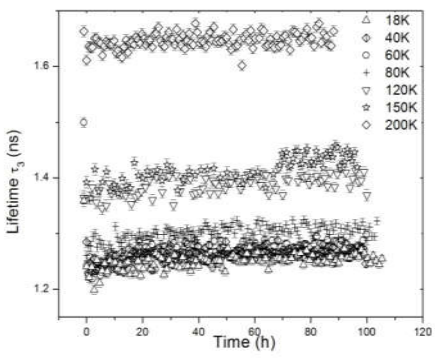

Fig. 2. Time dependence of lifetime τ_3 at different temperature for HDPE sample after directly cooling as in Fig. 1

Fig. 2 shows the variation of τ_3 corresponding to the I_3 data as shown in Fig. 1. The general trend of this Fig. shows that the value of τ_3 is larger for higher temperature. This increase is thus primarily due to the increase in free volume in sample. The monotonic increase of o-Ps lifetime τ_3 with temperature, is typical that was seen in polymers such as HDPE and PMMA (Suzuki et al., 2000; Wang et al., 1998).

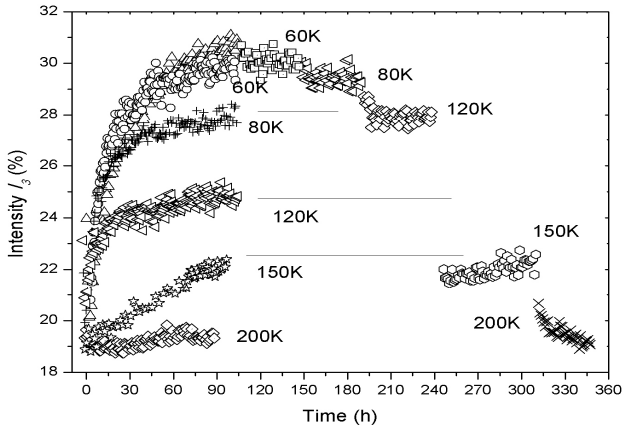

Fig. 3. o-Ps intensity I_3 with elapsed time those were obtained by heating at different temperatures after cooling at 20 K and compared with those obtained by directly cooling at the same temperatures. Straight lines shows the intensities obtained by directly cooling

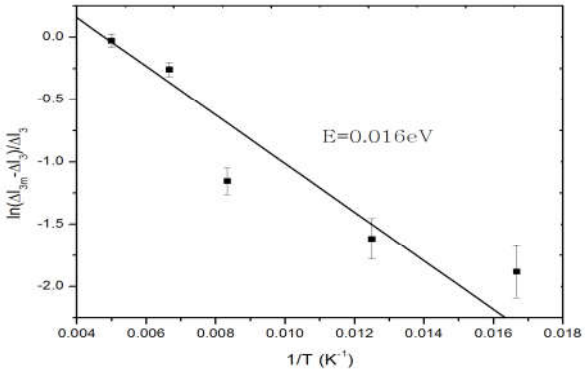

Fig. 4. Arrhenius plot of $\ln[(\Delta I_{3m}-\Delta I_3)/\Delta I_3]$ for I_3 data after samples have been at 20 K

In Fig. 3 I_3 has been plotted against elapsed time for the temperatures 20, 60, 80, 120, 150 and 200 K. At this time those I_3 values were obtained by heating gradually after a cooling at 20 K. This approximate annealing with time is shown by different symbols in Fig. 3 together with the first study as shown in Fig. 1.

One of the immediate findings from Fig. 3 is that the enhancement of I_3 (written as ΔI_3^{∞}) were generally higher than those obtained by direct cooling at the same temperature. Thus the observation is that:

$$\Delta I_3^{\infty} \text{ after passage through } 20K > \Delta I_3^{\infty} \text{ direct} \qquad (9)$$

This rule satisfies except at the higher temperatures (150 and 200 K). It is demonstrated more clearly in Fig. 3 as the direct I_3^{∞} has been plotted with the I_3^{∞} after passage through 20 K.

The value of I_3 can be used to determine the effective detrapping rate λ_d of the localized electrons through Eq. (8). Thus in order to find the activation energy an Arrhenius plot of $[(\Delta I_{3m}-\Delta I_3)/\Delta I_3]$ has been made to the saturated I_3 data after passing through 20 K as shown in Fig. 4. A straight line is obtained whose gradient gives activation energy of 0.016 eV.

It is necessary to show that the plot of $[(\Delta I_{3m}-\Delta I_3)/(\Delta I_3)]$ is indeed a plot of $\lambda_{eff}-\lambda_o$. The fraction of o-Ps that forms as a result of the localized electrons is ΔI_3. Since at high temperature no localized electrons remain, subtracting the high temperature (200 K) value of I_3 (19%) (shown in Fig. 1) from I_3 at different temperature we get ΔI_3. The value of I_3 at lowest temperature (20 K) where thermal detrapping is no longer possible (i.e. $\lambda_d = 0$) is I_{3m} and ΔI_{3m} is the maximum enhancement of o-Ps.

From Eq. 4 one has for (t→∞) when $dN_e/dt=0$ the asymptotic values of N_e given by:

At a general temperature T

$$J-\lambda_{eff}N_e = J-\lambda_{eff}\frac{\Delta I_3}{C}=0 \tag{10}$$

At low temperature (T→0),

$$J-\lambda_0 N_{em} = J-\lambda_0\frac{\Delta I_{3m}}{C}=0 \tag{11}$$

from which one has

$$\lambda_{eff}=\frac{JC}{\Delta I_3} \quad \text{and} \quad \lambda_0=\frac{JC}{\Delta I_{3m}} \tag{12}$$

And

$$\lambda_{eff}-\lambda_0 = JC\left[\frac{1}{\Delta I_3}-\frac{1}{\Delta I_{3m}}\right]=\frac{JC}{\Delta I_{3m}}\left[\frac{\Delta I_{3m}-\Delta I_3}{\Delta I_3}\right]=\lambda_0\left[\frac{I_{3m}-I_3}{\Delta I_3}\right] \tag{13}$$

from which one can see, apart from a constant factor of λ_0, the Arrhenius plot of $\lambda_{eff}-\lambda_0$ is the same as the plot of $[(I_{3m}-I_3)/\Delta I_3]$ or $[(\Delta I_{3m}-\Delta I_3)/(\Delta I_3)]$.

Discussion

In Fig. 1 the increase of Ps is generally understood to be due to the release of shallow trapped electrons which at the low temperatures provide an additional source of electrons for o-Ps formation at low temperature. The o-Ps formation at low temperature is therefore a function of time. It has been reported for many polymers that at low temperature o-Ps formation increase along with decreasing temperature (Suzuki *et al.*, 2003).

In Fig. 2 it has been shown that the value of lifetime τ_3 increases with temperature. This increase is thus primarily due to the increase in free volume. Closer inspection, however, reveals that the value of τ_3 also increases with the measurement time. The rise is about 0.4 ns over the 100 h period. The most likely interpretation for that is the trapped electrons cause o-Ps to form at specific free-volume sites and these sites are different from those general sites found the blob electron to form o-Ps.

An electron trapping site is a single fixed potential well with a binding energy E. This simplest idea has been taken to explain thermal history dependence of o-Ps formation as shown in Fig. 3. Thermal detrapping from the trap occurs according to the detailed balance between states in the continuum and the trapped state as shown in Fig. 5. As the temperature decreases the Boltzmann tail of the Fermi distribution decreases and detraping rate, $\lambda_d \rightarrow 0$. On this picture the population of the trap depends only on temperature.

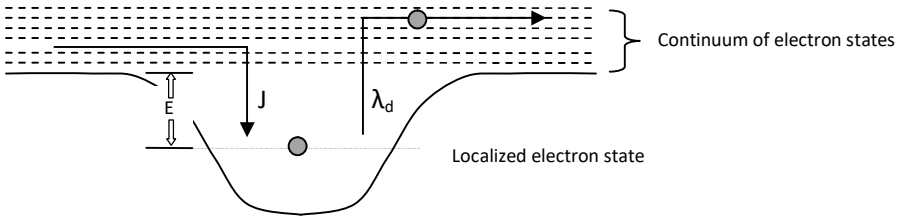

Fig. 5. A simple fixed potential trap. The population of such a trap is expected only to be a function of temperature

Based on the simple model of a localized electron state it would be expected that the occupied density of traps, N_e, and the enhancement of o-Ps produced by it, ΔI_3 , should only be a functions of temperature. Present experiment was devised to test this hypothesis.

But from Fig. 3 it is clear that the time saturated values of I_3 were generally higher than those obtained by direct cooling at the same temperature. This rule is clearly contrary to the expectation from the simple fixed potential trap model (Fig. 5), where the value of ΔI_3^{∞} should be solely a function of temperature (and not thermal history).

To explain the reason for this dependency of I_3 on thermal history is difficult. It can be assumed that there is some rotational and vibrational motion even at low temperature near and below the gamma transition temperature 150 K. This motion slowly freezes with cooling. This causes the electron traps to be more effective and raises the value of I_3 since the concentration of localized electrons becomes higher. The question is, why the saturation value of I_3 at different low temperatures depends on the thermal history?

One explanation for the result expressed in Eq. (9) is as follows. After spending time at 20 K the effective value of I_3 is maximal since at this temperature the localized electron density is maximal. No higher concentration is expected since all the trap sites are full. At low enough temperature, however, when the rotational and vibrational motions have effectively frozen the trapped electron, through its strong Coulomb force exerts some orientation on the molecular backbone causing some conformational change. Perhaps the electron causes an H- radical which fixes the motion of an H on the nearest neighbouring polymer, and this structure cannot be broken so effectively at temperatures below 100 K. After raising the temperature, localized electrons find themselves in a deeper potential due to the conformational change.

Conclusion

Ortho-positronium formation at low temperature has been studied for HDPE. It has been found from this study that the *o-Ps* formation at low temperature depends not only on the temperature but also on the thermal history. The reason for this dependency of I_3 on thermal history is difficult to explain. In this study it is assumed that due to some structural change at enough low temperature electrons find themselves in a deeper potential and cannot get released easily. Some more investigation about the structural change can make the concept more clear. This may be the good starting point of new research, such as study of local motion of polymers, *Ps* behaviour study in polymer etc.

Acknowledgement: This work has been performed at the Semiconductor laboratory, Physics Department of the University of Hong Kong. The author is grateful to lab-mates for providing the support and facilities to complete this research work.

References

He, C., Suzuki, T., Shantarovich, V.P., Ma, L., Matsuo M., Kondo, K. and Ito, Y. 2003. Positronium formation in low-density polyethylene. *Physics Letters*, *A* 313: 223-230

Hirade, T. 2003. Positronium formation in low temperature polymers. *Radiation Physics and Chemistry* 68: 375-379

Hirade, T., Maurer, F.H.J. and Eldrup, M. 2000. Positronium formation at low temperatures: the role of trapped electrons. *Radiation Physics and Chemistry* 58: 465-471

Kansy, J. and Suzuki, T. 2007. Delayed formation and localisation of positronium in polymers at low temperatures. *Radiation Physics and Chemistry* 76: 759-765

Kindl, P. and Reiter, G. 1987. Investigation on the low temperature transitions and time effect of branched poyethylene by the positron lifetime technique. *Physica status solidi*, *A* 104: 707-713

Levay, B., Lalovic, M. and Ache, H.J. 1989. Solid-solid phase transition and molecular motion in ling chain paraffin studied by positron annihilation techniques. *Journal of Chemical Physics* 90: 3282-3291

Stepanov S.V. and Byakov, V.M. 2002. Electric field effect on positronium formation in liquid. *Journal of Chemical Physics* 116 (14): 6178-6195

Suzuki,T., He, C., Shantarovich, V., Kondo, K., Ito,Y., Ma, L. and Matsuo, M. 2003. Relaxation behaviour of polymers probed by positron annihilation lifetime spectroscopy. *Materials Research Innovations* 7 (1): 31-36

Suzuki, T., Ito, Y., Kondo, E., Hamada, and Ito, Y. 2000. Radiation effect on positronium formation in low-temperature polyethylene. *Radiation Physics and Chemistry* 58: 485-489

Uedono, A., Kawano, T., Tanigawa, S., Ban, M., Kyoto, M. and Uozumi, T. 1997. Transition and Relaxation Process of polyethelene, polypropylene and polystyrene studied by positron annihilation. *Journal of Polymer Science*, *B* 35: 1601-1609

Wang, C.L., Hirade T., Maurer, F.H.J., Eldrup, M. And Pedersen, N.J. 1998. Free-volume distribution and positronium formation in amorphous polymers: Temperature and positron-irradiation-time dependence. *Journal of Chemical Physics* 108 (11): 4654-4661